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NANOSTRUCTURED POLYMERS, BLENDS AND COMPOSITES

Full Abstracts of Oral Presentations

MECHANISTIC ASPECTS OF SOLID STATE POLYAMIDATION PROCESSES

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INTRODUCTION

Solid state polymerization (SSP) is industrially applied for step-growth polymers, such as polyamides and polyesters; it involves heating the starting material (crystalline monomer or prepolymer) at a temperature below its melting point, permitting the initiation and propagation of typical polymerization reactions. Both chemical and physical steps occur during an SSP process, namely chemical reaction kinetics, reactive chain end movement in the amorphous phase, and condensate removal through convection. These phenomena are herewith discussed and correlated to operational variables, such as starting material nature and additives presence[1,2].

In particular, SSP starting from solid polyamide salts was investigated and found to be accompanied, depending on the reaction conditions, by a distinct transition of the process from the solid to the melt state (Solid – Melt Transition, SMT). Considering the hygroscopic nature of the reacting mass, a generalized mechanism for the effect of polycondensation water on reaction behavior was proposed and verified experimentally. It comprises water accumulation–hydration–transition to the melt, predominating in nylon salts of moderate structural organization, such as PA 6.6 salt. Furthermore, the SMT phenomenon was exploited through developing successfully a low-temperature two-stage prepolymerization technique, starting from dry PA 6.6 salt, and scaling up the process, through careful design of the experimental apparatus so as to handle properly the transitions of the reacting mass from solid to melt and solid again[3-6].

Turning to catalytic SSP, the efficiency of phosphorus-containing catalysts, serving also as antioxidants, was evaluated during PA 6.6 prepolymer SSP. The catalytic effect was correlated to the structure of the phosphonates, and, more specifically, to the additive mobility within the solid polymer, implying the possibility of partial incorporation of the catalyst molecule into the polyamide structure leading thus to reactivity enhancement[7-8].

Finally, nanofillers catalytic performance on SSP processes was proved in the current work, in the perspective of promoting their incorporation not only for the modification and/or improvement of materials properties, but also for exploring their performance as SSP “multifunctional” catalyst systems[9-10].

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Polymer Nanocomposites: Influence of Processing on Product Stability

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Polymer processing is a critical step in the manufacture of polymer articles. This step is even more critical when dealing with inhomogeneous polymer nanocomposites systems. Proper selection and tuning of the process variables should, in principle, lead to improved characteristics of the fabricated product. With multiphase systems, however, this is not straightforward and it is often the case that the process conditions are chosen initially to improve one or more desired properties at the expense of others. My aim in this lecture is to show how processing conditions affect thermoxidative stability of polypropylene nanocomposites (PPNCs) and how, in turn, aspects of stability may be used to better define these conditions so as to improve the manufacturing process of a specific formulation.

The melt blending approach is generally adopted for manufacturing polymer nanocomposites in which twin-screw extrusion plays a central part to achieving efficient mixing and compounding in a continuous production process. Co- and counter- rotating twin-screw extruders (TSE), with specially designed screw configurations, are used in a reactive processing approach to produce a product with optimal melt properties and characteristics suitable for further downstream conversion processes. For a specific screw size and design, temperature and screw speed can be used to control the production process for delivering the desired quality of the extrudate for a set of starting components. A systematic approach to studying the effects of these two process variables should, therefore, lead to a better definition of the process conditions required to produce polymer nanocomposites with target end-use properties. A stabilised PPNC system (containing Cloisite 15A & 20A) was used to perform the work reported here.

The design-of-experiment study was performed using a TSE fitted with an intermeshing co-rotating screw. Both temperature (210^{o}C & 230^{o}C) and screw speed (100 rpm & 300 rpm) were varied during the production process which was carried out under similar output process power so as to maintain similar stress levels on the melt. Profiles of properties of the extrudates were developed and related to their processing conditions. Properties examined include the thermoxidative stability (melt and solid) and impact strength of the extrudates.

A melt-recirculation (MR) test protocol using a micro-extruder with conical co-rotating screw geometry was used as a guide to assessing the melt stability. **Figure 1** shows changes in the torque in PPNCs under fixed conditions of shear (355 s^{-1}) and temperature (190^{o}C) with limited air ingress. It is clear that under both extrusion temperatures and screw speeds the PPNCs samples containing C20A nanoclay showed higher melt stability than those containing C15A.

Examination of the long term thermal stability (LTTS) of PPNCs containing C20A and C15A nanoclays, using air-circulating single-chamber Wallace Oven tests, shows that films containing C20A outperform also their C15A counterparts produced under the different extrusion conditions (see **Fig. 2a and b**) which agrees with the order of their melt oxidative stability described above. However, higher screw speeds under both extrusion temperatures tested gave much higher thermal stability (in both Wallace oven test in the solid state and DSC - OIT test in the melt), see for example **Fig. 2c**.

The organically modified C15A nanoclay contains more of the thermally unstable QUAT (quaternary ammonium surfactant). The higher amounts of the QUAT in the C15A nanoclay may contribute, at least in part, to the lower overall LTTS observed with PPNC-C15A films. However, there are some major differences in the distribution (surface vs bulk) of these two clays in these films which would influence their response to thermoxidative stresses. The structural differences of the PPNCs containing the nanoclays and the effect of the processing conditions on their overall behaviour will be elaborated.

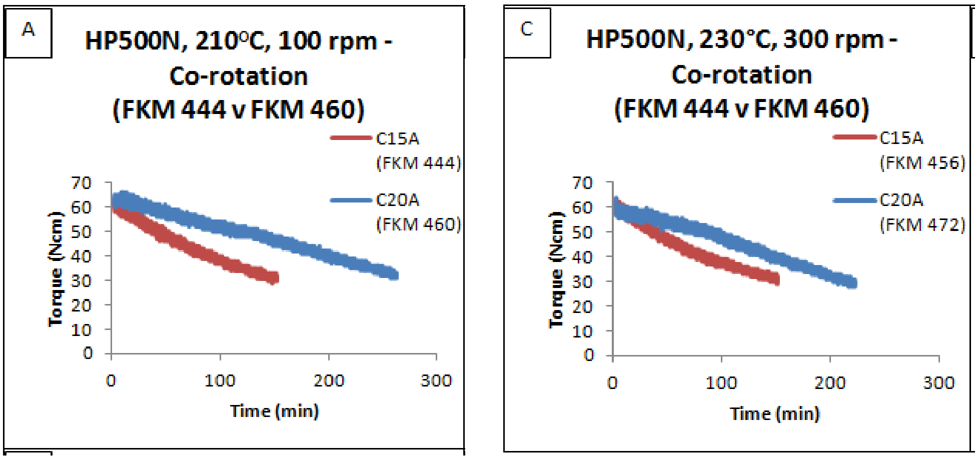

Fig. 1. Torque - time history from MR tests for C15A- (lower curves, in red) and C20A- PPNCs produced under different processing conditions.

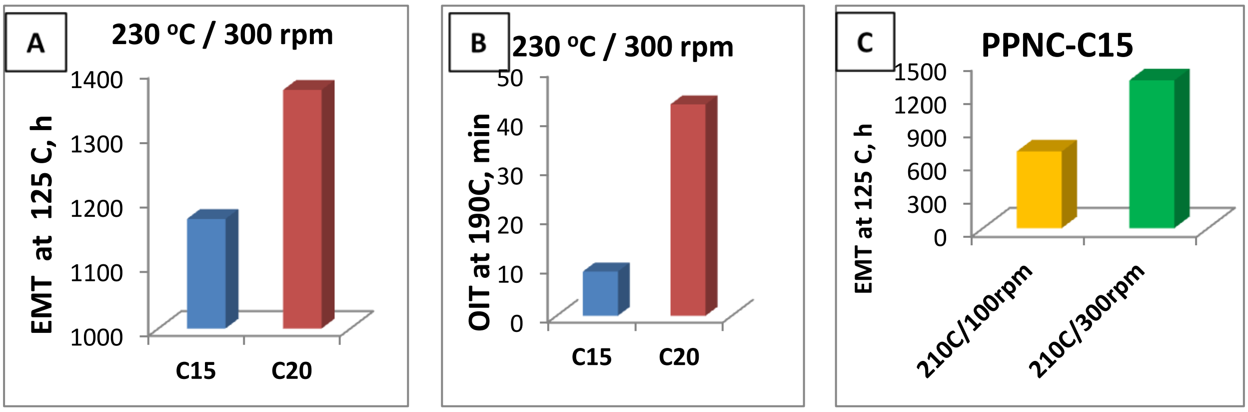

Fig. 2. Time-to-embrittlement from LTTS tests of PPNCs produced under different extrusion conditions.

INFLUENCE OF FUNCTIONAL NANOPARTICLES ON THE PHOTOSTABILITY OF POLYMER MATERIALS: RECENT PROGRESS AND FURTHER APPLICATIONS

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The polymer-nanoparticles/nanocomposites have been the exponentially growing field of research for developing the materials in last few decades. Research has mainly been focused on processing and properties of the materials. Inorganic nanoparticles have become attractive since they can simultaneously improve the physical, mechanical and flammability properties. Among various nanoparticles, clay minerals and carbon nanotubes were more often used, but functional nanoparticles were also incorporated into polymer as “nano-additives”. Depending on practical applications, nanoparticles of metal oxides (ZnO, TiO_2) were added for their photocatalytic and/or UV-screen effect. Luminescent oxides such as yttrium garnet (YAG:Ce^{3+}) were mixed with polymers (figure 1) for eco-energetic light devices.

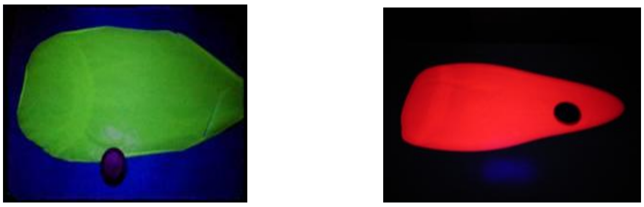

Figure 1.: Photos of polymer /phosphor nanocomposite films under UV excitation

Depending on their functionality, nanoparticles can impact the durability of the nanocomposite materials[1] under UV –light exposure. The behaviour of various types of nanocomposites submitted to UV-light exposure in presence of oxygen has been investigated and recent progress on the influence of functional nanoparticles on the polymer photodegradation will be presented.

Attention was firstly focused on the fate of nanocomposites with several polymers (PE, PP, EPDM, PS, epoxy …) and different nanofillers such as organo-montmorillonite[2] carbon nanotubes (NTC)[3] or Layered Double Hydroxides (LDH)[4]. Nowadays, montmorillonite is known to decrease the durability of polymer nanocomposites, whereas the effect of LDH or carbon nanotubes can be tuned. Stabilization of polymer/clay nanocomposites is then a bottleneck for industrial development of durable nanocomposites.

In the case of functional nanoparticles such as ZnO, TiO_2 or phosphors, one has to face two major questions:- i) what is the influence of the polymer degradation on the functional properties of the nanoparticles ii) do the nanoparticles impact the photostability of the polymer? The photochemical behaviour of nanocomposites will be explained with peculiar attention given to the influence of each component (UV absorber, photocatalytic particles and phosphors) on the rate of degradation of the polymeric matrix[5].

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TOUGHENIG OF UNSATURATED POLYESTER RESINS BY REACTING ADDITIVES

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Thermosetting materials based on Unsaturated Polyesters (UPR) are known to possess very low ductility. This means external energy applied on UPR (e.g. impact) has low chance to be dissipated as it occurs in rubbery materials, but is consumed on formation of cracks propagating fast from impact point to surrounding regions. Thus many attempts to apply reactive elastomers like CTBN did not lead to appropriate toughness of UPR resins. The same results were obtained for core-shell systems (Albidurs by Nanoresin) or nano-structured block-copolymers Arkema. The presence of reactive groups to link toughening agents to UPR structure did not show any visible effect on toughening of UPR used. On the other hand all above toughening agents showed good enough toughening effect in case we applied them in epoxy resin based composites. Low ductility means matrix of very low viscous properties and very low relaxation time. Within relaxation time period excitation is able to propagate to some distance from point of excitation to form crack or to be retarded by toughener. Basing on above approach we can consider polymer matrix as divided in elementary unit volumes. Each volume unit has to contain toughening element which is responsible for toughening of UPR matrix located in vicinity. The idea can be realized by using toughening additives of very low size to endeavor to fight with low relaxation time of extremely low ductile UPR matrix. In this regard the less is the toughening unit the better is toughening capacity. Toughening is only possible in case toughening additive exists as separated phase in solid UPR matrix. In case single phase solution of toughening additive in rigid matrix never toughening effect was observed. The main target of the work was to follow influence of epoxy toughener on properties of UPR. In contrast to classical toughening agents toughening effect of thermosets shows maximum upon concentration close to 0.1mol/kg of additive. Concentration of epoxy groups in toughening additive must be close to concentration of –OH and COOH end groups in UPR. In case of lower concentration it is not enough epoxy groups to link all UPR end groups. In case of higher concentration of epoxy groups not all epoxy groups are reacted or polymerization of epoxy groups can take place. Reaction of epoxy with Unsaturated Polyester end groups can decrease entropy change of solution of epoxy in UPR before and after reaction of epoxy groups with UPR ending groups. The number of possible states of linked epoxy is much less than numbers of possible states which in free epoxy can exist. It means:

$\Delta G_l = \Delta H_l - T\Delta S_l$ (liquid phase) (1)

$\Delta G_s = \Delta H_s - T\Delta S_s$ (solid phase) (2)

$\Delta S_s < \Delta S_l$ (3)

The main target to obtain toughened system is:

$\Delta G_l < 0$ and $\Delta G_s > 0$ (4)

In general terms epoxy structure interior UPR matrix can be related to interpenetrated network (IPN). Such toughening effect is related not to particular epoxy resin application but to formation of toughening IPN in UPR matrix by monomer of higher ductility. As mentioned above toughened polymer can be divided in elementary volumes each containing one toughening phase separated unit. Dimensions of elementary volume for regular rubbery toughening agents (about 0.5mcm) is likely large to provide effective transfer of exciting energy from UPR matrix to elastic polymer. Molecular level distances in IPR provide good toughening effect by very short time of energy transfer compared to relaxation time in UPR. Below are a few results of application of epoxy resin as toughening agent compared to regular toughening system in highly filled (87%w/w quartz) UPR composite.

Toughening effect of different additives on filled (87% quartz) UPR

Epoxy toughener, 0.1mol/kg, 3-functional	Albidur, Core-Shell, toughener, 12%	Unmodified UPR composite	
82.0	52.0	78.0	Ultimate Strength
2.2	1.0	1.0	Impact Strength, AU
91.4	81.0	9230	Tg, C

NATURAL SEPIOLITE NETWORK IN SBR NANOCOMPOSITES

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The addition of clay into elastomers generally leads to improvement in tensile stiffness, strength and toughness. Improved tensile properties are found by adding low amounts of organomodified clay to silicone rubber [1], polyurethane [2, 3] and EPDM rubber [4]. It has been shown that natural rubber/organomodified montmorillonite (MMT) nanocomposites [5], prepared by solution mixing, present mechanical properties that depend strongly on the level of intercalation/exfoliation of the clay within the matrix, and thus depends on the chemical modification of the clay. The stiffening effect can be easily observed in tensile tests and in low amplitude dynamic experiments [6-8].

Recently, needle-like silicates have shown a real impact on the mechanical behaviour of polymers [9] due to the good adhesion. It has been shown by Gonzalez Hernandez [10] that sepiolite based SBR compounds have lower viscosities than those produced using precipitated colloidal silica. The reinforcing effect of sepiolite used with silane coupling agent was much higher than kaolin.

The present work is aimed at studying the effect of natural sepiolite (needle-like clay) on the mechanical reinforcement and thermal behaviour of vulcanised SBR systems. A “networking” phenomenon has been observed and compared to the aggregated systems based on natural MMT (layered clay). The laboratory compounding process has been able to produce nanostructured materials as shown by TEM.

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RECYCLED PET/PP-EP BLENDS: INFLUENCE OF COMPATIBILIZER AND/OR MONTMORILLONITE CLAY ADDITION

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Introduction

Poly(ethylene thereftalate) (PET) is one of the most recycled plastics in the world. However, it is known that recycled PET presents inferior properties as compared to the virgin PET and that mixing with polyolefins can be an alternative to improve its properties[1]. Unfortunately, PET and polyolefins are immiscible resulting in a blend with poor adhesion among its phases. The compatibility of these blends can be improved commonly by reactive compatibilization processes[1]. Nowadays, some works have been shown that montmorillonite clay can act as a compatibilizer for polymer blends[2]. In this work, the morphology and mechanical properties of recycled PET/polypropylene (ethylene-propylene) heterophasic copolymer (R-PET/PP-EP) blends with addition of poly(ethylene-*co*-acrylic ester-*co*-glycidyl methacrylate) (P(E-*co*-MA-*co*-GMA)) and/or montmorillonite clay (MMT) was investigated.

Methods

R-PET/PP-EP blends were prepared in a twin-screw extruder. Both the genuine blends and the ones to which P(E-*co*-MA-*co*-GMA) (5wt.%) and/or MMT (5wt.%) was added were prepared in two steps. The compatibilizer and/or MMT was first mixed with the minor phase (PP-EP) and then blended with the matrix material (R-PET). Samples for tensile, impact tests and also morphological analysis were obtained by injection molding. Tensile and Charpy impact tests were performed according to standard conditions (ASTM D-638 and ASTM D256-D, respectively). The blend morphologies were characterized by scanning electron microscopy (SEM). The average dispersed phase diameter was obtained by measuring the diameter of 500 particles approximately. X-ray diffraction (XRD) analysis were performed using a CrKa radiation (k = 2.28 Å) with a step size of 0.08°/min from $2\theta = 1$ to 10°.

Results

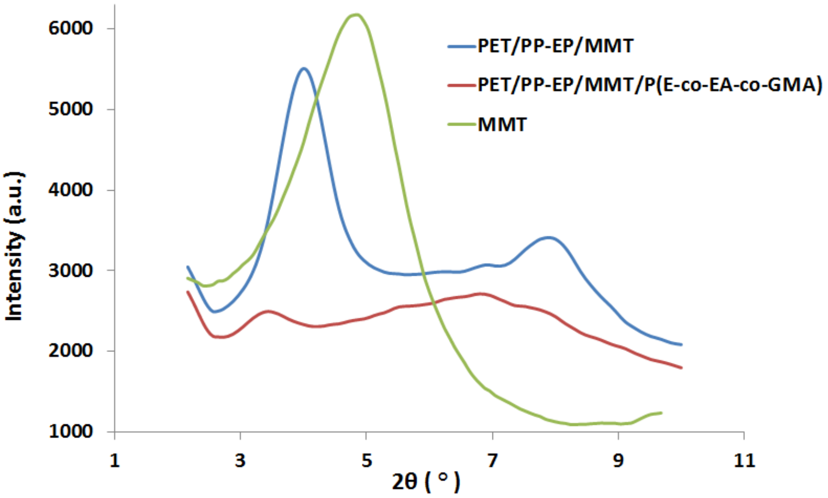

Figure 1: X-Ray difraction of MMT and PET/PP-EP blends containing MMT.

Table 2: Quantification of the morphology, tensile and impact properties of PET/EP blends**.**

Blend	**Diameter Average (µm)**	**Young Modulus (GPa)**	**Tensile strength (MPA)**	**Elongation at break (%)**	**Impact resistance (J/m)**
PET / PP-EP 90/10	1,50 ± 1,24	2,4 ± 0,1	46,0 ± 0,5	55,7 ± 28,8	18,0 ± 0
PET / PP-EP / MMT 85/10/5	0,89 ± 0,46	2,8 ± 0,1	46,7 ± 0,5	36,5 ± 17,0	27,0 ± 0
PET / PP-EP / P(E-*co*-EA-*co*-GMA) 85/10/5	1,21 ± 0,80	2,1 ± 0,1	41,5 ± 0,3	122,6 ± 34,3	27,0 ± 0
PET / PP-EP / MMT / P(E-*co*-EA-*co*-GMA) 80/10/5/5	1,01 ± 0,66	1,1 ± 0,4	38,0 ± 0,2	4,9 ± 0,9	18,0 ± 0

Conclusions

XRD analysis indicated that there was incorporation of polymer in MMT clay galleries. The addition of P (E-*co*-MA-*co*-GMA) or MMT separately promoted a decrease of the dispersed phase size. The addition of MMT in R-PET/PP-EP blend resulted in an increase of apparent Young modulus, tensile strength and impact resistance and a decrease of elongation at break. The addition of P (E-*co*-MA-*co*-GMA) resulted in an increased impact strength and reduction of other properties. The mechanical properties show a decrease when MMT and P (E-*co*-MA-*co*-GMA) are added simultaneously.

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PROPERTIES OF POLYAMIDE 6.6 COMPOSITES CONTAINING RECYCLED GLASS PARTICLES

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Glass powder from glass cullet has never been studied as a polyamide reinforcement. In this paper, PA-6.6 composites, reinforced with 10 wt.% of recycled, irregularly shaped, glass powder, and other common industrial fillers (glass fibers and microspheres, talc, and wollastonite), were processed in a double–screw extruder. Specimens were obtained by injection molding, and the following composite properties were measured: tensile strength, elastic modulus, elongation at rupture, and notchless Charpy impact strength.

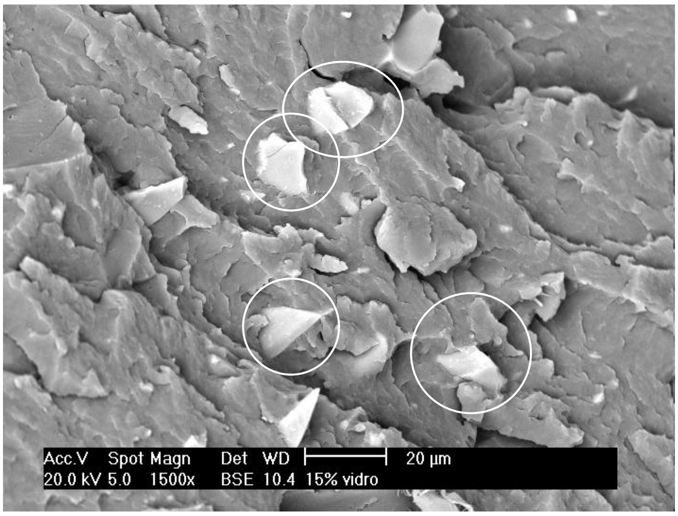

Figure 1: SEM micrograph (backscattered electrons detector) of a fracture surface of the composite containing glass particles. The circles identify some of the glass powder particles (note their assymetry and different contrast).

The glass powder was added to the matrix and processed, without the addition of any additives, either to alter the processing characteristics of the PA-6.6, or to increase the compatibility of the glass powder particles with the polymer matrix. Moreover, the recycled glass powder was particle size separated in standardized laboratory sieves, so that only the material containing particles less than 60 µm were used in the study. Since glass is a brittle material, the particle size distribution of the powder is very wide, even reaching submicrometer sizes, in its small end. The limit size of 60 µm was chosen because that is a typical (industrial) glass sphere size used as a filler (in general, with a very narrow particle size distribution). Table 1 summarizes the results.

Table 1: Measured mechanical properties of the PA-6.6 composites.

Filler	*Elongation at Rupture (%)*	*Tensile Strength (MPa)*	*Elastic Modulus (MPa)*	*Impact Strength (KJ/m²)*
No filler	5,3 ± 0,8	89 ± 1	3250 ± 69	208 ± 163
Talc	8,5 ± 2,1	77 ± 1	4140 ± 201	75 ± 4
Glass Fiber	2,4 ± 0,1	77 ± 1	4936 ± 175	29 ± 1
Glass Microspheres	3,0 ± 0,3	74 ± 2	3334 ± 74	20 ± 1
Wollastonite	12,2 ± 3,6	81 ± 1	4039 ± 106	89 ± 13
Glass Powder	4,8 ± 1,0	78 ± 1	3676 ± 100	33 ± 13
Standard	*ASTM D638–97*	*ASTM D638–97*	*ASTM D638–97*	*ISO 179-93*

The results indicate that it is possible to use particles of recycled glass with no surface modification in a PA-6.6 matrix, once the final composite properties are compatible to the ones of composites containing usual commercial fillers, particularly glass microspheres

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PREPARATION AND PROPERTIES OF PLASTICIZED POLY (VINYL CHLORIDE)/ORGANICALLY MODIFIED MONTMORILLONITE NANOCOMPOSITES

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Nanostructured polymers have attracted much attention in material science because of their unique properties and their applications in nanomaterials and nanodevices. In this study; an organophilic montmorillonite (OMMT), Cloisite 6A, was used as nanoclay. Plasticized poly(vinyl chloride) (PVC)/OMMT nanocomposites containing 1,3,5,7, and 10 wt% of Cloisite 6A were prepared via melt compounding using a twin screw extruder.

Compared to neat PVC the nanocomposite containing 5 wt% organoclay shows, from TGA, the greatest enhancement of decomposition temperature[1]. The interaction between PVC and silicate layer was studied by FTIR spectroscopy which confirms strong interactions between the nanometric silicate layers and PVC segments. Electrical conductivity σ measurements show that σ of nanocomposites increases with increasing temperature from 30 to 100°C, and show a considerable increase in the σ of plasticized PVC with increasing filler content up to 5 wt%, especially at higher temperatures (Table 1). The obtained values are situated between the two extremes of those of semiconductors (10^{-10} - 10^{+2} Ω^{-1} cm^{-1}).The activation energy E_σ was found to be lowest for the composite containing 5 wt% organoclay.The nanoscaled dispersion of silicate layers and strong interfacial interactions between silicate layers and PVC chains effectively enhance the tensile properties of plasticized PVC nanocomposites upon using 5 wt% organoclay.The dispersed behavior of organoclay in PVC matrix was identified by using XRD, TEM, and SEM analyses[2] which reveal the exfoliated structures in these nanocomposites when 5 wt% of Cloisite 6A was used (Figure 1).

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Table 1. Electrical conductivity (σ) of plasticized PVC mixed with various proportions of Cloisite 6A

Samples*	**σ x10^9 (Ω^{-1} cm^{-1}) at various temperatures (^{o}C)**							
	30	**40**	**50**	**60**	**70**	**80**	**90**	**100**
PVC-DOP-0	**--**	**--**	**0.01**	**0.02**	**0.04**	**0.06**	**0.09**	**0.12**
PVC-DOP-1	**0.02**	**0.04**	**0.14**	**0.31**	**0.74**	**2.12**	**4.79**	**9.80**
PVC-DOP-3	**0.05**	**0.15**	**0.51**	**1.12**	**2.63**	**7.51**	**16.98**	**34.60**
PVC-DOP-5	**0.07**	**0.20**	**0.69**	**1.52**	**3.59**	**10.37**	**23.66**	**48.50**
PVC-DOP-7	**0.06**	**0.18**	**0.61**	**1.35**	**3.18**	**9.14**	**20.73**	**42.30**
PVC-DOP-10	**0.04**	**0.13**	**0.46**	**1.01**	**2.37**	**6.81**	**15.40**	**31.53**

* The numbers in the names of the samples indicate the content of Cloisite 6A; for example, PVC-DOP-5 means a sample with 5 wt% of Cloisite 6A

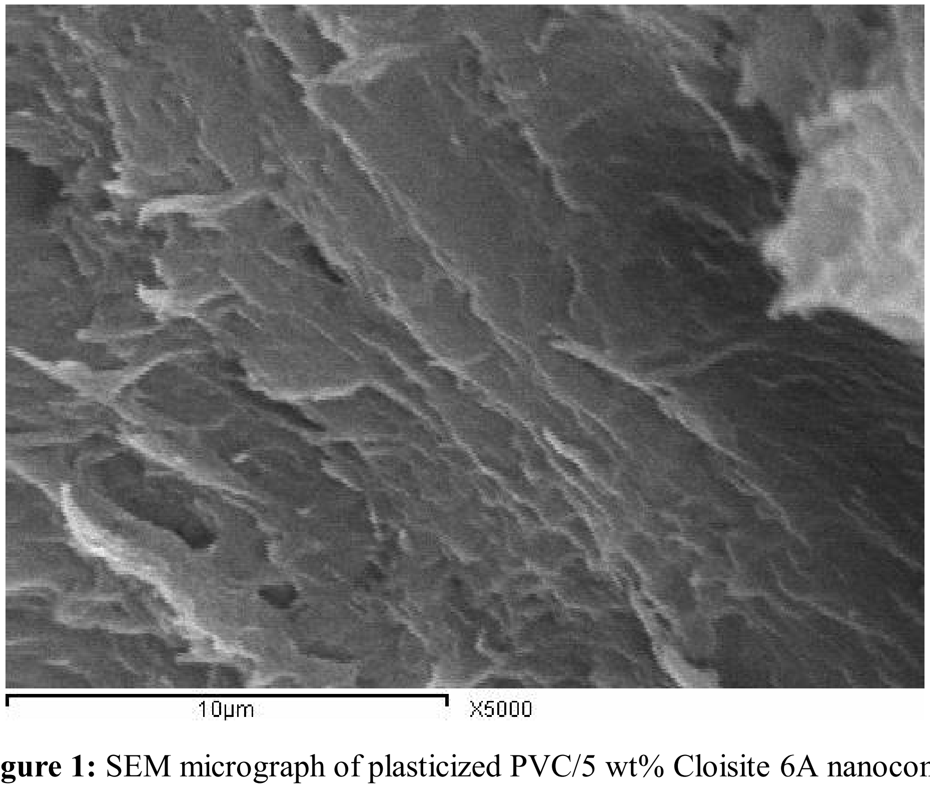

Figure 1: SEM micrograph of plasticized PVC/5 wt% Cloisite 6A nanocomposite

PREDICTION OF THE POLYMER BLEND MORPHOLOGY USING CONCEPT OF EFFECTIVE SHEAR FLOW

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One of the most successful routes of modification of polymer materials is blending polymers with complementary properties, e.g. high-modulus thermoplastics with rubbers. Because most polymer pairs are immiscible, morphology of their blends is formed during their mixing and processing. For achievement of materials with required properties, the morphology of polymer blends must be controlled. It is well known that the size of dispersed droplet of the minor phase in the matrix of the major phase in flowing blends is determined by the competition between the droplet breakup and coalescence. This effect is described quite satisfactorily for steady shear flow but not for complex flow fields in mixing and processing devices. Therefore, the important question is whether a complex flow field in mixers can be substituted by shear flow with an effective shear rate. With the aim to answer this question, we studied dependence the size of ethylene-propylene rubber particles form at steady mixing on the composition of polypropylene/ethylene-propylene rubber (PP/EPR) blends. Rheological properties of PP and EPR at mixing conditions can be found in Table 1. The results were compared with prediction of the theory for shear flow with effective shear rate, determined by common method[1] for mixing conditions.

Table 1. Storage modulus, *G'*, loss modulus, *G''*, and complex viscosity, $|\eta^*|$, of the blend components measured at angular frequency, ω, related to $\dot{\gamma}_{\text{eff}}$.

Material	ω (rad/s)	$G'\text{x}10^{-3}$ (Pa)	$G''\text{x}10^{-3}$ (Pa)	$\lvert\eta^*\rvert\text{x}10^{-2}$ (Pas)
EPR	18.5	17.4	44.9	25.1
EPR	185	159	203	9.85
PP	18.5	26.1	27.1	18.9
PP	185	126	88.2	4.2

The effective shear rate, $\dot{\gamma}_{\mathrm{eff}}$, in B 50 EHT chamber of a Brabender Plasticorder determined according to Bousmina et al.[1] was 185 s^{-1}. Besides it, also $\dot{\gamma}_{\mathrm{eff}}$ = 18.5 s^{-1}, related to lower limit of $\dot{\gamma}_{\mathrm{eff}}$ determined by other methods[2], was considered. Dependence of average Equivalent Diameter of EPR particles, determined by scanning electron microscopy, on weight fraction of EPR is plotted in Fig. 1. Average droplet diameter at zero EPR concentration and slope of the dependence was compared with prediction of the theory assuming dynamic equilibrium between the droplet breakup and coalescence in the shear flow[2,3]. It was found that *linear increase of the particle size with EPR concentration matches theory very well* but *calculated and experimentally determined particle sizes differ by order of magnitude.*

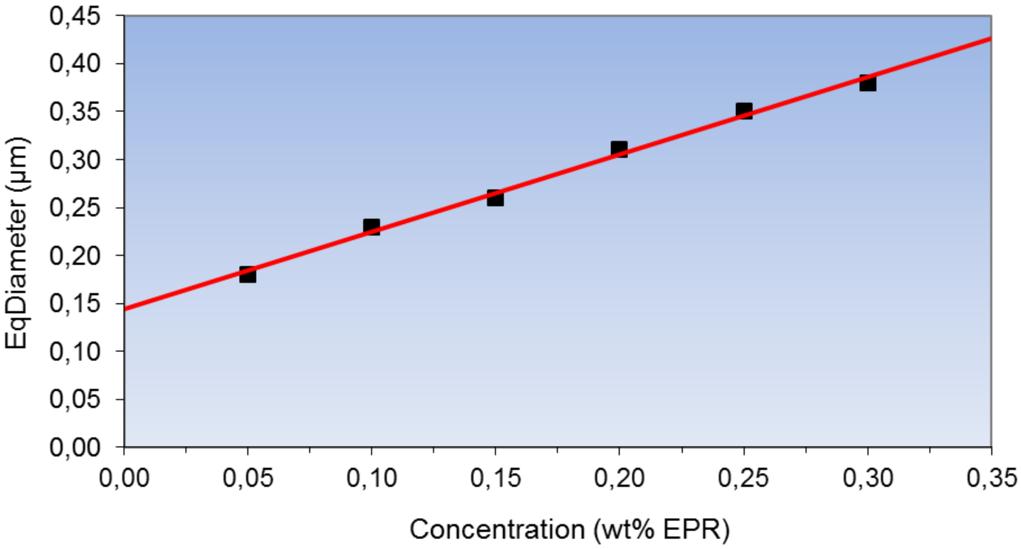

Figure 1. Dependence of number average equivalent diameter, ED, of EPR particles on their weight fraction in PP/EPR blends.

Acknowledgement. Financial support from the Grant Agency of the Czech Republic (grant No. P106/11/1069) is gratefully acknowledged.

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KINETIC MODELING OF A POLYMER BLEND THERMAL AGEING

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As rewiewed by Pospíšil[1], polymer blends generally oxidize with a different rate than their elementary constituents because of the existence of cooxidation reactions at the interfaces. In certain cases, however, cooxidation reactions would be negligible, as evidenced by microscopy analyses (such as TEM-EDX, AFM or SEM) focused on nodules changes in PE/PP blends, even if few heterogeneities were reported in PP matrix[2]. The aim of this communication is to check this last assumption from a kinetic modeling approach.

Methods

The experimental approach consists in fractionating the blend to study the ageing of each polymer phase separately (cf. figure 1). Blend fractionation was performed by solvent extraction and the fraction of soluble ethylene rich phase (ERP) was determined by mass loss. Ethylene fraction in ERP was also determined by NMR and FTIR using the classical Wei's law that leads to quite consistent results. At least, S-TEM analyses were made to characterize the blend morphology, in particular the nodules size.

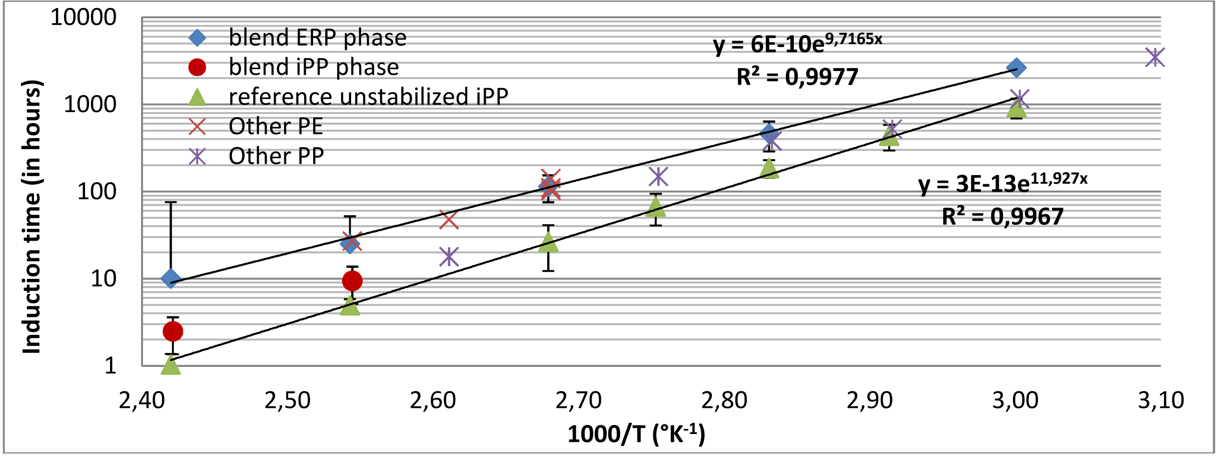

Figure 1 : Arrhenius plot of OIT determined in air for ERP and PP phases. ERP behaves similarly as PE because of its high ethylene content. The degradation kinetics of both phases are sufficiently different to envisage a two-steps degradation kinetic for the corresponding ERP/PP blend.

Kinetic modeling

For a sake of simplicity, the blend was represented by a series of ERP nodules regularly spaced in a PP matrix. The corresponding elementary cell used for kinetic modeling is given in Figure 2.

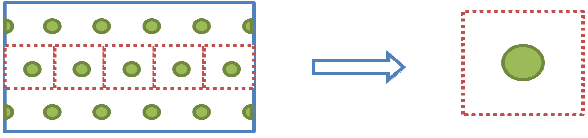

Figure 2: Schematization of an ERP/PP blend and the corresponding elementary cell.

In a first approach, it was assumed that each polymer phase degrades independently, i.e. that cooxidation reactions are negligible at the interface. Their thermal oxidation kinetics was simulated by a general kinetic model established for pure PP[3] and pure PE[4] in previous studies. This model considers only one type of reactive site: methyne group in PP and methylene group in ERP phase. Moreover, the oxygen concentration was determined by the classical Henry's law in PP and by a continuity equation in EPR phase:

$$C_{O_2}^{PP} = s_{O_2}^{PP}.P_{O_2} \qquad \text{and} \qquad C_{O_2}^{ERP} = C_{O_2}^{PP}.\frac{s_{O_2}^{ERP}}{s_{O_2}^{PP}}$$

with $s_{O_2}^{PP}$ and $s_{O_2}^{ERP}$ the respective oxygen solubility coefficients in each phase and P_{O2} the oxygen partial pressure in the environment.

As a result, the overall blend oxidation rate corresponds to the average value of phase oxidation rates:

$$r_{ox}^{blend} = X.r_{ox}^{ERP} + (1-X).r_{ox}^{PP}$$

with X the volume fraction of nodules in the PP matrix: $X = \omega_{ERP}^{blend}\frac{\rho_{blend}}{\rho_{ERP}}$.

It will be shown that this kinetic model allows to simulate a wide range of thermal oxidation behaviors by varying only one parameter: X. These simulations will be compared to experimental results in order to decide on the need to introduce interface effects in the kinetic model.

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IMPACT MODIFICATION OF POLY-4-METHYL-PENTENE-1 AND POLYPROPYLENE BY CONVENTIONAL AND NON-CONVENTIONAL ELASTOMERS

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Introduction: Poly-4-methyl-pentene-1 (PMP) is a semi-crystalline polymer for special applications requiring high stiffness and heat resistance. Even more than polypropylene (PP) homopolymers it suffers from a lack of impact strength. The relative effect of different elastomer types for impact modification was investigated for both PMP and PP.

Methods: Basic characterisation consisted of tensile and Charpy notched impact measurements. To gain insight into the related mechanisms both the morphology (via TEM) and the solid-state dynamic mechanical behaviour was investigated.

Results: Conventional impact modifiers, such as commercial ethylene/propylene-[1,2,3] (e.g. Vistamaxx) and ethylene/octene[4]-elastomers (e.g. Engage), were found to result in an acceptable stiffness/impact balance for both base polymer types. In addition a silane-crosslinkable LDPE/acrylate copolymer (Visico) was tested as a non-conventional impact modifier[5,6] which appears to deliver good impact properties for the case of PP only. Morphology investigations and the solid-state dynamic mechanical behaviour delivered some insight into the related mechanisms.

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Table 1: Stiffness-impact-balance for the PMP and PP blends.

Blend components	*Tensile Modulus ISO 527 [MPa]*	*Charpy ISO 179 1eA 23°C [kJ/m^2]*
PMP	1541	1.0
PMP + 30 wt-% Visico LE4481	888	1.9
PMP + 30 wt-% Vistamaxx 1120	1019	14.7
PMP + 30 wt-% Engage 8411	1004	5.3
PP	680	6.2
PP + 25 wt-% Visico LE4481	482	19.2

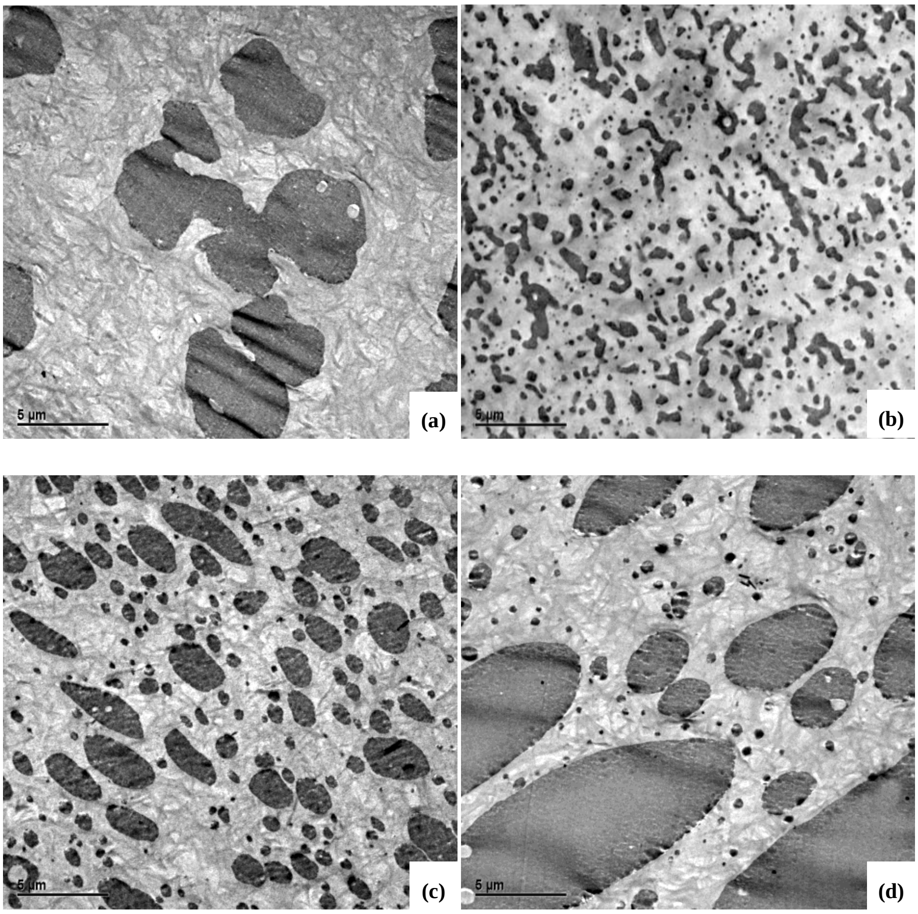

Figure 1: TEM micrographs of the blends: (a) PMP + 30% Visico, (b) PP + 30% Visico, (c) PMP + 30% Vistamaxx and (c) PMP + 30% Engage. The observed surface was perpendicular to the flow direction and the scale bar represents 5 µm.

STRUCTURE-PROPERTY RELATIONSHIPS IN END-LINKED MODEL PDMS NETWORKS – LINKING NETWORK ARCHITECTURE TO DEGRADATION BEHAVIOR AND MATERIALS PERFORMANCE

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Crosslinked Poly(dimethylsiloxane) (PDMS), elastomeric networks are an academically and technologically relevant sub-group of polysiloxane based materials, having wide-spread application in a large number of diverse technological, commercial and research areas[1]. Simple end-linked, unfilled, condensation, addition or peroxy cured PDMS networks typically exhibit poor mechanical properties and are of limited use as engineering elastomers. It is understood that in order to obtain the desired combinations of mechanical, physical and chemical properties for a specific real world application, such commercial 'silicones' must be formulated as complex multi-component systems - incorporating multi-modal distributions of chain lengths, varied crosslink topologies/densities, chemically modified free chain ends, non-stoichiometric excesses of reactive moieties, and often large volume fractions of a variety of reactive and/or passive filler materials[2]. The end result of this formulation effort is often a material with empirically tuned physical properties and a complex, yet often poorly defined network structure.

If we are to make accurate assessments and predictions of materials performance and lifetime over a broad range of environmental conditions (information that is of critical importance in many areas, including the electronics, biomedical implant and aerospace industries), there must be an understanding of this underlying network architecture and how it influences, physical properties, materials performance, stability and lifetime.

In this work, a combined, multilevel experimental approach towards understanding structure property relationships in silicone networks is discussed. Well defined, 'clean' model, end-linked PDMS networks have been formulated which incorporate individually and in combination, key structural elements: Mono- and bimodality, ranges of crosslink density, inter-chain molar mass, conventional silica and nano-scale filler materials (polyhedral oligomeric silsesquioxanes). By utilizing a combination of solid state NMR, analytical degradative thermal analysis and Multivariate data analysis, the influence of each basic structural component on the global properties of the system(s) as a whole have been investigated. Shown in Figure 1 is a ‘statistical map’ of the relation between sample network architectures and their components of thermal degradation.

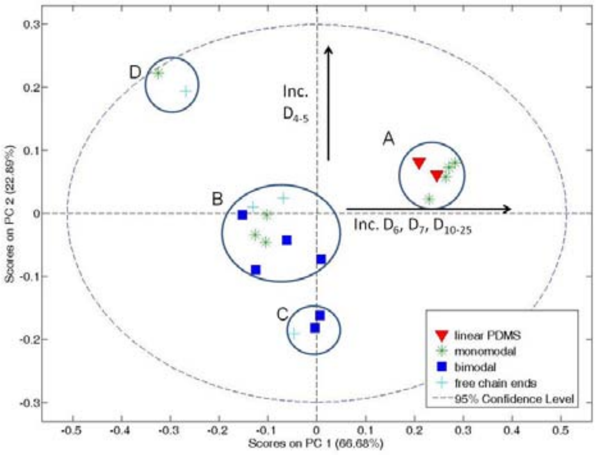

Figure 1. Multivariate statistical analysis of a matrix of model silicones. Statistical groupings of samples are circled and labeled A-D. Positive scores on PC1 (x-axis) have been correlated with increased relative yields of D_6 , D_7 & D_{10-25} cyclics. Positive scores on PC2 have been correlated with increased relative yields of D_4 & D_5 cyclics.

This work represents a step towards the construction of a valid a compartmental phenomenological model which progressively and realistically describes the effects of network architecture on the physical behavior of PDMS elastomers.

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ON THE PHOTO-OXIDATION BEHAVIOUR OF NANO-FILLED POLYPROPYLENE: ROLE OF THE FILLER TYPE AND COMPATIBILIZER

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The increasing interest in polymer nanocomposites over the last years is leading to a greater concern for their resistance to photo-oxidation, in particular for outdoor applications, where the action of direct sunlight, humidity and rain can lead to dramatic worsening of the main aesthetic and technological properties of polymers, due to its structural and morphological modification. The photo-oxidation behaviour of polyolefin based nanocomposites with layered silicate fillers has been investigated in the literature, and it has been found that their mechanical properties worsen at a higher extent, if compared to the neat matrices[1-3] while few data are available on those containing nano-calcium carbonate[4]. Literature reports also about the photo-oxidation behaviour of clay-filled nanocomposites in presence of compatibilizers such as maleated polyolefins, finding partially contrasting results, since Mailhot *et al.*[5] reported that maleic anhydride grafted polypropylene does not significantly modify the rate of photo-oxidation, while Qin *et al* [6] found that this compatibilizer can actually introduce some photoresponsive groups, leading to an acceleration of the photo-oxidation of PP when used in combination with organophilic montmorillonite.

In this work, the photo-oxidation behaviour of nanocomposites based on polypropylene and different nanofillers such as organo-modified clay and precipitated calcium carbonate has been investigated. Particular attention has been focused on the effect of a compatibilizer.

The materials used in this work were a general purpose polypropylene (PP) manufactured by Basell under the name Moplen X30G, and several types of nanometric filers. In particular, these were: an uncoated, precipitated calcium carbonate, produced by Solvay under the commercial name of Socal 31 (S31; mean particle diameter approximately 70 nm); two layered silicates (montmorillonites) produced and commercialized by Southern Clay Products as Cloisite Na+ (NaMMT; without organic modifiers) and Cloisite 15A (OMMT; modified with dimethyldihydrogenated tallow-quaternary ammonium chloride quaternary surfactant). Also a microsized calcium carbonate, commercialized by Solvay as MVM, was used for comparison purpose. The neat PP as well as the nanocomposites (5 wt%) and the comparison-purpose microcomposite were prepared by means of a Brabender counter-rotating intermeshing twin-screw extruder with a max. temperature set at 190 °C. The obtained materials were subjected to compression moulding and subsequent mechanical, FTIR and morphological characterization. These were performed on the samples before and after accelerated weathering in a Q-UV environmental testing apparatus. The photo-oxidation behaviour of these samples was directly compared to that of the corresponding composites were different amounts of a compatibilizer, polypropylene grafted with maleic anhydride (PP-g-MA) were used in order to assess its influence on the photodegradation rate.

Tensile test showed that the behaviour of the different nanocomposites is comparable, and there are not many differences with the reference microcomposite. Also the photo-oxidation rates of the various nanocomposites are comparable. Morphological characterization showed the presence of significant changes in the morphology upon increasing the photo-oxidation time. The use of PP-g-MA led to significant variations in the photo-oxidation behaviour, both in terms of photo-oxidation products formation and induction time.

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POLYMER-INORGANIC NANOCOMPOSITES: INVESTIGATION OF THERMAL DEGRADATION AND FLAME RETARDANT MECHANISMS

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Preparation of polymer/alumina and polymer/silica nanocomposites were accomplished using a single-screw extrusion technique (European Patent 1401924, Issued 20080709). The single screw extrusion technique creates a better interface than solution blending, an interface which is perfected on multiple extrusions. Less damage to particles is done versus twin screw extrusion. A systematic investigation of interfacial interactions, mechanisms of reinforcement, and the thermal degradation and flame retardant mechanisms was undertaken. Silica spheres of various dimensions, and alumina or alumina hydrate nanoparticles of various shapes (100/10 nm rods, 40-80 irregular, 15 nm spherical, and 2800/2-4 whiskers) were used. Several surface treatments were examined.

It was found that the stereochemistry of the polymer chains versus the shapes of the nanoparticles were extremely important. PMMA, polystyrene (PS), and polycarbonate (PC) were studied. It was found that aromatic polymers such as PC and PS have stronger interfacial interactions with needle or whisker-shaped nanoparticles than with spherical-shaped nanoparticles, while linear aliphatic polymers such as PMMA showed stronger interactions with spherical nanoparticles. It was found that the chemical nature of nanoparticles also plays a role in the thermal degradation of polymer nanocomposites. SEM studies of chars revealed that alumina nanoparticles moved to the surface of the nanocomposites, while silica nanoparticles stayed in the body of the material, which enhanced char formation.

While a 29% increase in tensile strength, a 34% increase in modulus, and a 60% increase in elongation at break was achieved for alumina whiskers at a 1% loading level in PC, lesser effect on mechanical properties was found for alumina in spherical shape (15 nm). In PC a 100/10 nm rod gave a 54% increase in tensile strength, a 97% increase in modulus, but a reduction in elongation at break. For PS, a 37 %

improvement in tensile strength, a 51% increase in modulus and no change in elongation at break was seen for whiskers at 1 % loading. But for 100/10 nm rods PS showed minimal increase in tensile strength, an under 29% change in modulus and no change in elongation at break. For 20 nm silica spheres PS showed a decline in tensile strength, a 50 % increase in modulus and no change or a decrease in elongation at break. For PMMA an up to 29% decline in tensile strength was seen for rods and whiskers. However, the 15 nm alumina spheres showed a 12% increase in PMMA at 1% loading, with a 9 % increase in modulus and a 40 % increase in elongation at break. Silica spheres (20 nm) showed a 3 fold increase in tensile strength, 2.8 fold increase in modulus, and 2.6 fold increase in elongation at break at high filler loadings (13%). The difference between alumina and silica spheres is the catalytic impact of alumina on the degradation of oxygen containing polymers.

For thermal degradation in TGA a 10 to 20 degree increase at 10% weight loss and 5 to 10 degree increase at 50% weight loss was generally seen regardless of resin, particle loading or shape. However, for Cone Calorimetry the 40 nm irregular particles for PC yielded a 33% reduction in peak rates of heat release at a 2% loading, while the 100/10 nm rods yielded a 45% reduction in peak rates of heat release. Silica (16 nm spheres) yielded only a 15% reduction in peak rates of heat release at a 3% loading. The highest increase in oxygen index (OI) was to 27.1 (versus 23.3 for neat resin)(3.8 units) for 100/10 rods at 2% loading. PC with 16 nm silica spheres showed no change in OI at particle concentrations from 1 to 5 percent. A 0.3 to 0.6 increase in OI was seen for PS/alumina nanocomposites, versus up to 1.2 units for 20 nm silica. For PMMA an oxygen index improvement of 0.3 to 0.6 units was seen for alumina nanocomposites, and a 3.7 unit increase for silica (20 nm) at 5% loading. PMMA nanocomposites showed a 22 to 27% reduction of peak rates of heat release with silica spheres. Clearly, different additives showed different impacts.

VOLATILE OUTGASSING INVESTIGATIONS OF EVA BASED MATERIALS IN SUPPORT OF SYSTEM LEVEL AGEING MODEL DEVELOPMENT

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There are many proven methods for predicting ageing trends in individual polymeric materials and components from data generated in thermally accelerated ageing experiments. Once materials are placed into systems in combination with others, however, a number of factors make the prediction of trends far more complicated. There may be important interaction between materials, which age at different rates and failure may result from degradation processes that are influenced by complicated diffusion pathways. A strategy of building up experimental complexity to interrogate, understand and de-convolute these factors has been pursued. The paper will briefly discuss the associated system model and detail the accelerated ageing experiments carried out on EVA based materials to populate the model currently being developed at AWE.

Our initial focus has been gas phase Infra-red (IR) spectroscopy for speciation and quantification of outgassing rates of key species. The release of inventory material dominates the early out gassing properties of the EVA materials. The species evolved are typically acetic acid, carbon dioxide and water, with acetic acid dominating the gas phase composition. For comparison purposes, we have also carried out studies on VCE binder material and the results of these initial trials will also be detailed in this presentation.

In each case, our studies show that inventory material (i.e species within the network produced from earlier degradation such as during processing or picked up during storage) dominants the outgassing and headspace composition. Under the conditions of interest, the production of species during the experiments (real-time) through chemical reactions appears to be negligible.

These activities are aimed at developing a robust ageing model that supports a larger system level ageing model. The development strategy including the key parameters of interest (such as quantification of inventory levels) will be detailed in this presentation.

FUNCTIONALIZATION OF CARBON NANOTUBES VIA PLASMA POST-DISCHARGE SURFACE TREATMENT: IMPLICATION AS NANOFILLER IN POLYMERIC MATRICES

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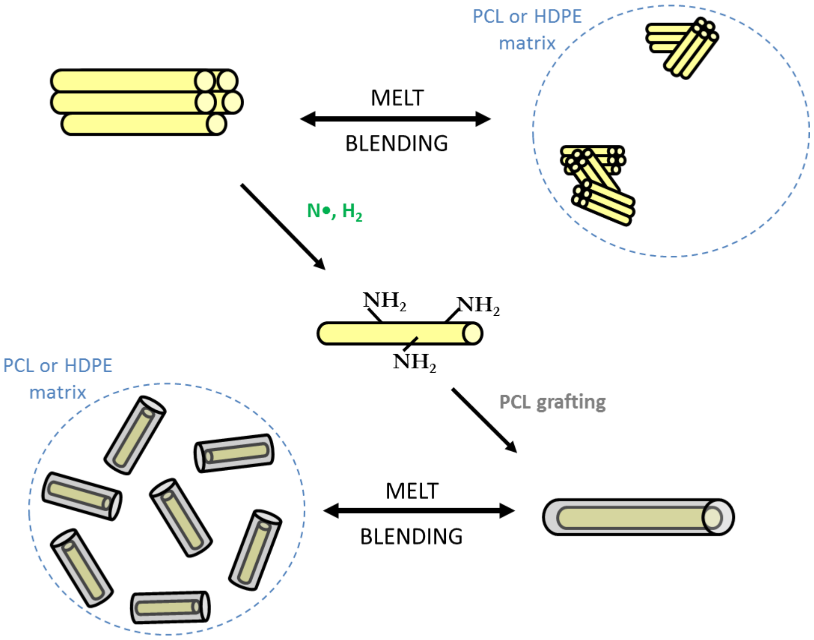
In the early 90's, the incorporation of carbon nanotubes (CNTs) in polymeric matrices was envisaged to improve the mechanical and thermal properties of polymers[1]. Due to their high electrical conductivity and high aspect ratio, CNTs can also percolate to form a conductive network in insulating matrices at low loading (1-3 wt%)[2]. The properties of the CNT-filled nanocomposite depend on several factors such as the polymer nature, the amount of impurities on CNTs and the dimensions of CNTs (aspect ratio). However, two key-factors remain the CNT dispersion quality and the interfacial interactions between CNTs and host matrix. Among the different proposed strategies to improve the CNT dispersion ability, the covalent functionalization has showed its potential for pre-disaggregation of CNT bundles that is the first step to achieve a good dispersion of CNTs[3].

In this study, CNTs were functionalized via an original covalent surface treatment that consists of exposing the CNTs to a reactive flow of atomic nitrogen[4,5]. The so-grafted primary amine groups were used as initiating sites for lactone polymerization forming CNT-g-polyester nanohybrids allowing the pre-destructuration of the CNT agglomerates. The CNT-based nanocomposites have been prepared by the melt blending of polymers with nanohybrids, used as highly filled chemical masterbatches, and their thermal, electrical and morphological properties have been characterized.

The amine grafting appeared to occur mainly at defects on the surface of CNTs, limiting any damages on the carbon nanotubes structure, and more likely preserving their physical properties such as electrical conductivity[6]. The investigation of two different polymer matrices, i.e. PCL (same nature than polyester-coating at the surface of the nanotubes) and HDPE, known for its non-compatibility with PCL chains, allowed to determine the influence of the CNT-polyester coating on the resulting electrical properties of the nanocomposites[7].



Schematic representation of the used strategy to disperse CNTs in polymer matrices.

The HDPE filled with PCL-coated CNT nanohybrids showed better electrical properties than HDPE filled with non-modified CNTs. The electrical properties improvement was associated to a better dispersion of the fillers and, also, to the exclusive presence of PCL coating in tunnelling junction between the CNTs. Moreover, the influence of CNTs on the semi-crystalline framework of the PCL composite was studied more in depth[8,9] and compared with those achieved with other nano-sized filler particles[10].

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BIODEGRADABLE POLYESTER NANOCOMPOSITES: THE EFFECT OF STRUCTURE ON MECHANICAL AND DEGRADATION BEHAVIOR

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The study describes the effect of the content and dispersion of the layered silicate on resulting mechanical behavior of poly(ε-caprolactone) (PCL) nanocomposites (NC) and its corresponding changes during the degradation in a phosphate buffer at 37 °C. Two nanocomposite systems are compared: intercalated and exfoliated nanocomposites. They were prepared by melt-compounding of a high-molecular-weight PCL with in situ polymerized silicate masterbatches or an organophilized montmorillonite (MMT). It has been shown that Young modulus increases with the increasing silicate content and at the same time, the highest increase in the modulus is observed for the exfoliated system. The stiffness enhancement is predominantly caused by the dispersed inorganic phase but it is also supported by the contribution of the low-molecular-weight PCL

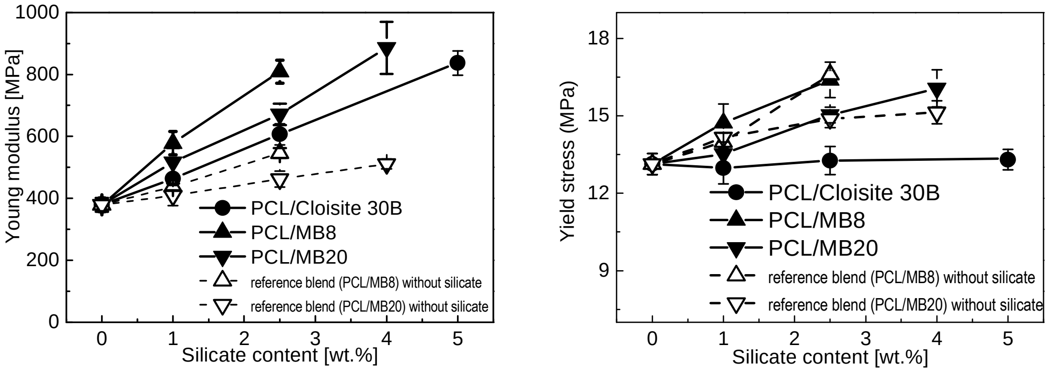

Figure 1: Young modulus (left) and yield stress (right) as a function of the silicate content. PCL/Cloisite 30B - intercalated NC prepared via melt compounding of PCL with MMT; PCL/MB8, PCL/MB20 - NC prepared via melt compounding of PCL with in-situ polymerized masterbatches with exfoliated (PCL/MB8) and intercalated (PCL/MB20) morphology. The composition of the reference blends without silicate corresponds to the nanocomposite composition (HMW/LMW PCL ratio).

(LMW PCL) fraction, which comes from the masterbatch, to the total degree of crystallinity. In contrast, the increase in the yield stress is driven mainly by the present LMW PCL with higher crystallinity.

The degradation behavior reflects both the presence of the layered silicate as well as the LMW PCL fraction. They accelerate the degradation in the phosphate buffer at 37 °C. The evolution of mechanical behavior during the degradation is affected by both secondary crystallization and the chain scission. Thus, Young modulus tends to increase with exposure time as a result of increasing crystallinity. The increase in the crystallinity causes also the increase in the yield stress. However, this increase is observed only up to certain degradation time (6 months). With prolonged exposure time in the degradation environment, the effect of the degradation processes prevails and both stiffness and strength tend to decrease. These trends are more pronounced for PCL/masterbatch systems with the highest silicate content. At the same time, the strain-at-break values of these nanocomposites are markedly reduced to 10 % after 6 month exposition. This significant drop in ductility is shifted to higher exposure times with decreasing silicate content and decreasing LMW PCL fraction. Observed evolution of mechanical behaviour reflects the nanocomposite structure and its changes during degradation.

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STRUCTURAL, THERMAL AND MECHANICAL CHARACTERISTIC OF THE POLYAMIDE 6/MODIFIED HALLOYSITE COMPOSITES

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Introduction:

The reinforcement of polymers thanks to the addition of nanofillers such as clay minerals or carbon nanotubes has attracted much attention in polymer engineering since decades [1-5]. Polyamide 6 (PA6) is an important semicrystalline engineering plastic which finds its application in automobiles, electrical appliances, construction materials and so on. However, the drawbacks such as limited mechanical strength and dimensional stability restrict its applications. Halloysite is a type of natural tabular nanoclay and has been recognized as an effective nanosized reinforcement of polymers for better mechanical and thermal properties [6-8]. The objective of this work is to investigate the influence of the surface treatment of halloysite by using gelatin on the mechanical and thermal properties of PA6 composites.

Experimental:

The first modification stage of the treatment of the mineral with ultrasound (HU) was performed for the purpose of the generation of structural defects on the crystallographic surface. The choice of organic compound used in modification was made taking the possibility of an active interaction with PA6 matrix into consideration. The effect of modification of halloysite by using gelatin (HUG) was measured by electron microscopy (SEM and SEM-EDS) analysis. As can be observed in the EDS-spectrum for the HUG filler, the peak from carbon is present. It indicates the presence of the organic compound on the surface of mineral. The composites based on PA6 containing 3 or 5 wt. % modified halloysite were prepared by using Brabender mixer. Mechanical and thermal properties have been investigated by tensile, flexural and impact strength testing and DSC and TG analysis.

Results:

Table 1. Mechanical properties of PA6/halloysite composites

Names of composites	Type of modifier / % contain	Tensile strength [MPa]	Young's Modulus [MPa]	Tensile strain [%]	Flexural strength [MPa]	Flexural modulus [MPa]	Charpy Impact [kJ/m^2]
PA6	-	57 ± 4,5	1284 ± 12	147 ± 2,0	61 ± 6,1	3030 ± 10	7,5 ± 2,1
1	HU/3	43 ± 4,0	1485 ± 14	76 ± 1,2	63 ± 5,8	3129 ± 13	6,5 ± 2,5
2	HU/5	42 ± 3,5	1442 ± 10	69 ± 2,4	56 ± 7,0	3126 ± 11	6,3 ± 2,0
3	HUG/3	73 ± 3,9	1592 ± 11	96 ± 1,9	74 ± 5,4	3190 ± 9,0	6,5 ± 1,0
4	HUG/5	75 ± 4,2	1517 ± 16	74 ± 2,3	68 ± 6,2	3146 ± 12	5,7 ± 1,5

Table 2. Thermal properties of PA6/halloysite composites, determined by DSC method

Names of composites	Type of modifier / % contain	DSC					
		ΔH_m [J/g]	T_m [ºC]	ΔH_c [J/g]	T_{cryst} [ºC]	X_c [%]	T_g [ºC]
PA6	-	57,9	222,4	65,1	186,2	30,7	54
1	HU/3	62,5	221,9	66,0	186,9	33	53
3	HUG/3	44,6	221,9	61,9	185,0	23,6	49
4	HUG/5	42,5	221,8	60,2	185,4	22,5	50

Conclusions:

Preparation and application of halloysite based modifiers in the filling of polyamide 6 have been presented. The chosen modification method was found to be effective in obtaining active fillers. Structural analysis, especially SEM/EDS and PCS methods confirmed an additional layer on the halloysite surface of an organic layer derived from the applied modifying compound. Our investigations reveal that the addition of HU favours the formation of the γ-modification for PA6. The determined mechanical properties indicate an advantageous influence of the filler on increasing the resistance of PA6.

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Effect of Silica Nanoparticles on Morphology and Properties of InjectionMolded Immiscible Polymer Blends

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The stabilisation of immiscible polymer blend morphology can be achieved by using compatibilizing agents which present a chemical affinity with the two polymer phases. Nanoparticles could present an interesting alternative to the use of these conventional compatibilizing agents since they can confine, under certain conditions, at the polymer blend interface and form a rigid barrier that prevents coalescence. Unlike organic compatibilizers that need to be chemically adapted to each polymer pair, nanoparticles can be localized at the interfaces by effects of nanoparticle-polymer affinity through the interfacial energy (1, 2) and their use could provide a universal way for the interfacial compatibilization of immiscible polymer blends, which could be advantageous especially for plastic recycling.

The purpose of this work is to investigate the effect of nanosilica, on morphological, mechanical and thermal properties of polyamide-6/ polypropylene (PA/PP) immiscible blends (3). Different morphologies were obtained as highlighted by transmission and scanning electron microscopies. The incorporation of 5 wt% of hydrophobic nanosilica that migrated mainly at the interface prevented dispersed phase domains from coalescence leading to a clear refinement of dispersed droplet size. The macroscopic properties of the hybrid blends were discussed and interpreted in relation with the blend morphology and melt mixing procedure. The control over coalescence allowed a morphology refinement of the blends (Figure 1) and improved mechanical properties except in the case of blends containing PA as minor fraction (Figure 2).

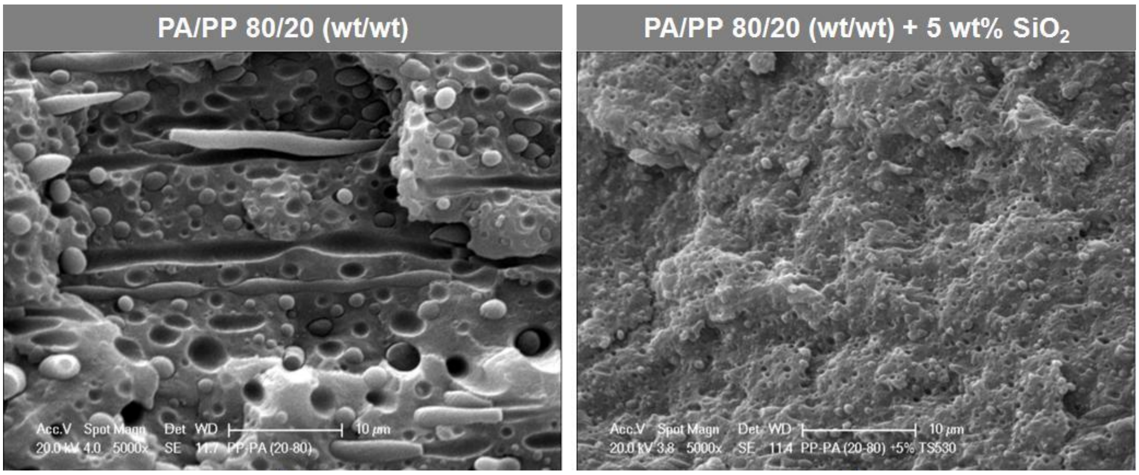

Figure 1 : effect of hydrophobic silica nanoparticles on PA/PP (80-20; wt/wt) blends morphology and ductility.

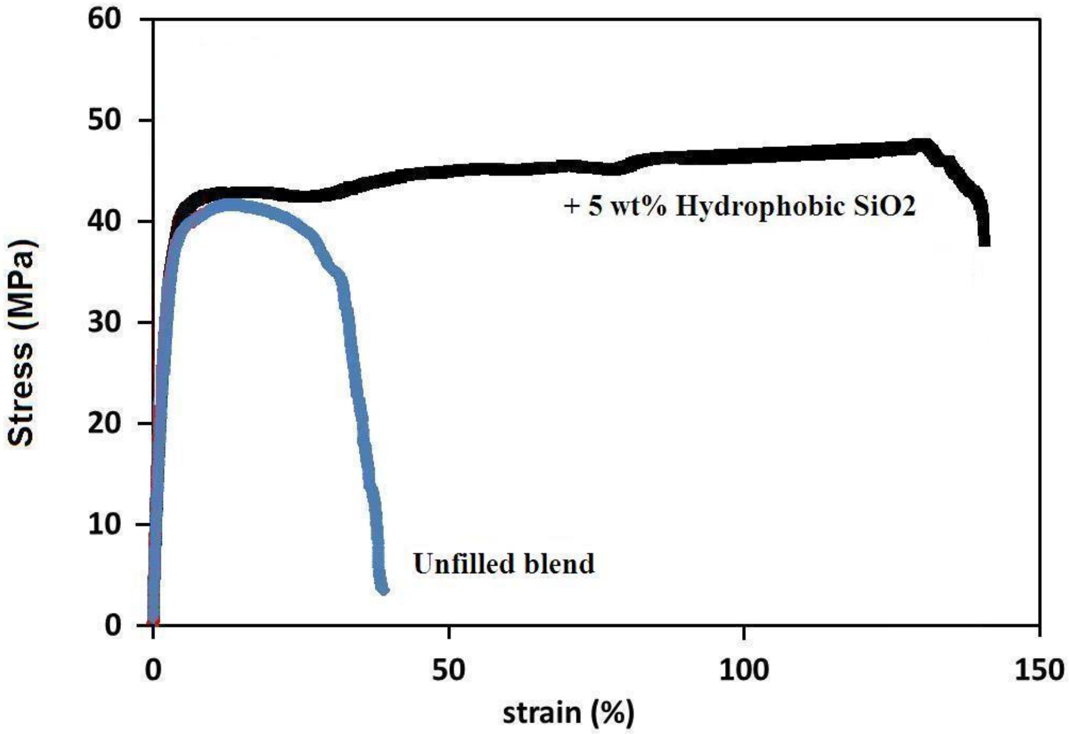

Figure 2 : Stress / Strain curves of PA/PP (80/20; wt/wt%) blends unfilled and filled with 5wt % of hydrophilic silica nanoparticles

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POLYOXYMETHYLENE/NANOSILICA NANOCOMPOSITES

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Introduction

During the last years a big increase in interest in the study of nanoscale materials has been noticed. One of the important areas of nanotechnology are polymer nanocomposites [1,2,3]. POM is an engineering polymer showing very good mechanical and chemical properties. The advantages like hardness, toughness, good dimensional stability of the polymer moulder and ease of processing make polyacetals very useful materials for the automotive, electronics and electrotechnical industries.

The results described in this paper concern the use of silica nanoparticles and its modified form. It was found that all the nanocomposites (with different quantity of fumed silica) showed better mechanical properties, higher thermal stability and resistance in use in comparison with non-modified polyoxymethylene.

Materials and Preparation

Polyoxymethylene (POM) in powder (grade Tarnoform) was supplied by Nitrogen Works in Tarnow-Moscice S.A., Poland and had a melt flow rate MFR = 10 g/10 min.

Fumed silica (14 nm) was provided by Aldrich and modified according to the process elaborated in Industrial Chemistry Research Institute [4].

Polyoxymethylene and fumed silica [5] were melt mixed using a Berstorff ZE-25x33D co-rotating twin-screw extruder (D = 25 mm, L/D = 33). Compouding was carried out using screw speed of 100 rpm and at the temperature profile 209-219^{o}C for the sequential heating zones. Than the product was dried and injection moulded.

Methods and Characterisation

A thermobalance (TGA/SDTA 851e Mettler - Toledo) was used to investigate the thermooxidative stability. The weight loss of a polymer annealed at 222 ^{o}C, after 10, 30 and 60 min (K_{222}) was measured. The content of the unstable fraction (UF) was calculated as weight loss of a polymer annealed for 1 h at 222^{o}C under pressure 50 Pa. Melt flow rate (MFR) was examined according to ISO 1133: 2002. The mechanical properties were obtained according to ISO 527 and ISO 179. The microstructures of nanocomposites were examined using a ZEISS-SUPRA scanning electron microscope.

Results

Table 1. Melt flow rate (MFR) and thermal properties of POM and POM nanocomposites.

	MFR *[g/10 min.]*	*UF* *[wt. %]*	K_{222} *[wt. %]*
Polyoxymethylene	**9**	**0.64**	**0.13__0.38__0.62**
Nanocomposites with modified nanosilica [wt. %] 0.25	10	0,60	0.07__0.17__0.28
0.50	10	0.65	0.06__0.14__0.22
1.0	9	0.67	0.07__0.15__0.25
2.0	9	0.72	0.11__0.25__0.40
4.0	8	0.89	0.26__0.52__0.78

The research in the field of thermal analysis (Table 1.,K_{222}) showed the influence of nanosilica on the polymer structure (the content of the crystalline phase) and on its thermal stability is very high. The results indicate the possibility of obtaining a material with high resistance in use.

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TAILORING OF CO-CONTINUOUS POLYMER BLENDS MORPHOLOGY: JOINT ACTION OF NANOCLAYS AND COMPATIBILIZERS

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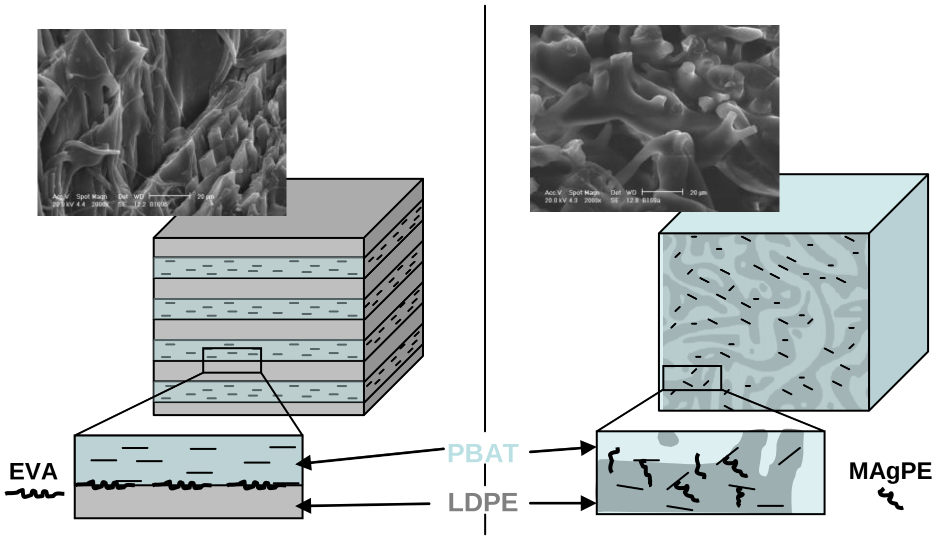
Polymer blends represent a large and rapidly growing fraction of all plastics produced. The opportune choice of the blend components and the control of microstructure can lead to multiphase systems with enhanced performances.

In a first part, the effect of both organically modified clay (Cloisite 30B) and compatibilizers (EVA copolymer or maleic anhydride grafted PE) on the morphology and mechanical properties of co-continuous structures is investigated. For that purpose, blends of low-density polyethylene (LDPE) and polybutyleneadipatetherephtalate (PBAT) (LDPE/PBAT 40/60 wt/wt) have been chosen as an environmentally friendly model. The influence of the nature of the nanoclay/compatibilizer pair on the morphology of the nanocomposite was thoroughly studied by means of scanning and transmission electron microscopies.



Depending of the compatibilizer, it has been found that the nanoclay can be selectively located in either the polyolefinic or polyester phase while the interphase is invariably stabilized by clay platelets. Remarkably enough, such a selection allows controlling the morphology of the polymer blends. The mechanical properties of the polymer blends were interpreted in the light of their morphology.

In a second part, the melt blending of poly(L-lactide) (PLLA) with biodegradable poly(butylene succinate) (PBS) is considered in a view to fine tune its mechanical properties. For this purpose, both maleic anhydride-grafted PLLA (MAgPLA) and maleic anhydride-grafted PBS (MAgPBS) were prepared and used as reactive compatibilizers. The influence of PBS melt viscosity on the morphology and the mechanical properties of PLLA/PBS blends are studied. Interestingly, the blending of low viscosity PBS with PLLA allows PLLA to be toughened while the use of high viscosity PBS led to PLLA/PBS blends exhibiting co-continuous morphology. The nanostructure of the co-continuous blends may be tuned through the joint action of organo-modified clays and reactive compatibilizers.

The so-obtained results evidenced that the joint action of nanoclay and compatibilizers allows tailoring the final properties of polymer blends, and pave the way for a new class of clay-based high-performance materials which combine the advantages of polymer blends and the characteristics of polymer nanocomposites.

Control of thermal degradation of PET/clay nanocomposites by chain extension reaction

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Polyethylene terephthalate (PET) undergoes severe thermal, oxidative, hydrolytic, and mechanical degradation during melt processing[1]. The organoclays accelerate chain scission of the PET matrix which leads to a matrix of a lower molecular weight[2]. In this work we employed a multifunctional epoxy based chain extender to rebuild the molecular weight as epoxide can form covalent bonds with the nucleophilic end groups of PET during the limiting time of extrusion. Joncryl® ADR 4368 (Joncryl) was used as the chain extender and Cloisite® 30B (C30B) and Nanomer® I.28E (N28E) were employed as organoclays. Figure 1 shows the complex viscosity and storage modulus as functions of frequency for the neat PET and PET nanocomposites with and without Joncryl. The addition of 1 wt% Joncryl during extrusion increased the complex viscosity of the neat PET from 400 Pa.s to more than 2000 Pa.s at low frequencies. All nanocomposites exhibit a shear-thinning behavior and the presence of the chain extender increased the complex viscosity and storage modulus of all samples. A gel content test was performed at room temperature to examine the probability of gelation or cross-linking in samples containing Joncryl. All samples were completely dissolved in a mixture of 60/40 wt% phenol and tetrachloroethane at room temperature within 30 min confirming that the samples containing the chain extender had no cross-linking. Extensive results on the effect of Joncryl on the rheological properties of PET and PET clay nanocomposites will be presented and discussed in light of the reaction mechanisms between PET and the chain extender.

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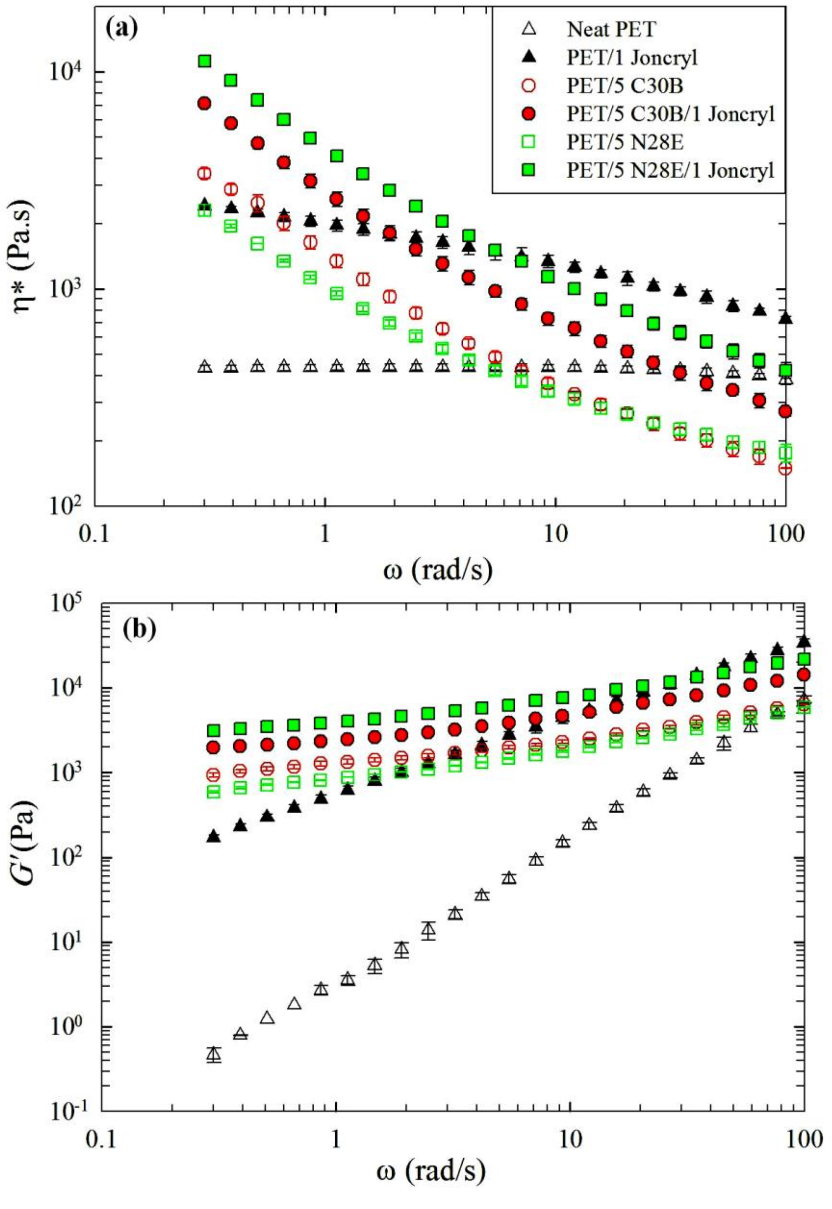

Figure 1 Complex viscosity (a) and storage modulus (b) as functions of frequency for the neat PET and PET nanocomposites with and without Joncryl.

NANOSTRUCTURED THERMOSETTING SYSTEMS DESIGNED USING BLOCK COPOLYMERS AS TEMPLATE FOR THERMO-, PHOTO- AND ELECTRO-RESPONSIVE MATERIALS

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In this work different block copolymers (BCP) were used as templates for generating nanostructured epoxy or unsaturated polyester matrices with long range order structure. Both amphiphilic [1-4] and epoxydized BCP [5] consisting of thermoset-miscible and thermoset-immiscible blocks were used to obtain nanostructured thermosetting systems, which act as template for designed thermo-, photo- or electro-responsive materials. Low molecular weight liquid crystals [1, 6-8], azobenzenes [4] and TiO_2 nanoparticles [1-3] were used as ternary component in order to develop novel nanostructured materials, which can respond to the external stimuli such as temperature, electrical field or laser beam.

The relation between morphology generated and thermo and electro-responsive properties of designed systems was investigated using atomic force microscopy (AFM). AFM images were obtained operating in tapping mode (Nanoscope IIIa scanning probe microscope (MultimodeTM, Digital Instruments) and Nanoscope IV (Dimension 3100, Digital Instruments)). The ability of alignment of low molecular liquid crystals and electrical properties of TiO_2 nanoparticles were studied by electrostatic force microscopy (EFM) (Nanoscope IV (Dimension 3100, Digital Instruments)) and tunneling atomic force microscopy (TUNA) (Nanoscope IV (Dimension 3100, Digital Instruments)). Additionally, electrical response of the nanocomposites was measured using a semiconductor characterization system (Keithley model 4200-SCS).

As show in the Figure 1 designed nanostructured thermosetting materials maintain properties of ternary components such as liquid crystals (LC), nanoparticles or azobenzenes that makes them interesting from the point of view of potential application in the field of thermo- and electro-optical devices, such as optical shutters, smart windows, optical sensors, memories and flexible display devices .

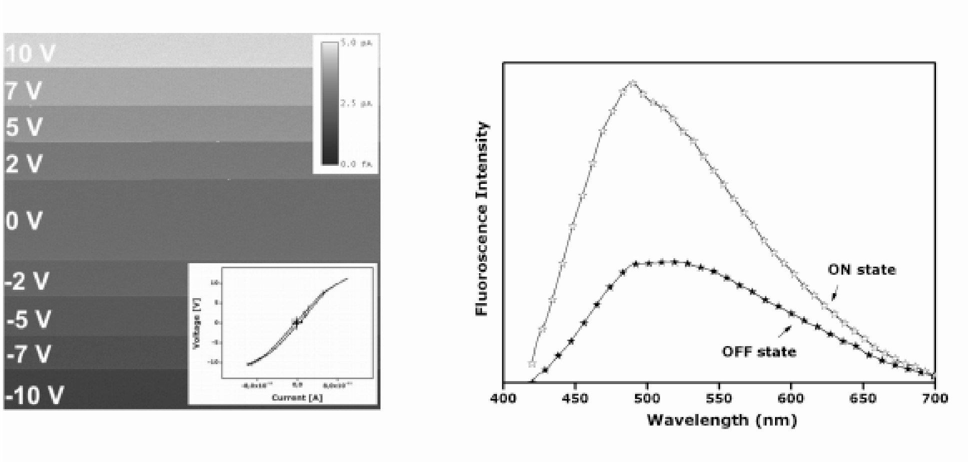

Figure 1. TUNA current map of the 1 wt % TiO_2/40 wt % LC-(DGEBA/MXDA) system obtained by applying different voltages. Fluorescence emission spectra of this system taken at 10 and 45 ºC

Acknowledgments

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SYNTHESIS OF NANOCOMPOSITE POLYURETHANE FOAMS BASED ON ORGANIC AND INORGANIC PHOSPHINATES

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Introduction The main aim of this work is to study the synergy between phosphinated flame retardants and layered silicates in polyurethane foams. Novel results on the synergism between organic phosphinates and ammonium modified clay on flame retardancy of PU foams will be reported and compared to the combined use of inorganic phosphinate and clays; moreover, also the effect of different clay amounts on the fire behavior and thermal stability will be considered.

Methods Polyurethane foams were prepared using a two steps procedure. A fixed amount of clays (3 or 5wt% on total foam mass) was dispersed in polyols mixture; clay dispersion was promoted using a microwave treatment[1]. After that, the catalysts, surface active agent, flame retardant (fixed amount, 10wt% on total foam mass) and blowing agent were added to the polyols mixture and stirred with a high speed mechanical stirrer. The isocyanate was added to this mixture; the components were mixed for 15 seconds and then poured into an open mould for free rise polymerization.

Characterization The thermal stability was studied by thermogravimetric analyzer, under air atmosphere with heating rate of 20°C min-1 from 25 to 800°C. Fire behavior was characterized by means of limiting oxygen index (LOI), according to ISO 4589, and cone calorimeter (CC) test according to ISO 5660.

Results: Fire behavior The use of both organic or inorganic phosphinate is very effective in enhancing LOI; however, inorganic phosphinate showed better performance. No significant effect of the nitrogen-based synergic compound can be seen. Moreover, further addition of layered silicate to phosphinates led to no significant variation, as already reported by other authors for analogous systems[2]. The cone calorimeter results shows very low ignition time (1s) for all samples tested because of the cellular structure of the material and the high radiant heat flux (50 kW/m2). After ignition, all materials exhibited a sharp increase in the heat release rate (HRR) until a first maximum was reached (peak of heat release rate, PHRR). The first PHRR was followed by a second peak, with lower intensity. The second peak was ascribed to the combustion process of an intermediary decomposition product or intermediary char. The use of phosphinates, both organic and inorganic, led to a decrease of the first PHRR more or less marked: the better results were obtained for IPA filled foams (Figure 1).

Conclusions For all analysed nanocomposite foams, the use of ammonium modified nanoclays seemed to depress gas phase activity, enhance the development of partly combusted products and increase the smoke released (TSR), thus showing no synergistic effect.

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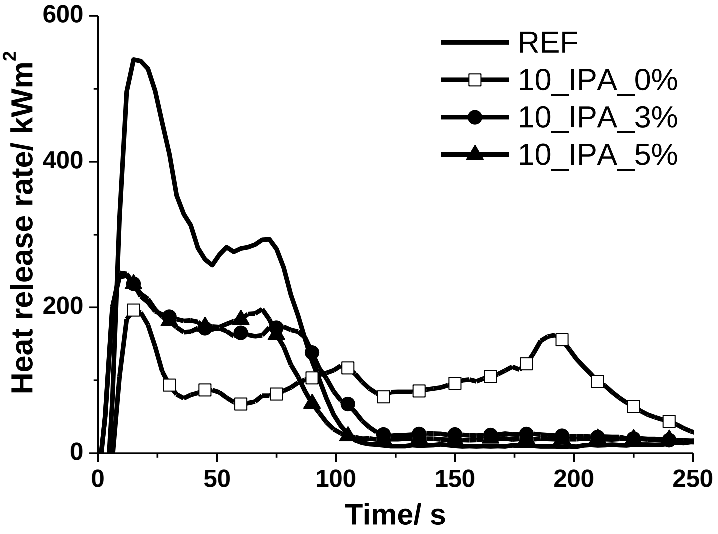

Figure 1 Heat release rate (HRR) for unfilled (REF) and IPA filled PU foams.

UNSATURATED POLYESTER-BASED HYBRID NANOCOMPOSITE

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The excessive ability of unsaturated polyester resin (UP) in meeting end-use necessities has been a consequential motivation in its extensive growth. The low resistance against crack propagation and high volume shrinkage of UP are the most important drawbacks for its widespread applications. The use of layered silicates such as organically-modified montmorillonites (OMMTs) as reinforcement and rubber materials as toughener are approaches to decline the above deficiencies [1-2].

In this research work, unsaturated polyester resin (UP) was reinforced by using an organically modified montmorillonite (OMMT) and toughened with core–shell rubber (CSR) particles. The effects of OMMT and CSR contents on the fracture behavior and tensile properties of UP have been investigated. The results showed that the incorporation of OMMT up to 3 wt% increased the UP fracture toughness (K_{IC}) on some extent, when further addition caused the fracture toughness to reach a constant level (Table 1). Dispersion state of OMMT platelets and CSR particles inside UP matrix were studied by using transmission electron microscopy (TEM) apparatus. TEM micrographs showed a good dispersion of organoclay tactoids with an intercalated structure or partial exfoliation for the UP reinforced by 1 and 3 wt% OMMT (Fig. 1). On the other hand, the addition of 5 and 10 wt% CSR particles to the UP increased the fracture toughness much more than the OMMT enhanced. Locally clustered but globally good CSR particle dispersion inside the UP matrix was observed for toughened UP specimens. Interestingly, a synergistic effect in fracture toughness was only observed for UP hybrid composite contains 1 wt% OMMT and 10 wt% CSR particles, when compared to other reinforced, toughened, and hybrid specimens. In this case, the OMMT platelets act as bridges between small rubber-particle agglomerates, which may accelerate the CSR particle cavitation and plastic deformation inside UP matrix. The incorporation of

OMMT increased Young’s modulus and also, decreased the tensile strength of the neat and CSR-toughened UP specimens with increasing the amount of OMMT.

Table 1. Fracture toughness and tensile properties

Code	OMMT (wt%)	CSR (wt%)	K_{IC} (MPa.m$^{1/2}$)	E (GPa)	σ (MPa)
UP	**0**	**0**	**0.890**	**2.30**	**42.70**
UPC1	**1**	**0**	**0.979**	**2.58**	**36.70**
UPC2	**2**	**0**	**1.059**	**2.58**	**34.60**
UPC3	**3**	**0**	**1.184**	**2.67**	**31.60**
UPC5	**5**	**0**	**1.166**	**2.81**	**29.46**
UPR5	**0**	**5**	**1.264**	**2.19**	**34.60**
UPC1R5	**1**	**5**	**1.224**	**2.51**	**34.16**
UPC2R5	**2**	**5**	**1.090**	**2.53**	**33.30**
UPC3R5	**3**	**5**	**1.104**	**2.65**	**30.74**
UPR10	**0**	**10**	**1.700**	**2.30**	**29.46**
UPC1R10	**1**	**10**	**2.189**	**2.58**	**32.02**
UPC2R10	**2**	**10**	**1.727**	**2.60**	**31.17**
UPC3R10	**3**	**10**	**1.179**	**2.70**	**30.74**

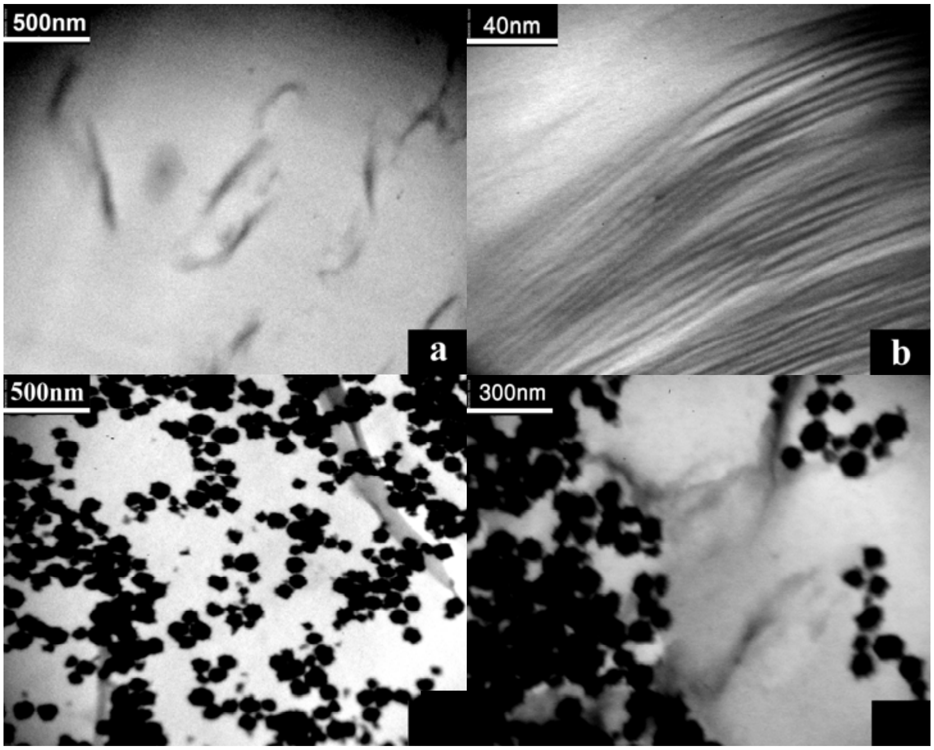

Figure 1. TEM micrographs of: (a, b) 1 wt% OMMT reinforced, (c) 10 wt% CSR toughened UP specimens, and (d) UP/OMMT/CSR hybrid nanocomposite.

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MODELING THE FATIGUE BEHAVIOR OF GLASS FIBER REINFORCED THERMOPLASTIC AND THERMOSETTING MATRICES

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The flexural fatigue behavior of continuous and short glass reinforced composites was investigated under four-point bending loading. The effect of mean stress and stress amplitude was identified. It was found that the fatigue life decreased rapidly with the decreasing stress ratio (i.e. the ratio between the minimum and the maximum stress). Further, the specimen lifetime for any loading mode increased with: (a) decreasing load range and decreasing stress ratio and (b) decreasing mean load and increasing stress ratio. From the above observations a brand new two-parameter model based on strength degradation was developed accounting for both the mean load and the load range, in order to express analytically the strength variation during fatigue cycle evolution.

NANOSTRUCTURED POLYMERS, BLENDS AND COMPOSITES

Full Abstracts of Poster Presentations

SYNTHESIS, KINETICS AND CHARACTERIZATION OF POLY(2-HYDROHYETHYL METHACRYLATE) BASED NANOCOMPOSITES

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1. INTRODUCTION

Dispersing nanometer-scale inorganic particles in a polymer matrix offers the potential of creating new materials, the properties of which arise from the synergies between the components[1]. While it is notoriously difficult to achieve a homogeneous distribution of nanometer-scale particles in highly viscous polymer melts, and aggregation of the particles cannot be avoided, dispersion in a suitable monomer followed by polymerization in situ is an attractive alternative route. It is tacitly assumed that inorganic particles are not interfering with the mechanism of free radical polymerization; however, it has been shown that this is not true, for example in the bulk polymerization of methyl methacrylate in the presence of nano-montmorillonite[2]. As a continuation to this work, synthesis of poly(2-hydroxyethyl methacrylate) based nanocomposites is investigated here using the in situ polymerization technique with dispersion of the nanoparticles into the monomer and subsequent bulk polymerization. Nano-fillers investigated include modified silica, organomodified montmorillonite (OMMT) and carbon nanotubes. The effect of the type and amount of the nanofiller on the reaction kinetics was investigated using DSC by recording the amount of heat released versus time under isothermal conditions and eventually calculating the time evolution of polymerization rate and monomer conversion. The final nanocomposites were characterized according to their structure using FTIR, their morphology with WAXD and TEM, their MWD with GPC, their glass transition temperature with DSC and their thermal stability with TGA.

2. EXPERIMENTAL

For the preparation of the nanocomposites, commercial OMMT clay, Cloisite 15A was used and kindly provided by Southern Clay Products Inc. (Texas/USA). The initial mixture was prepared by dispersing the appropriate OMMT in the monomer HEMA by adequate magnetic and supersonic agitation. In the final suspension the initiator benzoyl peroxide was added and the mixture was degassed by passing nitrogen and immediately used. The bulk free radical polymerization was investigated using the DSC-Diamond (Perkin-Elmer). The reaction exotherm at a constant temperature was recorded as a function of time. The rate of heat release measured by the DSC was converted into the overall reaction rate. A detailed description of the experimental procedure can be found elsewhere[2]. Following, the samples were cooled to 20°C and their glass transition temperature was measured by heating to 180°C. The final hybrid materials were characterized using XRD, FTIR, GPC and TGA.

3. RESULTS AND DISCUSSION

Indicative results of the effect of temperature and amount of OMMT on the conversion versus time curves appear in the following figure 1.

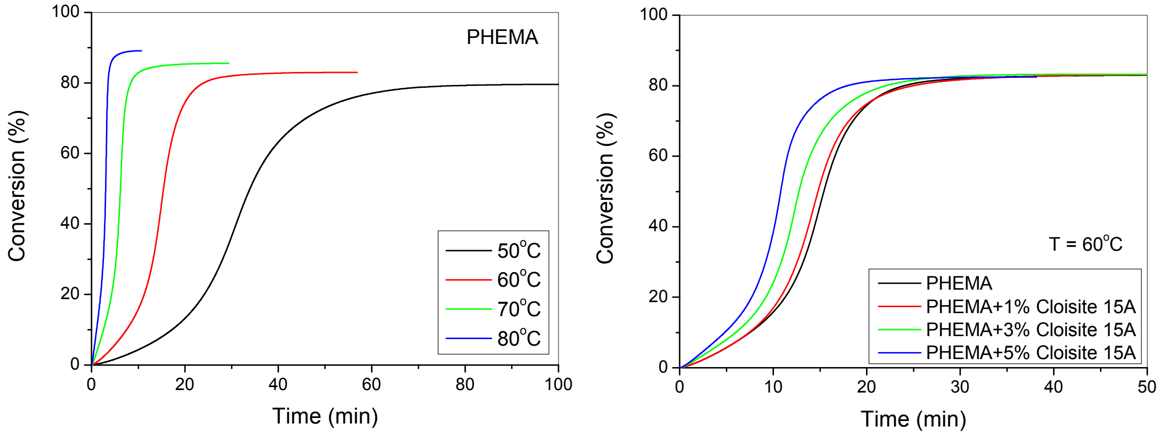

Figure 1: Effect of temperature and amount of Clay on the variation of conversion with time

Similar results were obtained when different types of nano-filler were used. Furthermore, from TGA measurements it was clear in all types of nano-filler, a shifting of the degradation curves to higher temperatures.

4. CONCLUSION

It was found that the type and amount of the nano-filler affect polymerization kinetics when strong diffusion controlled phenomena take place, while thermal stability of all nanocomposites is enhanced.

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PROPERTIES AND MORPHOLOGY OF PA BASED FILAMENT LOADED WITH MW-CNTS: EFFECT OF FILLER ASPECT RATIO AND SURFACE FUNCTIONALIZATION

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The addition of carbon nanotubes in various polymeric matrices leads to obtaining high-performance nanocomposites with mechanical, optical and electrical properties significantly higher than those of the neat matrix. However, in order to obtain nanocomposites with increased properties and performance is necessary to achieve a good distribution of the nanofiller within the matrix. The dispersion at nanometric scale in not easier because of their high interfacial area and of their incompatibility with the polymeric matrix[2]. To enhance the chemical affinity/compatibility between the nanoparticles and the polymeric matrix various reactive groups able to interact with the groups present on macromolecules are grafted onto the surface of carbon nanotubes[3]. The effect of elongational flow on the morphology and final properties of nanocomposites with the addition of carbon nanotubes has been studied by our research group[4] and the results obtained suggest that the elongational flow is effective to modify the morphology of nanocomposite polymer-carbon nanotubes, being able to align the nanofillers along the direction of stretching. In this work, the effect of CNTs aspect ratio and surface functionalization on the mechanical behaviour and morphology changes of polyamide based fibres is investigated. Composites are prepared by melt blending carbon nanotubes with PA, followed by melt-spinning. The purpose is to study how the different geometry and different functionalization interfere with the action of the elongational flow in obtaining nanocomposite having good mechanical properties. In Figure 1 the elastic modulus E and the two-dimensional SAXS patterns for unfilled PA and all CNTs filled PA fibres both as spun and drawn are reported. All used CNTs kinds exert reinforcement effect of the PA matrix, and in fact, the increase of the mechanical properties and dimension stability are more pronounced for highly oriented filaments. The achieved mechanical improvements and dimensional stability of the PA-based filaments follow the sequences: CNTs(l) > CNTs(th) > CNTs(uth). Moreover, CNTs(l) having large outer diameter, i.e. lowest aspect ratio show a great ability in orientation along the flow direction, while, the CNTs(th) and CNTs(uth) show the waviness in both condition before and after drawing. Additionally, the presence of functional groups onto the CNTs surface also hinders the nanotube orientation along the fibre direction because some interaction between functional groups presented both in the macromolecules and onto the nanotube surface occurs.

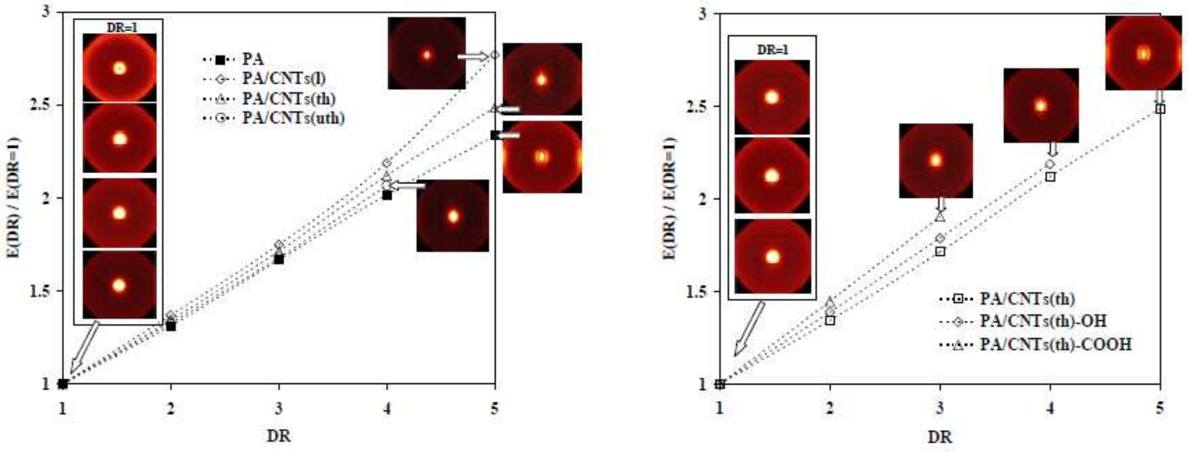

Figure 1 Dimensionless elastic modulus as a function of the draw ratio and SAXS patterns of unfilled and CNTs filled PA fibres

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EFFECT OF ORGANOCLAY ON MORPHOLOGY AND PROPERTIES OF BIO-BASED BLENDS OF PLA/PA11

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The present work is focused on the design of “engineerized” fully bio-based polymer blends with high amounts of Poly(lactic acid) (PLA) for technological applications at high temperature. The poor heat resistance and the inherent brittleness of PLA has been tackled by blending it with Polyamide 11 (PA11), a tough bio-polymer with good high temperature mechanical properties owing to its semicrystalline nature. Nanoparticles were added to manipulate the blend microstructure. Specifically, we aim at driving the localization of filler towards specific regions of the blend in order to convert drop-matrix morphologies into stable co-continuous ones with at low amounts of PA11. This is expected to radically improve the high temperature creep resistance owing to the interpenetration of the semicrystalline PA11 with the amorphous PLA [1, 2].

The PLA (2002D) was kindly supplied by NatureWorks. The PA11 (Nylon 11) was purchased from Sigma Aldrich. The filler is an organo-modified montmorillonite (OMMT, Cloisite 30B) from Southern Clay Products. Virgin and filled blends (PLA/PA11 70/30 and PLA/PA11 70/30 with 6 wt.% of OMMT) were prepared by melt-compounding the constituents using a micro co-rotating twin-screw extruder under nitrogen atmosphere at temperature T=215°C, average shear rates of ~50 s^{-1} and residence times of ~1 min. The extruded materials were compression-moulded in rectangular bars at T=215°C and pressure P=40 MPa for 5 min. Dynamic-mechanical thermal analysis (DMTA) were carried out using a Tritec 2000 DMA in single cantilever bending mode at a frequency ω=1 Hz, total displacement of 0.02 mm and heating rate of 2°C/min. Creep thermo-mechanical analysis were carried out in three point bending mode with a heating rate of 2°C/min under a load of 0.455 MPa.

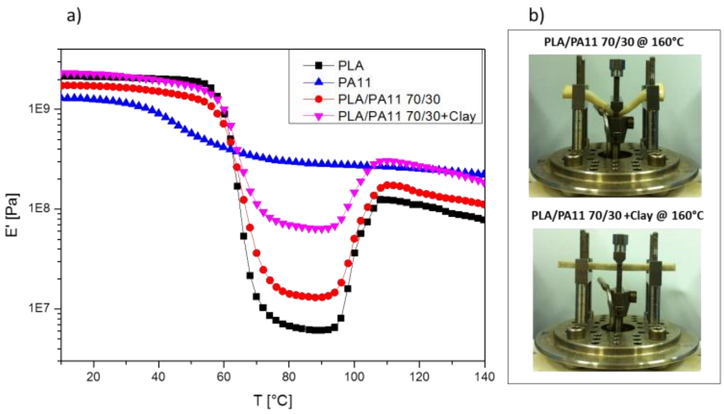

Figure 1 (a) E' vs. T curves for the samples; (b) Samples at the end of creep experiments.

The temperature dependence of the storage modulus, E', is plotted in Figure 1 (a) for the pure polymers and the neat and filled blends. The neat polymers share comparable glass transition temperature T_g, the drop of E' above the T_g being less pronounced for the PA11. The E' of PLA starts to increase at ~95°C because of cold crystallization. The overall shape of $E'(T)$ of unfilled blend PLA/PA11 70/30 looks like that of the major PLA phase owing to the globular morphology of the blend. Conversely, adding the filler to polymer blend causes a significant enhancement of E', especially in the high-temperature region. Besides the well-know reinforcing action of the nanoparticles, we believe that such an increment is due to the morphology transition from a sea-island structure to a co-continuous one induced by the organoclay. Despite the softening of the PLA matrix, which starts to flow aproaching its melting point (140÷160°C), the continuous framework of clay-rich PA11 phase serves as a mechanical scaffold until melting at T above 160°C [1, 2].

Our results show that the synergism between the reinforcing action of the filler and its ability to affect and stabilize the blend microstructure results in fully bio-based nanocomposite polymer blends with improved heat resistance. Analyses are currently in progress to evaluate the impact of the morphology change on the photo-oxidation resistance of the studied blends.

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NANOSTRUCTURED HYDROPHILIC HYDROPHOBIC AEROGEL AS HIGHLY EFFICIENT VOCS SORBENT

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Syndiotactic polystyrene (s-PS) is a cheap and robust commercial thermoplastic semicrystalline material. Particularly attractive for industrial applications are the nanoporous crystal form of sPS (delta). These crystal phase presents well-defined empty spaces distribute into the crystal lattice as cavities.[1] This crystalline form is able to rapidly absorb volatile organic compounds (VOCs) from air and water.[2] In order to increase the sorption kinetics of VOC, high porosity s-PS aerogels were prepared by removing the solvent from thermoreversible gels by using supercritical CO_2.[3] The advantage of using a supercritical extraction process to remove the solvent from the gel is the absence of surface tension and in these conditions a supercritical solution is formed between supercritical CO_2 and liquid solvent. Thus, it is possible to extract the solvent from the gel without collapsing the structure and the dimensions of a sPS gel remain unchanged during the supercritical CO_2 extraction and total removal of the solvent initially present in the gel.(Figure 1). The sorption kinetics of VOC from diluted aqueous solutions in aerogels with nanoporous crystalline phases can be further increased through a sulfonation of the sPS amorphous phase.[4] Indeed, as a result of the sulfonation, the aerogel becomes highly hydrophilic (Figure 2) allowing thus a faster diffusion of the VOC inside.
Figure 3 shows the comparison of sorption kinetics for three δ-form s-PS aerogels presenting different degrees of sulfonation of the amorphous phase (0; 2 and 7%) it's clear that the sufonation procedure of aerogels increases the their apparent diffusivity (D), in particular for the aerogel with only a degree of sulfonation S=7% there is an increase in dichloethane (DCE) sorption diffusivity of more than a magnitude order.

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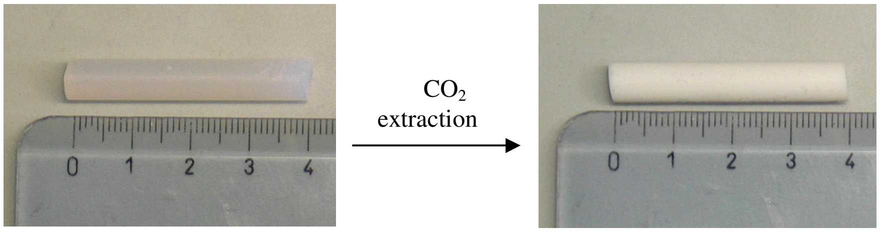

Figure 1. Photographs of a piece of sPS gel prepared in toluene before and after total solvent extraction with supercritical CO_2.

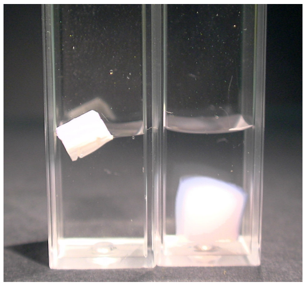

Figure 2. Photographs of a piece of s-PS aerogel dipped in water before (left) and after (right) sulfonation

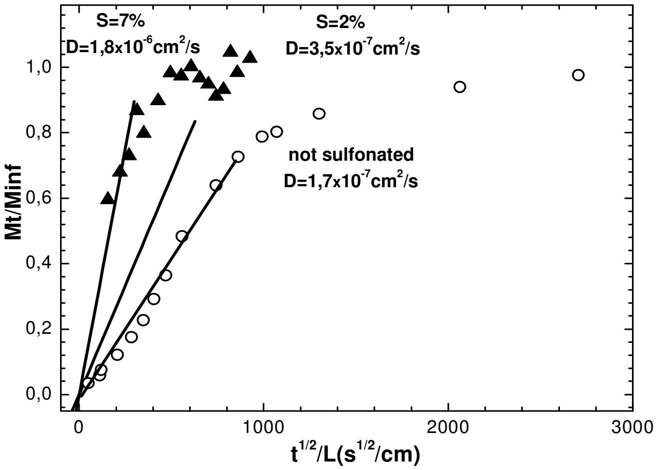

Figura 3. Sorption kinetics at room temperature of DCE from 100 ppm aqueous solutions, presenting different degrees of sulfonation of the amorphous phase

ON THE USE OF HYDROTALCITE IN PLA BASED COMPOSITES

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The interest in polymeric materials from renewable sources has been continuously growing both in the academia and in industry, due to the increasing need for differentiation of energy resources and reducing their environmental impact. In this context, poly(lactid acid) (PLA) becomes highly attractive for a substitution of fully petrochemical based polymers.

On the other hand, the large scale application of PLA is often limited by its mechanical and its barrier to gases and vapours. The addition of small amounts of lamellar nanoparticles as hydrotalcites (HT) in a polymer matrix can remarkably improve the mechanical properties of the matrix and enhance the barrier properties of these materials. However, the improvements of these properties depend on the nature of the final morphology of the material, the control of the dispersion and on the dimensions of the particles.

Aim of this work was to study the effect of the compounding methods on the morphology and on the properties of PLA-hydrotalcite composites. Moreover the influence of two different kinds of hydrotalcites – organically modified and not modified – and their concentration was evaluated. The filled materials were prepared using either a single screw extruder (SSE), a counter rotating twin-screw compounder (TSC) or a corotating twin-screw extruder (TSE).

The prepared materials were characterized by SEM, GPC analisys, mechanical and rheological measurements, The best morphology is exhibited by materials prepared with the corotating twin-screw extruder while the worse one by the samples processed with the single screw extruder. The increase of the hydrotalcite concentration leads to a worsening of the morphology, i.e. an increase of aggregates and worse dispersion. However the materials containing the organic modified filler show a better morphology. The viscosity of all the material containing the HT is lower in comparison with the viscosity exhibited by neat matrix in particular when the modified HT is used as showed in figure 1 in the case of the materials prepared with TSE. This is probably due to degradation phenomena occurring during the processing of the materials as revealed by the results of GPC analysis and by measurements of intrinsic viscosity.

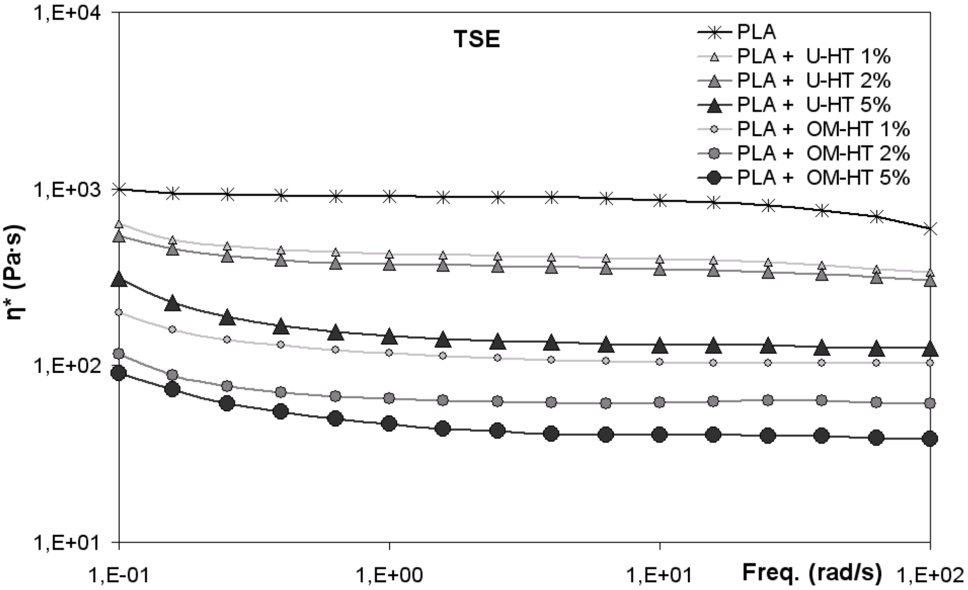

Figure 1 Complex viscosity as function of frequency for the materials prepared with TSE.

As regards the mechanical properties, the addition of HT caused only a slight increase of elastic modulus of filled materials even if the 5% of filler was incorporated. The tensile strength of the filled materials decreased if compared with the neat PLA, while the elongation at break is almost the same. Probably, the improvements that should be related to dispersion of the nanofiller in the systems are counterbalanced by degradation of matrix as reported for similar systems.

However, in full agreement with morphological analyses, the best performances were exhibited by materials prepared with the TSE while the worse ones by the samples processed with the SSE.

INNOVATIVE BIOCOMPOSITES BASED ON POLYLACTIC ACID AND LIGNIN: STRUCTURE AND PROPERTIES

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INTRODUCTION

The biopolymer sector still represents only a very limited share of the global market, however it is expected to have a huge potential for the future, due to the countless applications that polymers have gained in our society. Polylactic acid is a thermoplastic biodegradable and compostable polymer that can be made from annually renewable resources. Lignin is a natural amorphous polyphenolic macromolecule inexpensive and easily available.

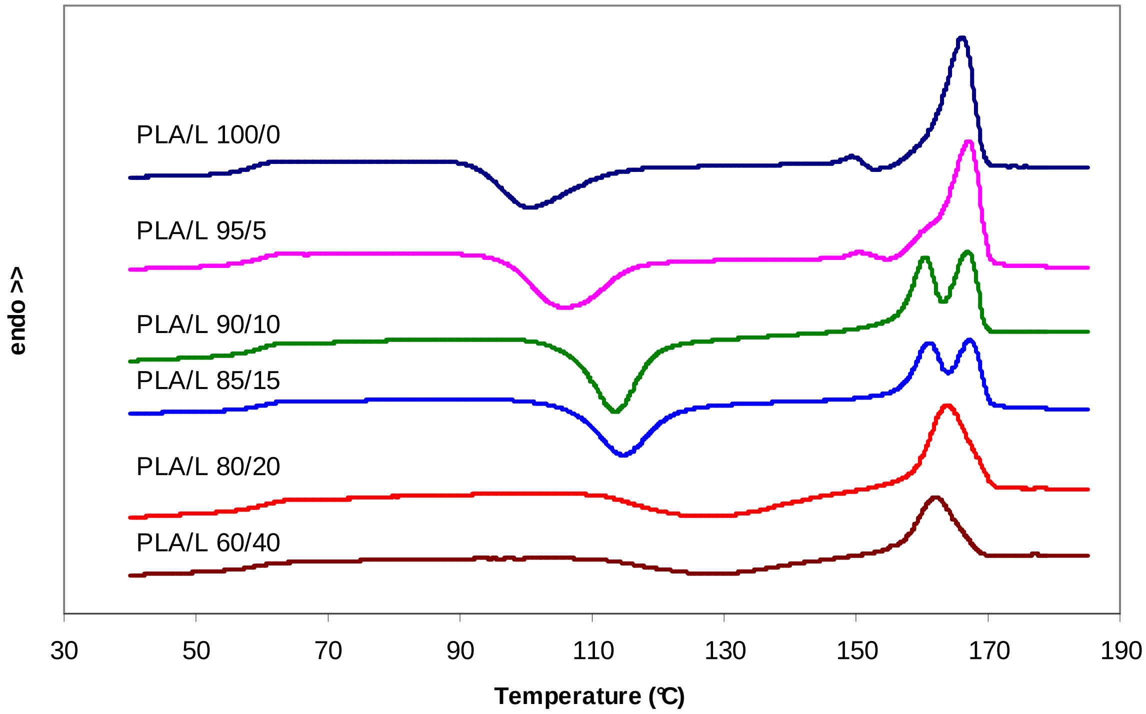
In the present study polylactic acid (PLA, NatureWorks, Ingeo 3251D) and acetylated lignin (hydrolitic lignin Aldrich acetylated in pyridine: acetic anhydride, 1:1) biocomposites were prepared by casting from chloroform solution to enable interactions at molecular level between lignin and biopolymer matrix. Structure, morphology, thermal properties and thermal degradation behavior of the PLA biocomposities containing from 5 to 40 wt.% of lignin, were investigated.

RESULTS AND DISCUSSION

Polarized optical microscopy carried out on the biocomposites showed a homogeneous distribution of lignin particles in the polymer matrix.

PLA can crystallize from the melt in the α and α’ forms, depending on the adopted crystallization conditions. During the annealing of PLA the transformation from α’ to α takes place via solid phase transition. The presence of the lignin in the biocomposites can interfere with the crystal transformation process.

The thermal behavior of PLA is influenced by the presence of the lignin. DSC scans of PLA and biocomposites quenched from the melt, show a glass transition, a cold-crystallization event and a complex melting region, constituted of several transitions. The cold crystallization shifts to higher temperature with increasing the lignin content in the biocomposite. The multiple melting profile changes as a function of the composition. The glass transition temperature of the biocomposites is not affected by the lignin presence.



DSC heating scan of amorphous PLA/Lignin biocomposites.

The PLA crystallizes from the melt in a typical spherulitic morphology. In the biocomposites the addition of lignin causes a decrease of the spherulite radial growth of the PLA.

The effect of the lignin presence on the stability of the biocomposites was studied by means of TGA carried out under inert and oxidative conditions. In general, the thermal decomposition temperature decreases with increasing the amount of lignin in the biocomposite, while the char yield is proportional to the lignin content. The positive barrier effect due to the char residue was evidenced in thermo-oxidative degradation.

Acknowledgment. The authors thank Regione Lombardia for financial support of the project "VeLiCa – From ancient crops, materials and products for the future".

PREPARATION AND CHARACTERISATION OF UHMWPE/MODIFIED NANO-SIO2 COMPOSITES

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Excellent properties in terms of wear, fatigue and fracture resistance have made ultra high molecular weight polyethylene (UHMWPE) the material of choice in a number of applications in which low frictional coefficients and high abrasion resistance are required[1]. Filling with nano-powder can improve mechanical properties of polymers, however due to the extremely high viscosity of molten UHMWPE, the pristine powder is effectively processed only by compression moulding, rendering the filling with other materials to make a composite a challenging task. In this work we dispersed SiO_2 nanoparticles modified on the surface with vinyl groups, with the aim to render them reactive with the free radicals formed into UHMWPE during the e-beam irradiation.

We used a GUR 1020 UHMWPE (Ticona), filled with Silicon Dioxide Nanoparticles (Sigma–Aldrich, spherical particles: Ø=15–20 nm, density: 2.2 g/cm^3, specific area: 140–180 m^2/g). Vinyltrimethoxysilane (VTMS, Sigma Aldrich) was used as received as silane coupling agent. The preparation of the composite proceeded in four steps: in first place, we performed the functionalization of nanosilica surface with VTMS by sol-gel process; secondly, we dispersed both the UHMWPE powder and the modified nanosilica (1% wt) in acetone and the resulting suspension was ultrasonicated in a water bath for 1 hour, using low power at room temperature, in order to favour an uniform mixing; then the solvent was evaporated and the mixture was compression molded into a sheet of 1cm thickness, using a Saspol T60 hydraulic press. The whole sinter cycle took about 6 h and reached a maximum temperature of 200 °C and a pressure of 100 bar. Finally, the composites were e-beam irradiated to 60 or 120 kGy (Bioster SpA, Seriate, IT) to promote the formation of chemical bonding between the matrix and the filler.

The characteristic FTIR absorption bands of the modifier[2] (C=C stretching and bending at 1602 and 1410 cm^{-1}, respectively) were absent in the spectra of the resulting composites, indicating that grafting of the modified nanosilica via radical reaction had likely occurred during processing of the composite, prior to irradiation. Irradiation caused further cross-linking of the polymer matrix, via the reaction between the remaining vinyl double bonds and the alkyl radicals generated during irradiation.

Tensile testing supported this observation (Figure 1): the composite exhibited increased yield strength, decreased elongation at break and a general increase in strength at the same elongation, when compared to pure polyethylene. The same trend was observed after irradiation of both polyethylene and composite.

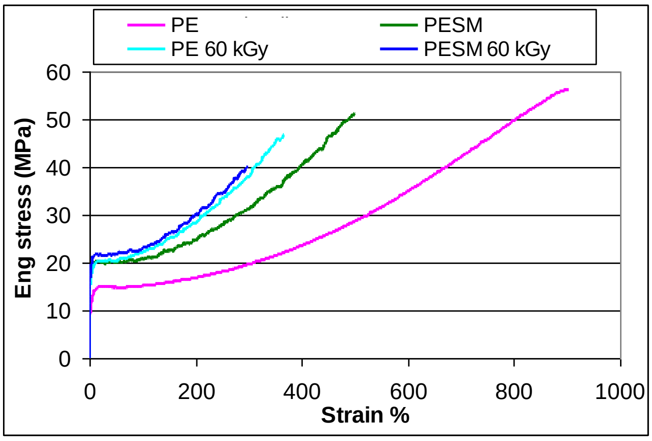

Figure 1: Tensile testing of virgin polyethylene and polyethylene-modified silica composite, before and after e-beam irradiation.

TGA was used to assess the thermal stability of the composites both in inert and oxidizing environment. While no significant differences were observed in nitrogen atmosphere, the composite showed a slightly lower stability to thermal degradation in air, when compared to the virgin polymer. A further slight destabilization effect was noticed on both the polymer and the composite at increasing irradiation doses. However, the formation of a more stable residue was also observed during the first degradation step.

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EFFECT OF DIFFERENT ORGANIC MODIFIERS ON THE CRYSTALLIZATION KINETICS OF POLY(3-HYDROXIBUTYRATE) NANOCOMPOSITES BASED ON MODIFIED CLAYS.

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Poly(hydroxybutyrate) (PHB) is produced as intracellular storage materials by different types of microorganisms from renewable sources. Not only they are biodegradable and biocompatible, but they can also be produced by bacterial fermentation from renewable resources like cane sugar[1].

Films of PHB and its nanocomposites with the addition of 4% of different commercial clays (CNa^+, C93A, C15A) were obtained by casting process[1]. Thermal behavior and crystallization kinetics were performed using a Perkin-Elmer Pyris 1 DSC. Isothermal crystallization experiments were done by heating the sample from -30°C to 195°C at a scanning rate of 30°C/min and holding it temperature for 1 min. Then, the sample was quenched to a desired isothermal crystallization temperature, Tc.

The effective activation energy was calculated through the model-free isoconversional method, which accounts for their dependence on the whole range of the relative degree of crystallinity[2]. Isoconversional analysis was performed by modifying the Equation 1 for an isothermal process, obtaining the Equation 2:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = \left[\frac{\partial \ln(k(T))}{\partial T^{-1}}\right]_{\alpha} + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_{\alpha} \qquad \text{Eq. (1)}$$

$$\ln t_{\alpha,i} = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E_{\alpha}}{RT_i} \qquad \text{Eq. (2)}$$

where $g(\alpha)$ is the integral form of the kinetic model, t is the time, T is the temperature, A is a constant, R is the gas constant and $E\alpha$ is the isoconversional effective activation energy. From the slope of the plot of $\ln(t_{\alpha,i})$ vs $1/T_i$, E_α values of the samples were obtained at each α, without assumption of a kinetic model. Figure 1 describes the variation of the activation energy of PHB and its nanocomposites with the relative degree of crystallinity. The effective activation energy of PHB, PHB +4%CNa$^+$ y PHB +4%C93A increase with the relative crystallinity, in a similar way. Instead, the activation energy of nanocomposite with C15A remained almost unchanged with the degree of crystallinity. However, its value of the effective activation energy is the highest at the beginning of the crystallization process. This could be associated with a decrease in the diffusion rate of polymer molecules[3] in the most tortuous morphology due to the good dispersion of C15A in the PHB, as it was observed in the DRX patterns.

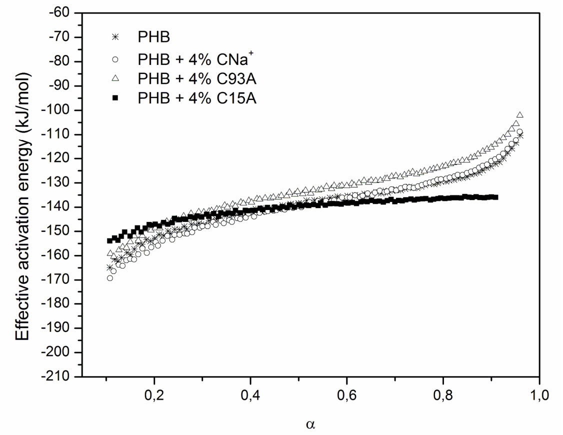

Figure 1 Activation energy of PHB and its nanocomposites varying with relative crystallinity.

It can be concluded that the incorporation of the C15A clay decreases the crystallization rate of PHB chains, without increasing the level of crystallinity. It was related to the best dispersion of this type of clay in the polymer. So, the crystallization kinetics was greatly affected by the structure and dispersion of the clay. Different type of clay organic modifiers results in different effects on the crystallization behavior of PHB.

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BIODEGRADABLE POLYMER/NATURAL FIBER BIOCOMPOSITES: PROCESSING AND MECHANICAL PROPERTIES

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Introduction

Lower performance in mechanical properties is the main problem of some biodegradable polymers. The solution for that is the using of some filler to prepare composites[1-3]. Natural fibers like juta, sisal and curauá are one of the most used. However, during the composite preparation the length of the fiber is decreased because the high rate of shear on extrusion process. A coupled device extruder was used to prepare biocomposites made with natural fibers. This device was positioned after extruder matrix avoiding excessive fiber degradation. An injection machine was used to prepare bars according ASTM for mechanical properties analysis (tensile). The surfaces fractures of the biocomposites were analyzed by Scanning Electron Microscopy (SEM).

Experimental

The polymers used were poly(buthylene adipate-co-terephthlate) – PBAT and poly(lactide acid)/poly(buthylene adipate-co-terephthlate) – PLA/PBAT blend. Two types of biocomposites were prepared:

- Sisal and poly(buthylene adipate-co-terephthlate);
- Juta and poly(lactide acid)/poly(buthylene adipate-co-terephthlate) blend;

Fibers were mixed with the polymers by coupled device extruder and “fiber pellets” were obtained. Any treatment was done on fiber to improve the compatibility with the polymers. After that injection-moulded samples were produced using an injection-moulding machine with dimensions according to ASTM D638 for tensile tests (100mm/min). Extrusion and injection process were conducted at temperatures below 200 ^{o}C. Two compositions were prepared for each biocomposite. One of them using 100% of “fiber pellets” and the other using 50% of “fiber pellets” plus 50% of neat polymer. Mechanical analyses also were done with neat polymers.

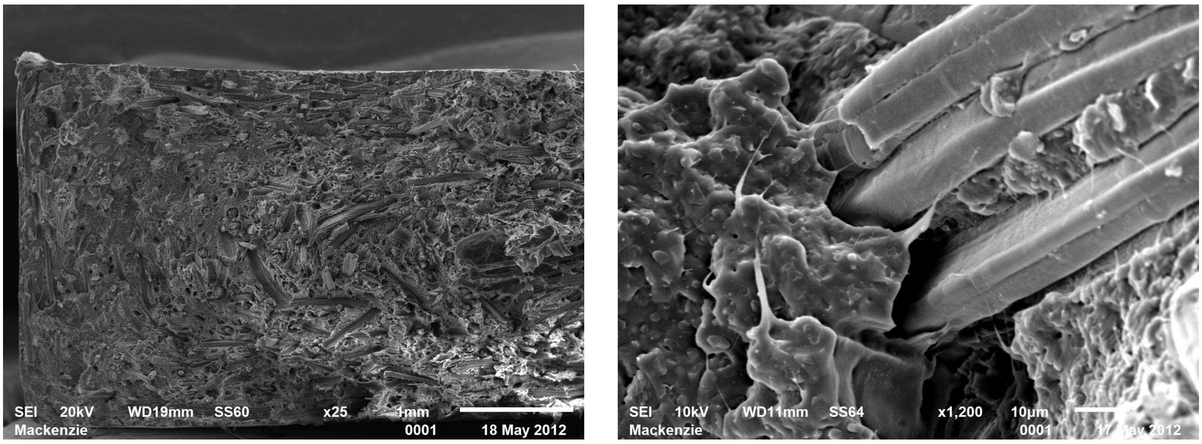
Results and discussion

The results from mechanical analysis are showed on Table 1. For both biocomposites the presence of natural fiber increase the elastic modulus and yield stress. At the same time the yield strain decreased. The major influence is observed for biocomposites prepared with only “fiber pellets”. These results indicate that sisal and juta fibers are good reinforcement for PBAT and PLA/PBAT blend. The increase of elastic modulus and yield stress for PBAT 100 compared with neat PBAT was 200 and 20%, respectively. In the case of PLA/PBAT 100 the values of elastic modulus and yield stress increased 77 and 13%, respectively, when compared with neat PLA/PBAT blend.

Table 1: Mechanical properties of neat polymers and biocomposites.

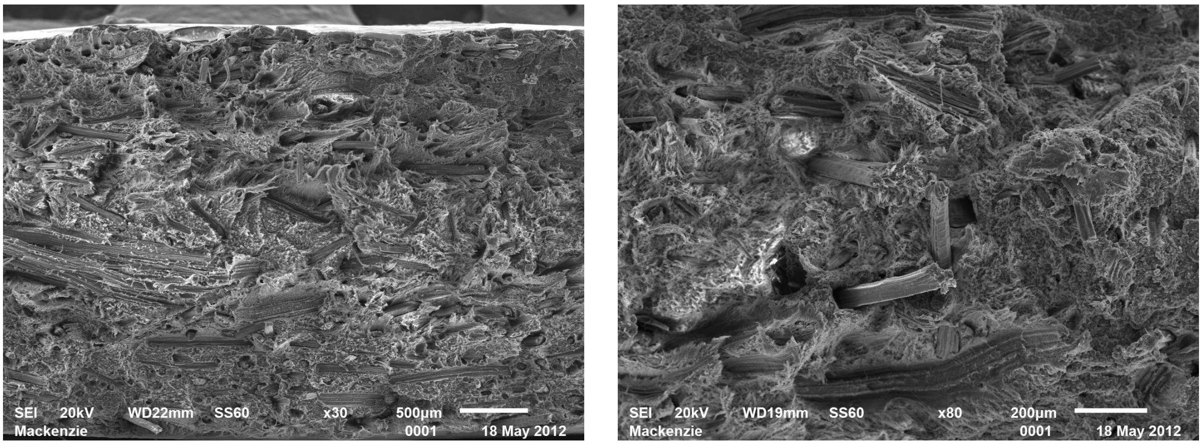
Sample	***Elastic Modulus (MPa)***	***Yield stress (MPa)***	***Yield strain (%)***
PBAT	80.3 ± 07.5	7.1 ± 0.5	20.6 ± 3.4
PBAT 50/50	122.0 ± 14.6	7.9 ± 0.6	11.8 ± 1.5
PBAT 100	236.6 ± 12.7	8.5 ± 0.2	9.0 ± 0.9
PLA/PBAT	825.8 ± 68.6	18.1 ± 0.7	6.8 ± 0.8
PLA/PBAT 50/50	867.5 ± 76.3	16.5 ± 0.3	5.6 ± 0.9
PLA/PBAT 100	1462.4 ± 204.1	20.5 ± 0.6	2.5 ± 0.3

The Figure 1 and 2 shows the surface fracture of PLA/PBAT 50/50 and PLA/PBAT 100, respectively. The Figure 1a depicts several holes that were left after the fibers are pulled-out from the matrix. Visible gaps can be found between fiber and polymer matrix in Figure 1b, suggesting poor interfacial adhesion. The same behavior can be seen for PLA/PBAT 100 biocomposite (Figure 2a and 2b).



(a) (b)

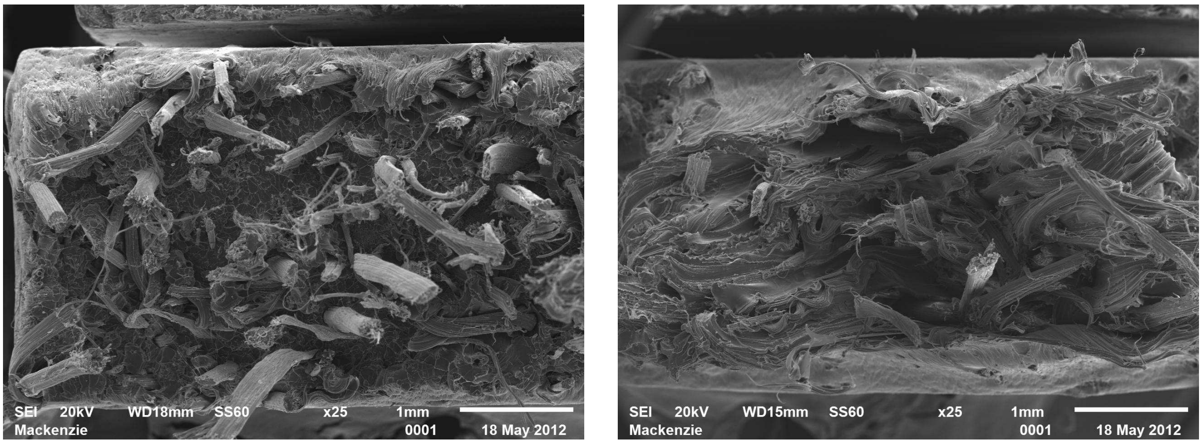
Figure 1 - SEM micrograph of tensile fractured surface of PLA/PBAT 50/50 biocomposite.



(a) (b)

Figure 2 - SEM micrograph of tensile fractured surface of PLA/PBAT 100 biocomposite.

The Figure 3a and 3b shows the surface fracture of PBAT 50/50 and PBAT 100, respectively. Unlike of PLA/PBAT biocomposite, a better adhesion between fiber and matrix is seen on PBAT biocomposite. This result justifies the better mechanical performance of PBAT composite.



(a) (b)

Figure 3 - SEM micrograph of tensile fractured surface of PBAT 50/50 (a) and PBAT 100 (b) biocomposite.

Conclusions

The mechanical properties of natural fiber biocomposites have been measured and evaluated. The presence of sisal and juta fibers improved significantly tensile properties of the PBAT and PLA/PBAT blend.

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MOD-0145

PROCESSING AND PERFORMANCE OF POLYMER NANOCOMPOSITES (PPNCs)

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Introduction

For a given size and configuration of a twin-screw extruder (TSE), the proper choice of the process variables is essential to ensuring that the process environment result in materials with optimal nano-structures without affecting adversely the chemistry of the constituents. This work examines in detail how changes in temperature and screw speed in a small TSE affect selected end-properties or PNCs

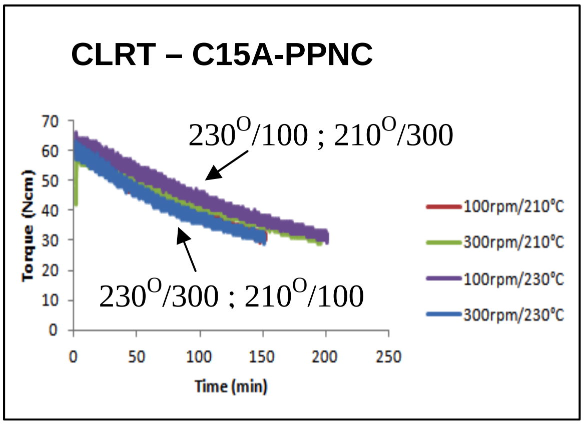
Experimental

Pre-mixed (at ambient conditions) dry blends of isotactic polypropylene (Lyndon-Basell iPP, MFI=12g/10min at 230°C), 5% w/w maleated-PP (Chemtura, MFI=120), 5%w/w organo-modified montmorillonite clays (Cloisite 15A, 20A) and a stabiliser system were processed in a 27 mm intermeshing co-rotating TSE at different temperatures (210/230°C) and screw speeds (100/300 rpm) with variable output rates (7-11 kg/h) while maintaining almost similar levels of motor power. The products were then subjected to testing and ageing to assess their mechanical and thermo-oxidative stability both in the solid (film, plaque) and melt states. Complementary techniques, e.g. spectroscopic (FTIR), thermal (DSC), microscopic (TEM), mechanical (impact) and rheological (closed loop recirculation test, CLRT), were used to elicit some ‘process’ variables – ‘product’ properties relationships.

Results and Discussion

Fig.1 shows a plot of torque generated, during CLRT in a micro-extruder (Haake), by the PPNC samples produced under the four different processing conditions used; changes in the torque (or relative viscosity) is used here as a guide to assessing the stability of melts under fixed conditions of shear ($355\ s^{-1}$) and temperature (190°C) with limited air ingress. **Fig. 2** shows the melt stability of the same samples determined using the standard DSC methodology for determining the oxidation induction time (OIT) of thin films under a flow of oxygen at 190°C. Results from CLRT indicate that for C15A-PPNCs, samples extruded at 100rpm/230°C and 300rpm/210°C show resilience and retain their viscoelasticity more than their counterparts produced at 100rpm/210°C and 300rpm/230°C (see Fig.1). Clearly, temperature (and its effects on viscosity and surfactant stability) and residence time (and its effects on the reaction chemistry and distribution/dispersion of nano-structures) are critical process variables that determine the ultimate properties of end-products.

Oxidation stability tests for the same samples portray (see Fig. 2) a different behaviour. Under the static test conditions (of OIT by DSC), the nature of melt surface in contact with oxygen (as against limited air ingress in CLRT) is critical; oxygen diffusion into the melt is mediated by changes in the nanoclay concentration (and migration depending on size and state of aggregation) at the surface during the test.



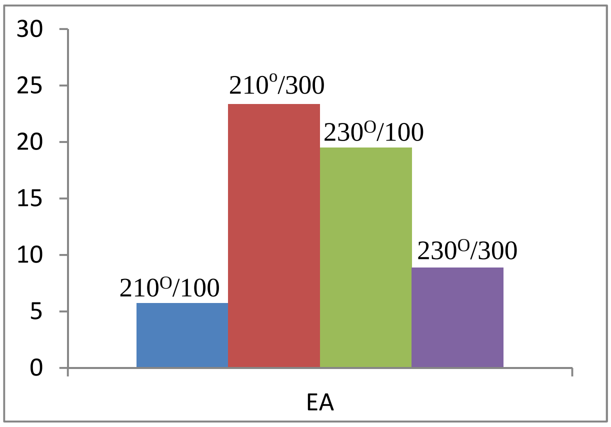


Fig. 1. Torque-time history for C15A-PPNCs

Fig. 2. OIT (min) for C15A-PPNCs

Conclusion

Temperature and residence time are critical parameters in TSE production of PNCs and a proper balance must be found to achieve target end-properties given an initial set of boundary conditions, i.e. TSE design and chemistry.

FLOW INDUCED COALESCENCE IN MOLTEN POLYMER BLENDS

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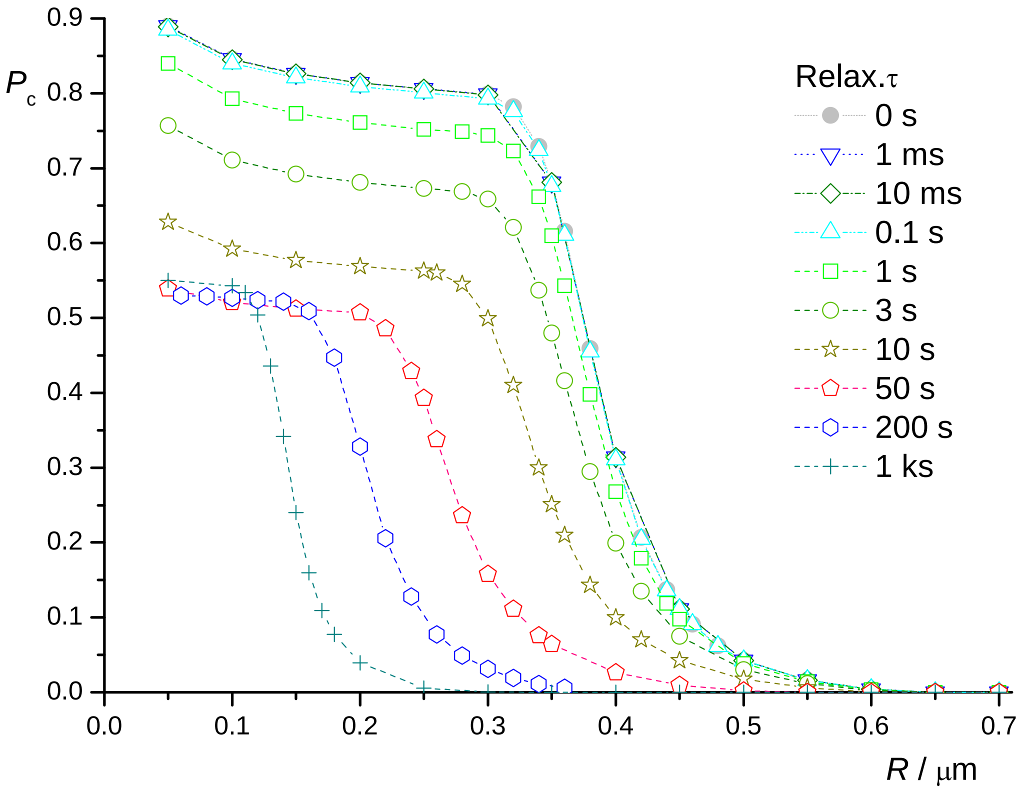
Introduction. Properties of polymer blends are given among other by their phase structure, which is controlled among other by the competition between the droplet breakup and coalescence. The course of coalescence can be split into four steps: Approach of the droplets, drainage of the matrix between the droplets, breakup of the matrix at critical inter-droplet distance, and shape relaxation of coalesced droplet. Our current research focuses on the second step of coalescence induced by flow. Both shape and size of the deformed droplets codetermine the final state of their approach. The effect of matrix drainage is quantified using the probability P_c that the collision of droplets, calculated for non interacting droplet pairs, will be really followed by their fusion. Theories considering drops keeping the spherical shape[1] or highly flattened shape[2] through the whole coalescence event or combining both approaches[3] were derived for Newtonian droplets in Newtonian matrix. Our recent papers[4] have proposed the theory combining the formulae describing approaching of strongly flattened and of spherical Newtonian droplets in viscoelastic matrix. We are now presenting the influence of a relaxation time on coalescence.

Results and discussion. Elasticity of the matrix does not change the shape of dependence of P_c on R. The increase in relaxation times τ_m decrease probability of coalescence P_c, as well as a critical droplet radius R_c from which P_c starts to decrease steeply. However, the P_c for small droplets (corresponding to P_c of rigid spherical droplets) seems to reach its limit value or even increase after reaching a minimum. The effect is not significant for $\tau_m < 1$ s, but it is pronounced for relaxation times in order of seconds. Substantial part of grades of commercial thermoplastics has $\tau_m < 1$ s. Therefore, the effect of elasticity on flow induced coalescence seems to be important only for systems with high molecular weight matrix.



Coalescence probability dependence on droplet radius for different relaxation times. Jeelani and Hartland model,... Shear rate 0.1 s^{-1}, interfacial tension 1 mN/m, viscosities of both phases 1 kPa.s, $h_0/R = 0.3$, $h_c=5.10^{-9}$ m.

Conclusion. Increase in the matrix elasticity, related to the relaxation time of its Maxwell model, decreases coalescence probability and causes a decrease of a critical droplet radius R_c from which P_c starts to steeply decrease.

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INFLUENCE OF SELECTED ADDITIVES ON FLAMMABILITY OF FLAME RETARDED, HALOGEN-FREE POLYOLEFINIC COMPOSITES

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Nowadays, the problem of flame retardation is of great interest, especially in the field of plastics' industry since RoHS directive was issued. There is a possibility to get flame-retarded plastics with the use of inorganic fillers like aluminum or magnesium hydroxide. However, in such case the mechanical properties, especially elongation at break of highly filled plastics suffered greatly.

As far as ethylene (co)polymers are concerned, the problem of nanocomposites synthesis is especially challenging because of the hydrophobic character of the polymer matrix and processing difficulties associated with complex viscoplasticity of the systems.

One of the promising, perspective ways for obtaining new generation of halogen-free, flame-retarded plastic materials, including polyolefinic ones, is the usage of nanotechnology. Basing on theoretical assumptions and on experimental results obtained up to date, nanocomposites seem to be very promising.[1]

The main object of our work is to obtain new kinds of flame-retarded, halogen-free materials based on ethylene (co)polymers filled with metal hydroxide and nanoclays, with improved mechanical and fire properties. The beneficiary effects are obtained due to the use of specific auxiliary materials.

An experimental part of our work includes methods like limiting oxygen index (LOI), UL94 tests, cone calorimeter experiments and tensile measurements.

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ELASTOMERIC MATERIALS CONTAINING BISMUTH OXIDE, GADOLINIUM OXIDE AND TUNGSTEN ABSORBING X-RAY

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X-ray computed tomography is extensively used for nondestructive evaluation, medical and biological imaging[1]. The breasts are one of the most radiation-sensitive organs in the human body. The tissue weighting factor has been recently revised from 0.05 to 0.12. Therefore, radiation dose reduction for the breasts is important to avoid stochastic risk when diagnostic X-ray examinations such as CT, mammography, and thoracic radiography are performed[2].

Many studies on medical radiation shielding have been conducted because the shielding is related directly to radiation poisoning of patients and radiation workers[3]. Polymers could be rendered radiopaque by blending them with radiopaciting agents like boron, lead or their compounds, barium sulfate or barium bromide, bismuth halides[4,5].

The purpose of the study was to determine the composition of the elastomers characterized by absorption properties of the X-ray radiation.

The polymeric matrix consisted of natural rubber (RSS I). Fillers and simultaneously active substances were bismuth (III) oxide (Bi_2O_3), gadolinium (III) oxide (Gd_2O_3) and tungsten (≥99.9% trace metals basis). To vulcanize the elastomer, sulfuric cross-linking systems were applied (sulfur, zinc oxide and MBT (2-Mercaptobenzothiazole)).The mechanical properties and hardness [^{o}Sh] (Shore method) of the vulcanizates were examined. The degree X-rays absorption was determined through the appointment of the mass absorption coefficient (μ/ρ cm^2/g) and the lead equivalent (Pn_{eq}, mm) relating to the thickness of lead X-ray attenuation of the energy in the same way as the specified thickness of the protective material. Radiation source was^{57}Co (E_γ = 122 keV) with activities of 115 kBq.

The use of bismuth in the elastomeric material leads to a reduction in the dose of X-rays. However, studies show that the absorption of radiation with energies above 96 keV leads to the emission of fluorescent radiation of additional bismuth, which may adversely affect the quality of CT images. In order to reduce the emitted fluorescence radiation tungsten oxide was added to a mixture, which showed high values of absorption coefficients for X-ray emission of bismuth. Tungsten was also a source of additional X-rays, but with a much lower emission quantum yield of lower energies. Minimization of the secondary radiation was achieved by introducing into the composition of gadolinium oxide, which absorbs X photons from tungsten.

The effect of fillers on mechanical properties, hardness, mass atteenation coefficient and lead equivalent of natural rubber composites.

Compound	*Tensile strength MPa*	*Hardness ${}^{o}Sh$*	*Mass attenuation coefficient cm^2/g*	*Lead equivalent mm* [E_γ = 122 keV]
NR/50 Bi_2O_3/50W/50Gd_2O_3	16	50	1.33	0.08
NR/50 Bi_2O_3/30W/30Gd_2O_3	14	49	1.17	0.05
NR/50 Bi_2O_3/15W/15Gd_2O_3	18	47	0.87	0.04
NR/50 Bi_2O_3/5W/5Gd_2O_3	22	46	0.85	0.03

The composites characterized by good strength properties. The lead equivalent was from 0.03 to 0.08 mm.

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NATURAL RUBBER COMPOSITES PROTECTING AGAINST X-RAYS

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The most common form of radiation used in radiation medicine, nuclear engineering and technology is the high-energy photon[1]. Energy associated with γ radiation (e.g. γ rays emitted by ^{60}Co) is high enough to break the molecular bonds and ionize atoms[2]. The simplest way to minimize the exposure is via shielding. The lead is a good shielding material for gamma rays and X rays[3], it has high atomic mass number and high density but this element influences on health and environmental[4].

The purpose of the study was to determine the composition of the elastomers characterized by absorption properties of the X-ray radiation. Natural rubber (RSS I) was applied as the elastomer matrix and bismuth oxide (Bi_2O_3), gadolinium oxide (Gd_2O_3), tungsten oxide (WO_3) and antimony oxide (Sb_2O_3) were added as fillers; used as crosslinking system: sulfur, zinc oxide and (2-Mercaptobenzothiazole) and stearic acid. Mixing was done on a laboratory size two roll mixing mill at friction ratio of 1:1,13. Dimensions of mixing mill rolls were about 400 x 200 mm. Thin 1 mm composites plates were prepared by vulcanization of rubber mixture in 150^oC under pressure of 15 MPa for 15 minutes. Test for measuring the tensile strength were carried out according to PN-ISO 37:1998. The stretching velocity of the sample was 500 mm/min. Crosslink densities were determined rubber sample. The crosslink density was calculated using the Flory - Rehner equation. Intensity of absorbed radiation were using by typical Canberra spectometry system with well collimated 3`` NaI(Tl) detector. As radiation source ^{57}Co (122 keV) were applied.

The natural rubber composites containing different amounts of oxide were characterized by the lead equivalent (Pn_{eq}) value between 0.03 mm and 0.06 mm. The mechanical properties of this composites were above 12 MPa.

Mechanical properties and crosslink density of composites with different oxides

Sample	*Stress at elongation100% MPa*	*Tensile strength MPa*	*Elongation at break %*	*Crosslink density mol/cm^3*
$50Bi_2O_3/10Gd_2O_3/10WO_3$	1.24	18	537	$25.3 \cdot 10^{-5}$
$50Bi_2O_3/10Gd_2O_3/10WO_3/10Sb_2O_3$	0.97	15	555	$24.9 \cdot 10^{-5}$
$50Bi_2O_3/15Gd_2O_3/10WO_3$	1.05	14	521	$25.0 \cdot 10^{-5}$
$50Bi_2O_3/15Gd_2O_3/10WO_3/10Sb_2O_3$	1.02	12	505	$26.0 \cdot 10^{-5}$
$50Bi_2O_3/25Gd_2O_3/25WO_3$	1.67	16	485	$28.0 \cdot 10^{-5}$
$50Bi_2O_3/25Gd_2O_3/25WO_3/25Sb_2O_3$	1.26	15	521	$27.0 \cdot 10^{-5}$

Lead equivalent of natural rubber composites ($E_\gamma = 122$ keV)

Sample	*Lead equivalent mm*
$50Bi_2O_3/10Gd_2O_3/10WO_3$	0.04
$50Bi_2O_3/10Gd_2O_3/10WO_3/10Sb_2O_3$	0.04
$50Bi_2O_3/15Gd_2O_3/10WO_3$	0.03
$50Bi_2O_3/15Gd_2O_3/10WO_3/10Sb_2O_3$	0.04
$50Bi_2O_3/25Gd_2O_3/25WO_3$	0.06
$50Bi_2O_3/25Gd_2O_3/25WO_3/25Sb_2O_3$	0.05

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MAGNESIUM ALUMINIUM LAYERED DOUBLE HYDROXIDES MG-AL LDHS AS REINFORCING FILLERS AND AS CURING AGENTS FOR CARBOXYLATED NITRILE RUBBER

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Recently there is a growing tendency in application of layered double hydroxides LDHs as novel fillers for rubber composites such as: EPDM[1], NBR[2], XNBR[3], CR[4], silicone[5], polyurethane[6]. The purpose of work was to study the effect of magnesium aluminium layered double hydroxides Mg-Al LDHs with varying Mg/Al ratio on the crosslink formation and mechanical properties of carboxylated nitrile rubber XNBR. Following types of Mg-Al LDH were applied: Hydrotalcite (Sigma Aldrich), Pural MG 30 HT, Pural MG 63 HT and Pural MG 70 HT (Sasol) which contained respectively 50, 30, 63 and 70 % wt. of magnesium. The XNBR/Mg-Al LDH composites were prepared by blending rubber and filler (10, 20 and 30 phr) in internal mixer Brabender without using conventional metal oxide curative. These compounds were characterized by infrared spectroscopy IR, dynamical mechanical analysis DMA and scanning electron microscopy SEM. Ability of LDHs to interact with XNBR was proven by FTIR analysis, cause with increasing content of LDH or magnesium concentration the intensity of the band corresponding to free –COOH decreases remarkably (Figure 1). Also an appearance of secondary tanδ peak at higher temperature (conducting DMA studies) might indicate the formation of ionomeric clusters in the XNBR/Mg-Al LDH composite (Figure 2). These investigations confirmed that magnesium rich LDH can be applied at once as active filler and as curing agent in carboxylated elastomer. The advantage of layered double hydroxides with respect to other conventional fillers lies in chance of partial replacement or full elimination of harmful zinc oxide from the XNBR (or its hydrogenated counterpart HXNBR) curing process what has a potentially great importance for the rubber industry.

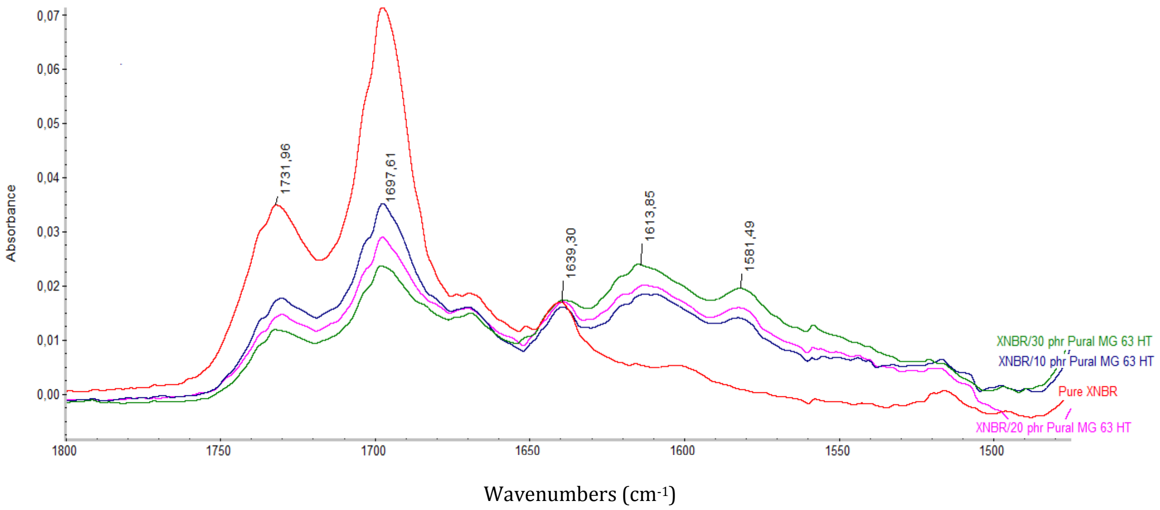

Figure 1 ATR spectra (range 1800 – 1475 cm^{-1}) of the unfilled XNBR sample and XNBR filled with 10, 20 and 30 phr of Pural MG 63 HT.

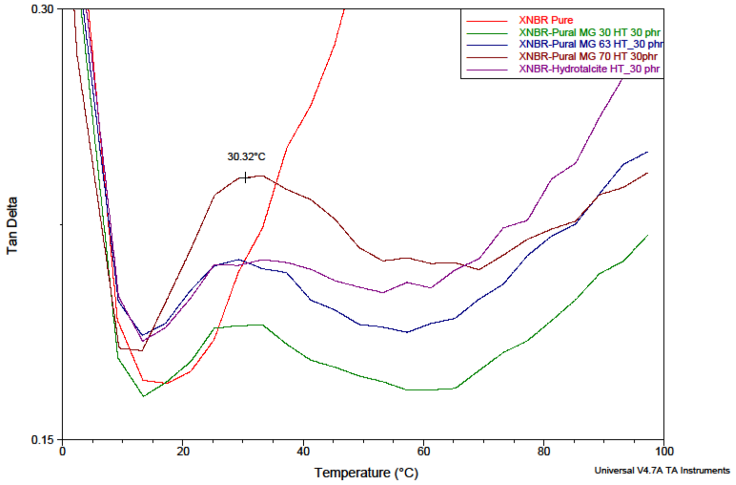

Figure 2 Relation between Mg/Al ratio and intensity of secondary peak in temperature region from 11˚C to 65˚C that may indicate the possibility of ionomeric structure in the composites XNBR/Mg-Al LDH

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EFFECT OF IMIDAZOLIUM IONIC LIQUID TYPE ON THE PROPERTIES OF CARBOXYLATED NITRILE RUBBER/LAYERED DOUBLE HYDROXIDE COMPOSITES

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Over the last decade layered fillers as well as ionic liquids ILs have attracted research attention for their unique structural and chemical properties. The advantage of layered double hydroxides LDHs with respect to other conventional fillers lies in possibility of partial replacement or full elimination[1,2] of zinc oxide from the XNBR (or its hydrogenated counterpart HXNBR) curing process what has a potentially great importance for the rubber industry. Nowadays there is also a systematically growing tendency in employing of ionic liquids as performance additives in rubber compounds formulation. The most common reason for application of ionic liquids in elastomer filed is improvement of nanofillers dispersion (carbon nanotubes[3], halloysite nanotubes[4], carbon black[5]) in hydrophobic matrix as well as enhancement ionic conductivity, thermal and mechanical properties of polymer composites.

The purpose of our work was to investigate the impact of hydrophobic and hydrophilic imidazolium ionic liquids characterized by high ionic conductivity on morphological, thermal, mechanical and ionic conductivity properties of XNBR/Mg-Al LDH composites. Magnesium-aluminium layered double hydroxide Mg-Al LDH (also known as hydrotalcite) was applied in XNBR as a reinforcing filler and as a curing agent simultaneously. The filler (30 phr) was modified with different contents (2.5, 5, 10 and 15 phr) of EMIM TFSI and EMIM SCN by grinding it till a homogeneous paste was obtained. Compounding of XNBR with paste was performed in an internal mixer Brabender, subsequently compounded rubbers were milled in open two-roll mill and cured at 160 ºC.

Table 1 Type and short characterization of used ionic liquids ILs.

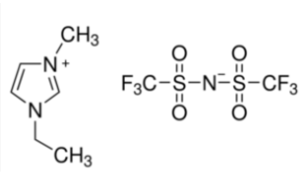
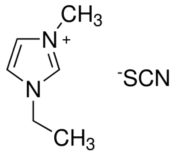
Full name of IL and abbreviation	*Chemical structure*	*Molar Mass, g/mol*	*Ionic conductivity at 25°C, mS/cm*
1-ethyl-3-metylimidazolium bis(trifluoromethylsulfonyl)imide EMIM TFSI (hydrophobic)		391.31	3.5
1-ethyl-3-methylimidazolium thiocyanate EMIM SCN (hydrophilic)		169.25	27.0

Table 2 The effect of 5 phr IL concentration on glass transition temperature Tg, mechanical properties, curing density and ionic conductivity of XNBR/Mg-Al LDH composites.

Type of IL	*IL content*	*Tg °C (DSC)*	*300% modulus, MPa*	*Tensile strength MPa*	*$V \cdot 10^{-5}$ Mol/cm^3*	*Ionic conductivity 25°C, S/cm*
Without IL	0	-23	5.5	18.0	9.0	4.2×10^{-10}
EMIM TFSI	5	-26	5.7	20.5	10.2	1.6×10^{-8}
EMIM SCN	5	-23	8.5	20.5	13.2	5.5×10^{-9}

The application of these imidazolium type ionic liquids strongly influenced not only properties presented above but also effected on Mg-Al LDH filler dispersion in elastomeric matrix what was confirmed by SEM and TEM technique.

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PREPARATION OF EVA CONTAINING ALUMINIUM NANOPARTICLES

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The synthesis of aluminium nanoparticles in a EVA matrix, by sol-gel process in the melt, was investigated. Two EVA with different vinyl acetate (VA) content and aluminium isopropoxide were used as organic and inorganic phases. The nanocomposites were prepared in a batch mixer under constant processing conditions and were analysed by several characterization techniques. Even though aluminium nanoparticles were synthesised with both EVAs, smaller and better dispersed nanoparticles were achieved with EVA with higher VA content. Aluminium isopropoxide presented a low activation energy allowing the synthesis of the nanoparticles without a post step treatment. The nanocomposites prepared exhibited higher stability than EVA and improved fire resistance.

The influence of imidazolium ionic liquids on the properties of NBR/A380/RTILs composites

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Ionic liquids (ILs) exhibit intriguing properties that make them a good replacement of volatile compounds in many chemical and industrial processes. Ionic liquids (ILs) are gaining widespread recognition in chemistry for their unique properties including negligible vapor pressure, good thermal stability, nonflammability, high ionic conductivity and miscibility with water and organic solvents. Also some properties (conductivity, tensile strenght etc.) of the rubbers can be affected by the addition of ionic liquids. The influence of the ionic liquids on the properties (mechanical properties, conductivity, cross-link density nad temperature glass transition) of acrylonitrylo-butadiene rubber (NBR) in this work was conducted. Two ionic liquids: 1-allyl-3- methylimidazolium bis(trifluoromethylsulfonyl) imide AMIM TFSI and 1-allyl-3-methyl imidazolium chloride AMIMCl (hydrophilic), were examined (Table 1). NBR vulcanization was carried out in the presence of curing agents (sulfur, mercaptobenzothiazole, zinc oxide, stearic acid), filler (Aerosil 380) and mentioned ionic liquids at different loadings (5 phr, 10 phr, 15 phr). The morphology of filler in the elastomer matrix containing AMIM TFSI was estimated using scanning electron microscopy (Fig.1). We found that 1-allyl-3- methylimidazolium bis(trifluoromethylsulfonyl) imide, effected on increase of conductivity NBR composites whereas only a slight decrease in Tg was observed. NBR compounds containing AMIM TFSI at each loading also exhibited good mechanical properties, tensile strength and cross-link density increased with amount of AMIM TFSI in composite. The presence of AMIMCl in the NBR compounds slightly affected the increase in the conductivity and led to the decrease Tg and cross-link density as well as deterioration of the mechanical properties (Table 2).

Table 1. Chemical structures of the ionic liquids

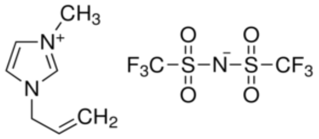
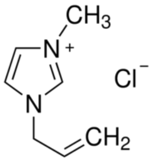
Chemical name	**Given name/nature**	**Structure**	**Supplier**
1-allyl-3- methylimidazolium bis (trifluoromethylsulfonyl) imide	AMIM TFSI/ hydrophobic		Sigma Aldrich
1-allyl-3-methyl imidazolium chloride	AMIMCl/ hydrophilic		Sigma Aldrich

Table 2. Properties of NBR composites

Sample		SE_{100} [MPa]	TS [MPa]	EB [%]	v_T*10^{-5} [mol/cm^3]	Tg [^{0}C] DSC	σ [S/cm] 1kH, T=26 ^{0}C DEA
NBR		1,17	2,9	445	5,91	-28	2,06 x 10^{-10}
NBR/A380		2,23	18,9	676	5,34	-30	6,70 x 10^{-10}
NBR/A380/ AMIM TSFI	5	1,87	18,9	734	4,82	-29	1,64 x 10^{-8}
	10	1,11	19,4	695	5,91	-30	2,45 x 10^{-8}
	15	1,57	20,2	683	6,00	-32	1,1 x 10^{-7}
NBR/A380/ AMIM Cl	5	1,68	11,7	714	4,95	-33	4,02 x 10^{-10}
	10	1,19	4,03	938	2,65	-34	5,68 x 10^{-10}
	15	0,91	1,67	857	2,11	-35	2,63 x 10^{-9}

SE_{100} – stress at 100 % elongation [MPa], TS – tensile strength [MPa], EB – relative elongation at break [%], v_T – curing density [mol/cm^3], σ - conductivity [S/cm]

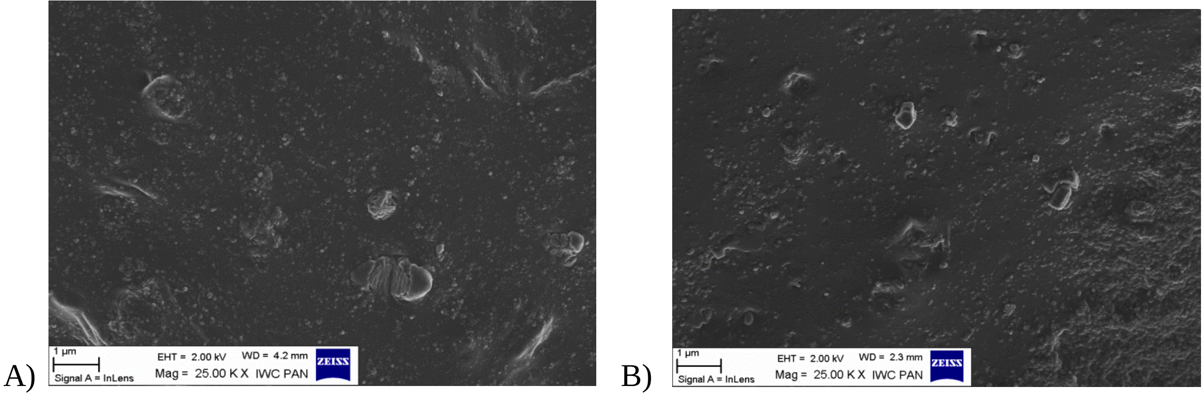


Fig. 1 SEM images of: A)NBR/A380, B) NBR/A380/AMIM TFSI

Dyes-modified silicas as fillers of butadiene-acrylonitryle rubber (NBR)

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One widely used in the rubber industry of the group of elastomers is acrylonitrile-butadiene rubber (NBR). The main disadvantage of conventional NBR rubber is its small resistance to thermal aging, ozone and weathering. This phenomenon is caused by the presence of C = C bonds in the chain main and the side vinyl groups. Factors like light and temperature are the main initiators of polymer degradation. They contribute to the formation of free radicals that react with oxygen. The ageing processes of materials bring about irreversible changes in structural properties, which is an undesirable effect. Nowadays the industry uses anti-ageing substances in the form of derivatives of aromatic amines, phosphoric derivatives and substituted phenols. In this work we have proposed the organic dyes as anti-aging substances: 2-hydroxy-1,4-naphthoquinone (lawsone) and berberine chloride (Table 1). Both substances exhibited high half-wave potentials ($E_{1/2}$): 2,20 V and 1,36 V respectively for 2-hydroxy-1,4-naphthoquinone and berberine chloride (Table 2). Our aim was to study composites system filled with antioxidant/ionic liquid supported on silica towards the aging stability and functioning as reinforcing additive for rubber

NBR vulcanizates filled with silica modified ionic liquids and lawsone showed a slight increase in tensile strength TS in comparison with blend containing unmodified Zeosil 175. The ageing resulted in deterioration of mechanical properties of the vulcanizates but in a less extent than in the case when nonmodified SiO_2 was used as filler.

Table 1. Chemical structures of the dyes

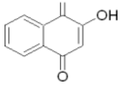
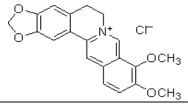
Compound name	**Structure**	**Supplier**
2-hydroxy-1,4-naphthoquinone		Sigma Aldrich
Berberine chloride		Fluka

Table 2. Cyclic voltammetry and molecular orbital parameters for the compounds studied

Compound	$E_{1/2}$,V	E_{HOMO}, eV	Enthalpy ΔH, kcal/mol
Berberine chloride	1,36	-8,5696	-47,9729
2-hydroxy-1,4-naphthoquinone	2,20	-10,1882	-62,0149

Table 3. Effect of modified Zeosil 175 silica on properties of NBR

Sample name	Sample condition	SE_{100}, MPa	*TS*, MPa	*EB*, %	v_T*10^{-5}, mol/cm^3	K
NBR/Z175	niestarzona	1,92	17,6	744	5,86	0,24
	starzenie UV	2,81	7,44	417	6,76	
NBR/Z175/berberine	niestarzona	1,55	11,6	527	6,35	0,81
	starzenie UV	2,17	10,0	498	6,75	
NBR/ Z175/berberine/ $[C_8MIm]$ $[BF_4]$	niestarzona	2,17	14,4	540	6,30	0,52
	starzenie UV	2,31	8,69	464	6,75	
NBR/Z175/berberine/ $[C_4MIm]$ $[(CH_3(CH_2)_2O(CH_2)_2OS_3O)]$	niestarzona	1,94	13,1	556	6,24	0,66
	starzenie UV	2,19	9,7	4,98	6,57	
NBR/Z175/lawsone	niestarzona	1,99	18,4	885	5,86	0,88
	starzenie UV	2,03	18,2	784	6,06	
NBR/Z175/lawsone/ $[C_8MIm]$ $[BF_4]$	niestarzona	2,17	21,2	741	5,31	0,74
	starzenie UV	2,02	16,0	728	5,78	
NBR/Z175/lawsone/ $[C_4MIm]$ $[(CH_3(CH_2)_2O(CH_2)_2OS_3O)]$	niestarzona	2,03	19,0	756	5,90	0,77
	starzenie UV	2,21	15,4	719	5,97	

SE_{100} – stress at 100 % elongation [MPa], *TS* – tensile strength [MPa], *EB* – relative elongation at break [%], v_T – curing density of vulcanizates calculated using the Flory Rehner equation [mol/cm^3], K - ageing coefficient; (K= EB x TS)$_{\text{after aging}}$ / (EB x TS)$_{\text{before aging}}$

UNDERSTANDING THE PHYSICAL AND/OR CHEMICAL INTERACTION IN POSS-POLY(ETHYLENE-CO-ACRYLIC ACID) NANOCOMPOSITES

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Polyhedral oligomeric silsesquioxane, so-called POSS, is a class of organosilicic three-dimensional compounds with cage frameworks with different degrees of symmetry and their general formula is $(RSiO1.5)_n$, where n is an integer number and R is an organic group. The organic pendent groups can be designed to achieve the desired affinity with the host polymeric matrix[1]. Using POSS in polymer based nanocomposites is a promising issue for the design of materials with high-performance in several applications[2].

Partial cage POSS with different pendent organic groups were melt blended with acrylic acid functionalized polyethylene (Escor) in order to investigate the interaction between the –OH POSS's groups and the carboxylic functionalities of the matrix. Beyond, PE/POSS compounds were prepared in the same processing condition for sake of comparison.

Usually, the POSS molecules act as plasticizer[3], but if interactions between matrix and POSS are present, these molecules can act as anti-plasticizer. In particular, Escor/POSS compounds show increased complex viscosity than the values of neat matrix at low frequencies while at high frequencies the values are similar, see Figure 1 (a). PE/POSS systems show lower viscosity in the hole investigated frequency range than the pristine matrix, see Figure 1 (b). It is interesting to highlight that the storage modulus as a function of the temperature in dynamic temperature sweep test shows an unexpected increase in temperature range between 105 and 120 °C for Escor/silanol-POSS nanocomposites. After 120 °C the storage modulus decreases for all investigated systems. The rheological behavior can be understood considering the formation of physical network, due to hydrogen bonds between of the –COOH groups in the matrix and the –OH groups in the POSS molecules.

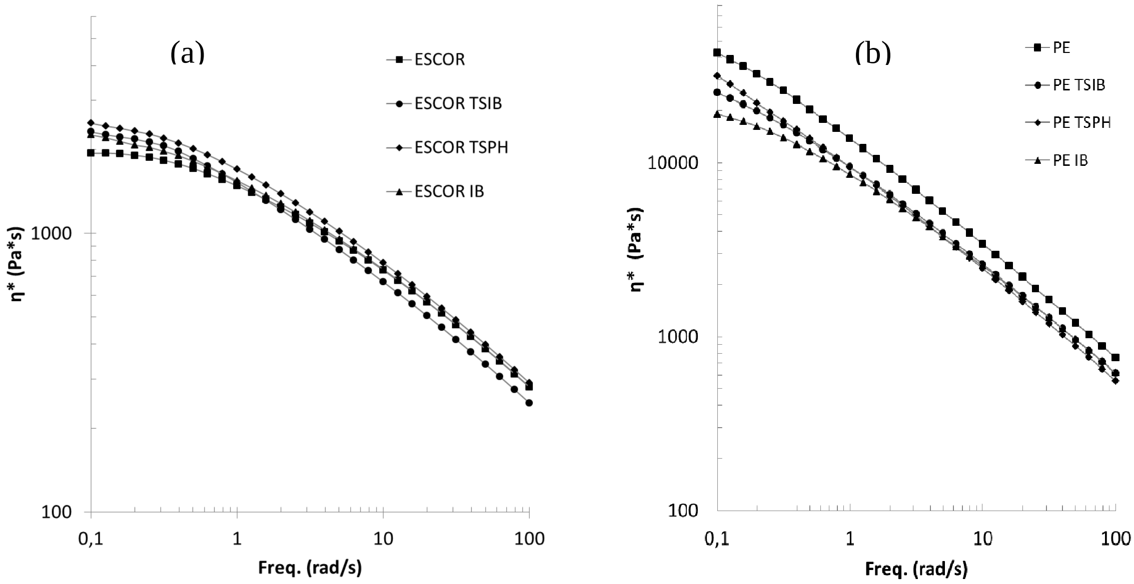

Figure 1: Complex viscosity for Escor, PE, Escor-POSS and PE-POSS nanocomposites

The mechanical results obtained by tensile test confirm the anti-plasticizing effect of the POSS for systems where the interaction between the macromolecules and the POSS molecules are present. However, the inorganic framework of POSS exerts a plasticizer effect and all measured properties are results by two contrasting phenomenon, i.e. the plasticizer and reinforcement effect.

Moreover, a peculiar cold crystallization of the pristine Escor under stress was not modified by POSS loading. This consideration was made considering that the values of the fusion enthalpies of Escor/POSS systems are similar to the value of the fusion enthalpy of Escor, obtained by DSC measurements.

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EFFECT OF MULTIPLE REPROCESSING CYCLES ON THE PROPERTIES OF POLYETHYLENE/CLOISITE 15A NANOCOMPOSITES

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Introduction

Recycling of polymer based materials is a consolidated technique and, in particular, recycling of polymer based nanocomposites is gaining interest because of the increasing use of these materials in the industry. In this work, the effects of multiple reprocessing cycles on the main properties of LDPE based nanocomposites were investigated.

Experimental

The materials used in this work were a low density polyethylene (LDPE) and a nanofiller -Cloisite 15A organomodified montmorillonite- added to the polymer at 5 wt%. The components have been processed in a Brabender single-screw extruder equipped with a slit die (T = 210 °C) and up to four reprocessing cycles have been performed. Some of the results were compared to those observed on the same systems prepared in a Brabender batch mixer at 210 °C. The mixing time was, in this case, chosen to be 1 hour.

Results and discussion

The results of tensile tests are reported in Table 1.

Some interesting observations can be drawn from the comparison between the materials upon the first extrusion and the fourth reprocessing. As regards the neat LDPE, only minor variations occur between the material extruded one and four times, respectively. Similar considerations may be done with regard to the 5 wt% filled LDPE-Cloisite 15 A nanocomposite: the multiple reprocessing leads to an increase in the elastic modulus and only small reductions (below 10%) of tensile strength and elongation at break. Therefore, it can be stated that multiple extrusion cycles do not significantly alter the tensile behavior of LDPE and LDPE-Cloisite 15A nanocomposites, while investigations on similar systems based on polypropylene or Nylon 6[1, 2] found more significant variations in the main properties upon multiple reprocessing cycles. The influence of higher processing times on the properties can be taken into account by observing the mechanical properties of the neat polymer and the nanocomposite upon one hour mixing at 210 °C and comparing them with the properties of the extruded samples. As regards the LDPE, the tensile properties show only minor differences. The nanocomposite, on the other hand, has significant reductions of tensile strength, and especially elongation at break. This allows to state that only higher processing times can significantly worsen the mechanical properties of the nanocomposites, while the neat polymer is not much affected.

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Table 1 Tensile properties of the investigated samples.

Material	*Elastic Modulus [MPa]*	*Tensile Strength [MPa]*	*Elongation at break [%]*
LDPE	110	15	450
LDPE 4th reprocessing	120	14.1	390
LDPE+5%CL15A	138	10.7	370
LDPE+5%CL15A 4th reprocessing	151	10	340
LDPE mixer 210°C	120	12.2	347
LDPE+5%CL15A mixer 210°C	154	9.2	87

EFFECT OF THE ORGANO-MODIFIED FILLER ON THE THERMAL PROPERTIES OF POLY(3-HYDROXYBUTYRATE) (PHB) NANOHYBRID MATERIALS

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INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is an aliphatic biodegradable polyester produced by microorganisms from renewable resources. Due to its unique properties, it has attracted the interest of the scientific community recently. However, its thermal instability in temperatures a little higher than its melting point[1] constitutes a drawback in its applications and uses. In the present work, nanohybrid materials of PHB and organo-modified silicate clays (montmorillonite) were produced by the melt mixing method. The effect of the nanofiller on the thermal stability of the pure polymer was investigated by thermogravimetry (TGA) and the results are presented here.

EXPERIMENTAL PART

The silicate clays were modified via a cation exchange reaction using alkylammonium salts with different numbers of carbon atoms. Following a design of experiments approach, the organo- modified silicate clays were also prepared in differed concentrations equivalent to 0.5×, 1.5× and 2.5× the cation exchange capacity (CEC) of the clay. The nanohybrid materials were prepared by the melt-mixing method in a micro-extruder/compounder at 175^{0}C and 130rpm and under constant nitrogen flow, which prevented the thermal decomposition of the polymer matrix. Hybrid materials with

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clay loadings of 1%, 3% and 5% wt were produced. The structure of the hybrids was investigated by X-ray diffraction. The 2θ scanning range spanned from 1.5^0 to 10^0. The thermal properties of both the pure polymer and the nanocomposites were studied by TGA, under nitrogen flow and at a heating rate of 10^0C/min.

RESULTS AND DISCUSSION

Figure 1a shows some representative TGA derivative thermographs of PHB and its nanocomposites, while fig.1b presents the effect of the nanofiller on the initial thermal decomposition temperature (T_i) at 2% polymer mass loss.

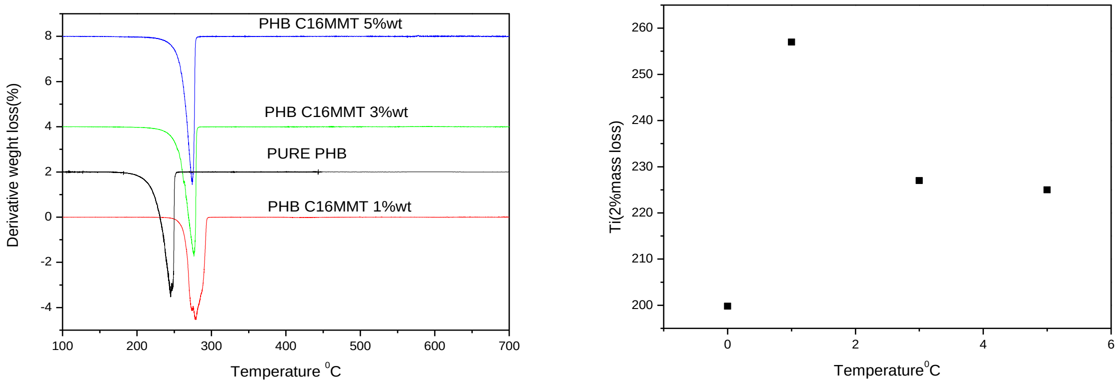

Figure 1 (a) Representative TGA derivative thermographs and **(b)** initial decomposition temperature (2% mass loss) of PHB and its nanocomposites with different clay loadings but with the same modified clay (C_{16}MMT at 250× CEC)

It is clear that the presence of the nanoclays inside the PHB matrix enhances the thermal stability of the pure polymer. More results regarding the structure of the nanohybrid materials produced and their thermal stability will be given and will be analyzed during the presentation.

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EPOXY THERMOSET/THERMOPLASTIC BLENDS: INFLUENCE OF THE THERMOPLASTIC MOLECULAR WEIGHT ON THE PHASE SEPARATION, MORPHOLOGY AND THERMAL STABILITY

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A common procedure for preparing thermoset/thermoplastic blends is through the mechanism of Polymerization-Induced Phase Separation (PIPS). In PIPS mechanism, the thermoplastic component is initially miscible in the thermosetting precursors and then is separated into phases during polymerization. Different types of morphologies can be generated by PIPS depending on the blend composition and cure conditions.

The aim of this work is to study the influence of the concentration and molecular weight of modifier on the phase separation, developed morphology and final properties in thermoplastic-modified epoxy-amine thermoset blends.

The epoxy-amine system was constituted by diglycidylether of bisphenol A (DGEBA) and the diamine 4,4´-methylenebis(2,6-diethylaniline) (MDEA). The thermoplastic modifier was polystyrene (PS). Two PS with different molecular mass and polydispersity were used to study the effect of molecular mass (PS↓: Mn=140000 g.mol^{-1}, Mw=230000 g.mol^{-1}; and PS↑: Mn=170000 g.mol^{-1}, Mw=350000 g.mol^{-1}).

Two final properties were studied, the glass transition temperature, measured by differential scanning calorimetry, and the thermal and thermooxidative stability, measured by thermogravimetric analysis.

Cloud-points of the blends during cure were determined in two steps: first, the cloud-point time, t_{CP}, was determined in a transmitted light device; and then, the cloud-point conversion, p_{CP}, was calculated from a differential scanning calorimeter.

Experimental cloud-point curves obtained for the DGEBA/MDEA+PS blend during cure at 120ºC for the two PS of different molecular mass are shown in Figure 1. Figure 1 also shows the final morphology developed by some of these blends.

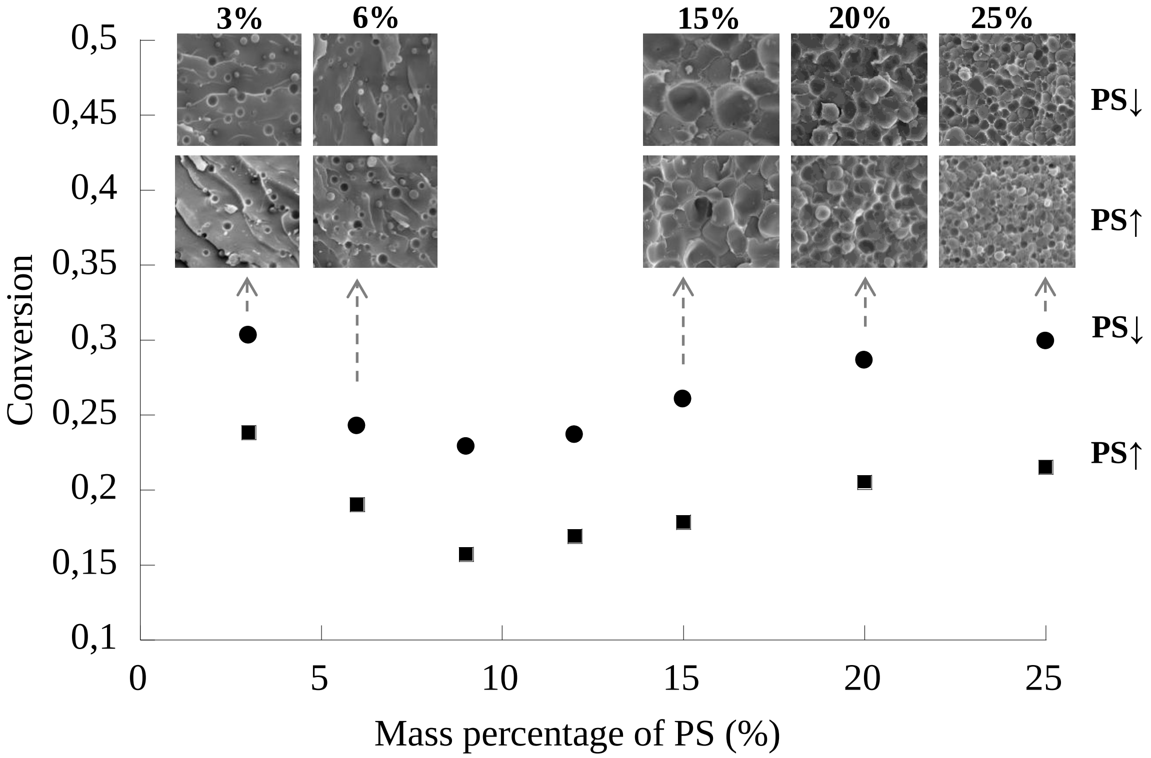

Figure 1 Cloud-point conversion and final morphology for the DGEBA/MDEA system modified with different amounts of PS cured at 120ºC for two PS with different molecular mass: PS↓ = 140 000 g.mol^{-1} (●) and PS↑ = 170 000 g.mol^{-1} (■) in number average.

An increase in PS molecular weight decreased the miscibility of blend starting the phase separation at lower conversions. This affected the size and concentration of dispersed particles in the developed morphologies.

The PS-modified blends showed two glass transitions with values close to the Tgs of the pure materials, indicating the existence of two separate phases which were not pure but contain amounts of the other component.

The degradation of the blends started at lower temperatures in oxidizing atmosphere. The thermooxidative degradation occurred in several steps leading to the total mass loss around 600 °C, while thermal degradation occurred in one step remaining a final residue at 700ºC. The PS modifier did not affect the thermal and thermooxidative stability of materials.

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MULTIFUNCTIONAL FIBERS BASED ON POLYAMIDE 6 AND PLASMA FUNCTIONALIZED CARBON NANOTUBES

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Commercial (CNT 1) and *ad hoc* synthesized carbon nanotubes (CNT 2) were plasma treated under oxygen atmosphere and then added to polyamide 6 (PA 6) in order to prepare multifunctional fibres by melt spinning. For comparison, pristine nanofillers were used too. The effect of functionalization and of filler characteristics on the morphological, rheological, mechanical and electrical properties of the fibers was studied by TEM and SEM, rheological measurements, tensile tests and electrical conductivity tests. The amalysis of Raman spectra put into evidence that the intensity of D-band (correlated with the degree of functionalization by the different vibration mode of carbon atoms in the presence of defects[1,2]) increased after plasma treatment, thus confirming the oxidation of nanotubes. The rheological measurements showed that the increments of MS are more intense when CNT 2 are added and when functionalized samples are used. Therefore, the highest increase of melt strength (MS) is observed for the systems PA6/f-CNT 2 while the lowest is observed in the system PA6/CNT 1. These results can be interpreted considering that the presence of polar oxygen moieties in the functionalized CNTs is responsible of a better adhesion between the nanofiller and the matrix. This higher interaction between the two phases causes an increase of the elongational viscosity and, finally, an increase of the MS. In this sense, f-CNT 2>CNT 2≈f-CNT 1>CNT 1. The results carried out from tensile tests followed the same trend observed in the case of MS and demonstrated that the functionalization led to a higher mechanical performance. The morphological analysis confirmed that the adhesion, the dispersion and the alignment of the nanotubes within the polymer matrix were improved when using functionalized CNTs. In PA6/CNT 1, Fig. 1a, it is possibile to identify single nanotubes with smooth surface, evidencing the absence of any adhesion with the matrix. The morphology of PA6/f-CNT 1, Fig. 1b, is different as the nanotubes are partially covered with PA6, indicating a higher affinity between the two components. The adhesion is further improved when using f-CNT 2, Fig. 1c-d. In this case it is possible to see several isolated nanotubes that are wrapped into PA6. This higher affinity between the matrix and CNTs allows their better orientation, as evidenced by the preferential alignment along the drawing direction. Electrical tests marked that functionalization slightly reduced the conductivity of materials and, in general, the effect of the characteristic of filler (L/D, purity) plays the most important role on this property.

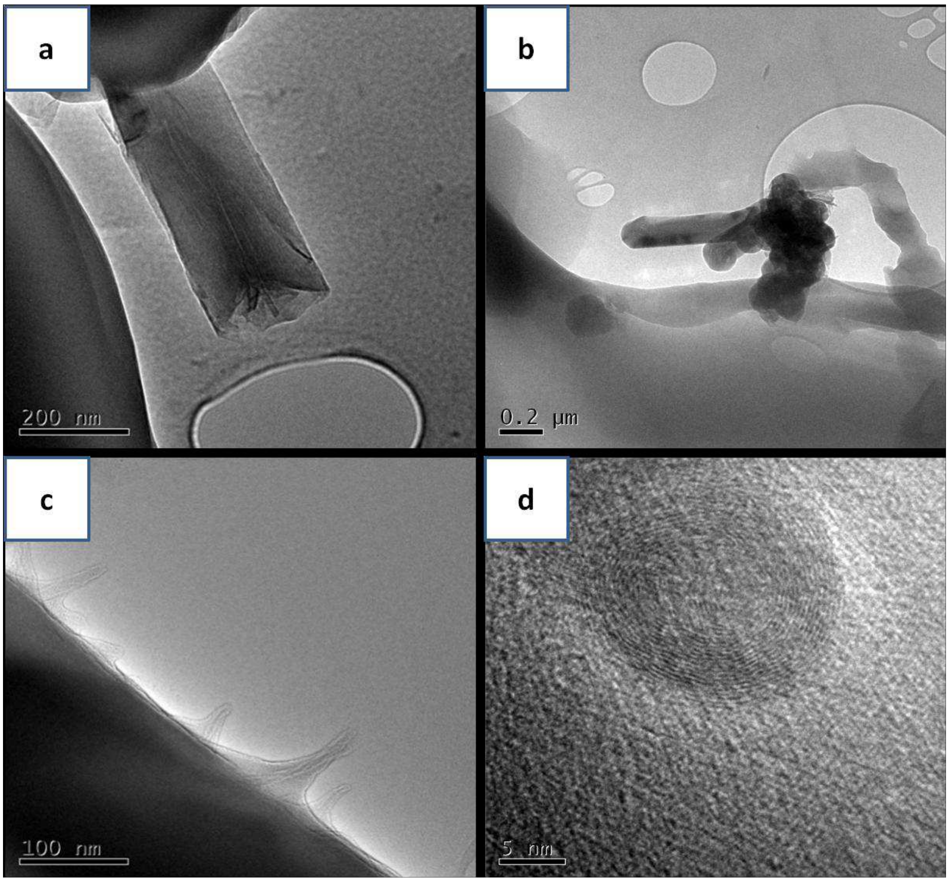

Figure 1 TEM micrographs PA6/CNT 1 (a), PA6/f-CNT 1 (b), PA6/f-CNT 2 (c-d).

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PROCESSING – MORPHOLOGY – PROPERTIES RELATIONSHIPS IN HDPE/PA6/CLAY NANOCOMPOSITES

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In our previous works[1-2] we presented the properties of high density polyethylene (HDPE) and polyamide 6 (PA6) blends containing an organically modified montmorillonite (OMM). We evaluated the effect of different compatibilizing systems on the properties of the blends. The results indicated that, despite a good morphology achieved in the filled blends and a moderate intercalation level, the mechanical performance and especially the properties at break, were not satisfactory. This behaviour was attributed to degradation phenomena involving the organic modifier of the blends that were reduced by using a stabilizing system.

Aim of this work was to evaluate the influence of morphology, at nano and micro scale, achieved by different processing methods and sample preparation, on the rheological and mechanical properties of blends of HDPE/PA6 in the presence of OMM and different compatibilizing systems. In particular, three compatibilising systems were used in this work: ethylene-co-acrylic acid copolymer (EAA) together with a 2,20-(1,3-phenylene)-bis(2-oxazoline) (PBO); high-density polyethylene modified with acrylic acid (HDAA) together with PBO; ethylene-co-glycidyl methacrylate copolymer (EGMA).

The nanocomposites were prepared using different procedures. Some blends were prepared by premixing all the components in the solid state and then feeding them all together into the extruder (E1). In another procedure, part of the blends pellets was further re-extruded adopting the same conditions in order to evaluate the effect of re-processing (E2). In another procedure, blends with the same final composition were prepared using a masterbatch of the compatibilizer (EAA, HDAA or EGMA) with OMM prepared in a separated stage at 180 °C in a batch mixer (MB).

The morphology of the blends was studied by XRD, TEM and SEM analyses while the mechanical behaviour was studied by tensile and impact tests.

The XRD and TEM analysis showed that the re-extrusion improves slightly the morphology probably because to the supplementary stresses induced on the blend by the second processing. This would allow a further dispersion/redistribution of the nanofiller with consequent higher intercalation level.

A further improvement of the morphology, in terms of lower clay dimension and better dispersion, can be observed in the blends MB. These results can be explained considering that the preparation of the compatibilizer-clay masterbatch may induce a certain initial intercalation/expansion of the clay that becomes more intense during the subsequent extrusion processing.

The results of the mechanical tests, table 1, showed that reprocessing (E2) induced an increase of all the properties for all the three systems. This improvement is in full agreement with the better blend morphology and with the improved clay distribution and intercalation after the second processing, as commented above. A further general increase of the mechanical properties was showed by the blends MB. These results confirm that the pre-dispersion of the clay in the compatibilizer helps in achieving a further dispersion in the final material.

Table 1 Elastic modulus (E), tensile stress (TS), elongation at break (EB) and impact strength (IS) of all the nanocomposites prepared in this work.

Sample	*E (MPa)*	*TS (MPa)*	*EB (%)*	*IS (J/m)*
PA6/HDPE/EAA/PBO/15A/E1	1283 ± 32	23.6 ± 0.3	3.1 ± 0.1	24.0 ± 1.0
PA6/HDPE/EAA/PBO/15A/E2	1348 ± 39	23.4 ± 0.4	3.4 ± 0.2	28.5 ± 0.9
PA6/HDPE/EAA/PBO/15A/MB	1452 ± 43	23.8 ± 0.3	4.0 ± 0.2	33.3 ± 1.1
PA6/HDPE/HDAA/PBO/15A/E1	1169 ± 27	17.3 ± 0.6	1.9 ± 0.2	23.7 ± 0.9
PA6/HDPE/HDAA/PBO/15A/E2	1229 ± 33	21.6 ± 0.4	2.4 ± 0.1	30.3 ± 1.0
PA6/HDPE/HDAA/PBO/15A/MB	1353 ± 41	22.6 ± 0.5	2.9 ± 0.1	31.2 ± 0.8
PA6/HDPE/EGMA/15A/E1	1173 ± 28	23.3 ± 0.8	5.0 ± 0.3	28.3 ± 0.7
PA6/HDPE/EGMA/15A/E2	1287 ± 34	26.7 ± 0.6	5.9 ± 0.3	36.4 ± 1.1
PA6/HDPE/EGMA/15A/MB	1297 ± 28	27.3 ± 0.7	7.5 ± 0.4	42.0 ± 1.3

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MECHANICAL AND RHEOLOGICAL PROPERTIES OF BLENDS TYPE TPV HDPE/GROUND TIRE RUBBER DEVULCANIZED BY MICROWAVE

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Experimental

Mechanical and rheological properties of blends TPV HDPE/Ground tire rubber (GTR) devulcanized by microwaves were analysed by tensile strength in a Instron universal testing machine 3369 (50mm/min) and by oscillatory rheometry in a parallel plate rheometer Anton Paar CTD450 (diameter 25mm, gap 1,3 mm, 0,5 % strain at 170 °C). The blends were prepared in an internal mixer Haake coupled to a torque Rheometer Polylab 900 (160° C, 80 rpm and mixing time of 15 minutes) in concentrations of 20% HDPE and 80% devulcanized GTR, 80% HDPE and 20% devulcanized GTR in mass. Blends of the same HDPE, but with 5% of organically modified clay Cloisite 20A in the HDPE phase, were also prepared. The nomenclature of the blends is of the type XHDPE 20A/YGTRZ AD, where X represents the % amount of HDPE in mass, Y the % amount of GTR in mass and Z represents the time of GTR exposure to the microwaves, 20A represents the presence of clay and AD the presence of vulcanization additives. The rubbers were also mixed with vulcanization additives prior the mixing with the thermoplastic.

Results

The evolution of storage modulus (G') and complex viscosity (η^*), and mechanical properties of blends HDPE/GTR containing or not Cloisite 20A are summarized in Figure 1.

The complex viscosity decreases with the frequency, which clearly exhibits pseudoplastic behavior of the blends, assuming the Cox Merz rule [1]. The decrease in the G' values of the (blends without clay) with the increase in the time of exposition of GTR to microwaves is probably due to the better compatibility between the rubber and the matrix, enhancing stress transference to the more rigid rubber particles. On the other hand, while η* remains almost the same, G' decreases in the TPVs with clay in comparison with the other blends, which was not expect, since the clay usually increases both elasticity and viscosity of the matrix. Usually, the crosslinks in the rubber phase facilitates the dispersion of the lamellaes in the blend, which improves the interaction between polymer/clay [2]. The presence of clay can also influence the vulcanization reaction in the rubber phase [3], and can decreases the particles size of dispersed phase [4]. Deeper investigation is needed to explain the present behavior.

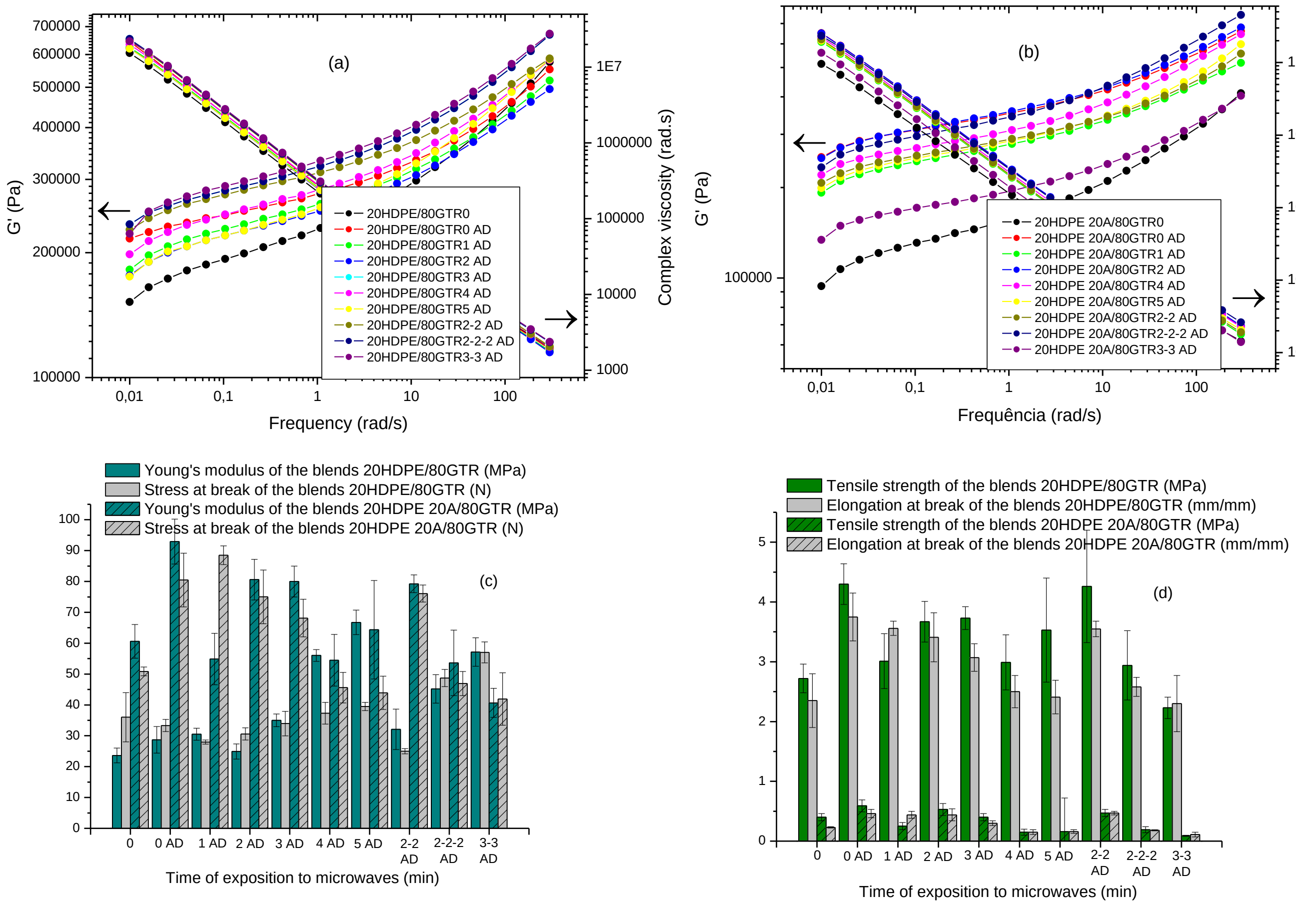

Figure 1 Evolution of G' and η* (a,b) and mechanical properties (c,d) of the analysed blends.

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THERMAL PROPERTIES OF BLENDS TYPE TPV HDPE/GROUND TIRE RUBBER DEVULCANIZED BY MICROWAVE

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Experimental

Thermal properties of blends TPV HDPE/Ground tire rubber (GTR) devulcanized by microwaves were analysed by Differential Scanning Calorimetry (DSC) in a DP Union DSC Q200 (20° C/min from -90° C to 300° C). The blends were prepared in an internal mixer Haake coupled to a torque Rheometer Polylab 900 (160° C, 80 rpm and mixing time of approximately 15 minutes) in concentrations of 20% HDPE and 80% devulcanized GTR, 80% HDPE and 20% devulcanized GTR in mass. Blends of the same HDPE, but with 5% of organically modified clay Cloisite 20A in the HDPE phase, were also prepared. The nomenclature of the blends is of the type XHDPE 20A/YGTRZ, where X represents the quantity of HDPE in mass, Y represents the quantity of GTR in mass and Z represents the time of GTR exposure to the microwaves, 20A represents the presence of clay. The rubbers were also mixed with vulcanization additives prior the mixing with the thermoplastic.

Results

The thermal properties results of blends HDPE/GTR containing or not Cloisite 20A are in the Table 1.

The melting temperature of HDPE phase was not influenced by the presence of rubber and the clay. In relation to the melting enthalpy, in blends 80HDPE/GTR with or without clay, the real values were below than the theoretical values (234,4 and 222,7 J/g with clay), while in blends containing 20HDPE/GTR with or without clay, the real values were lower than the theoretical values (58,6 and 55,7 J/g with clay) only for those

GTR exposed to the microwave for short periods of time. Probably due to the high concentration of rubber and presence of cross-links, there was a greater difficulty in the melting of the thermoplastic phase, being required greater levels of energy for melting occurs, which increased the melting enthalpy in these cases. According to Magioli et al. [1], the reduction in the value of melting enthalpy of the thermoplastic phase in blends type TPV in relation to the theoretical value is the result of a good interaction between the phases.

The presence of rubber and the occurrence of dynamic vulcanization influenced the HDPE cristallinity degrees in the blends. In general, the HDPE cristallinity degree in the blends was smaller than in the neat HDPE, with the exception of some blends, in which were verified very high values. Such values are probably due to the best dispersion of rubber phase in the matrix, the fast cooling of the blend, and the fact of sample be from a region of high cristallinity degree.

Table 1 Values of melting temperature (T_m), melting enthalpy ($\triangle H_m$) and cristallinity degree (χ_c) of HDPE phase in the polymeric blends analysed.

Sample	**T_m (^{o}C)**	**$\triangle H_m$ (J/g)**	**χ_C (%)**	**Sample**	**T_m (^{o}C)**	**$\triangle H_m$ (J/g)**	**χ_C (%)**
HDPE	141,74	183,72	62,7				
20HDPE/80GTR0	132,12	33,57	57,29	80HDPE/20GTR0	143,05	178,86	76,31
20HDPE/80GTR2	133,53	40,43	68,99	80HDPE/20GTR2	137,46	140,93	60,12
20HDPE/80GTR4	133,81	39,02	66,59	80HDPE/20GTR4	139,2	184,6	78,75
20HDPE/80GTR5	135,79	119,32	203,62	80HDPE/20GTR5	137,77	130,67	55,74
20HDPE/80GTR2-2	133,46	51,75	88,3	80HDPE/20GTR2-2	138,12	158,89	67,79
20HDPE/80GTR3-3	133,77	87,76	149,75	80HDPE/20GTR3-3	138,45	155,75	66,45
20HDPE 20A/80GTR0	133,71	36,41	65,4	80HDPE 20A/20GTR0	139,32	171,11	76,84
20HDPE 20A/80GTR2	132,56	41,21	74,03	80HDPE 20A/20GTR2	138,19	137,54	61,76
20HDPE 20A/80GTR4	135,24	118,24	212,39	80HDPE 20A/20GTR4	134,92	116,94	52,51
20HDPE 20A/80GTR5	136,47	119,24	214,19	80HDPE 20A/20GTR5	135,53	135,86	61,01
20HDPE 20A/80GTR2-2	133,81	41,72	74,94	80HDPE 20A/20GTR2-2	140,35	133,31	59,87
20HDPE 20A/80GTR3-3	134,77	43,25	78,62	80HDPE 20A/20GTR3-3	141,95	171,66	77,09

References:

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EFFECT OF POLYMER BLEND PHASE ARRANGEMENT ON RELEASE KINETICS OF INCORPORATED BIOACTIVE SUBSTANCE

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The main goal of this work is to correlate morphological parameters of the partially biodegradable binary blend of polyamide 6 (PA6) and a polylactide based biodegradable co-polyester blend (BioFlex) with the release kinetics of the incorporated bioactive compound.

The blends of PA6/BioFlex were prepared in ratios of 100/0, 90/10, 75/25, 60/40, 50/50, 40/60, 25/75, 10/90 and 0/100 by thermoplastic mixing. In addition, 1 wt. % of the bioactive compound (Tris(4-(dimethylamino)phenyl)methylium chloride) was incorporated into blends during the preparation step. Their morphology was studied by using scanning electron microscopy and solvent extraction method. The occurrence of co-continuous morphology was observed within the range of 40 to 60 wt. % of BioFlex (Figure 1).
The release kinetic were observed in three various aqueous media (distilled water, physiological solution, buffer pH = 2 and pH = 9). The obtained dependences of cumulative concentrations (determined by UV-VIS spectroscopy) of released bioactive compound on time were evaluated by using first-order kinetics (Equation 1) and the regression was processed by the least square method.

$$C_{REL} = C_{MAX} \times \left(1 - e^{-kt}\right) \qquad (1)$$

where, C_{REL} (mg/g) is the experimental concentration of CV that was released at time t, C_{MAX} (mg/g), means the maximal theoretical concentration of CV released from 1 g of the sample, and -*k* (h^{-1}) represents the rate constant i.e. time needed to reach C_{MAX}

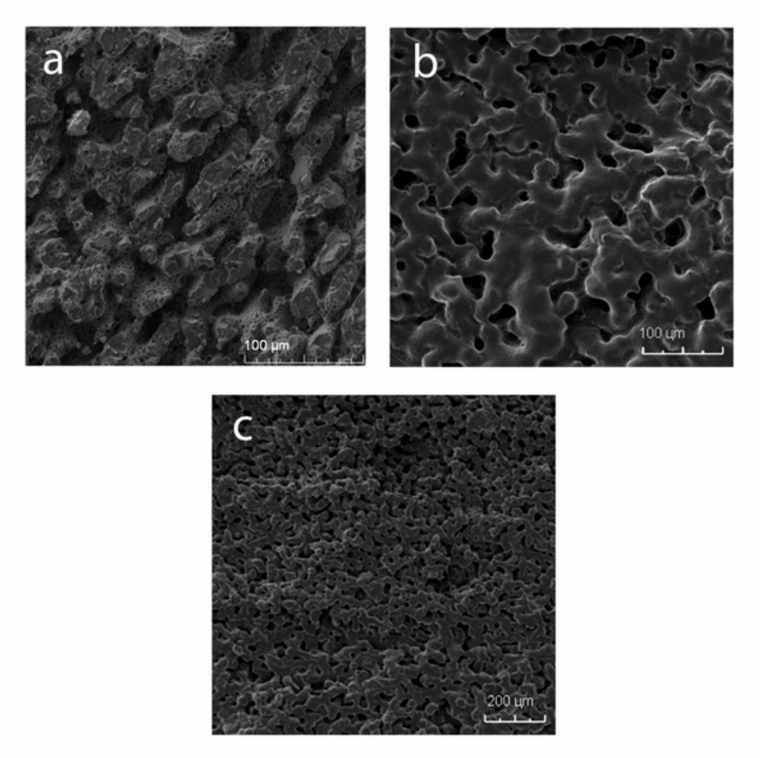

Figure 1 SEM pictures of the cold fractured specimens of PA6/BioFlex blends (a) 50/50, (b) 40/60, (c) 40/60 after chloroform treatment

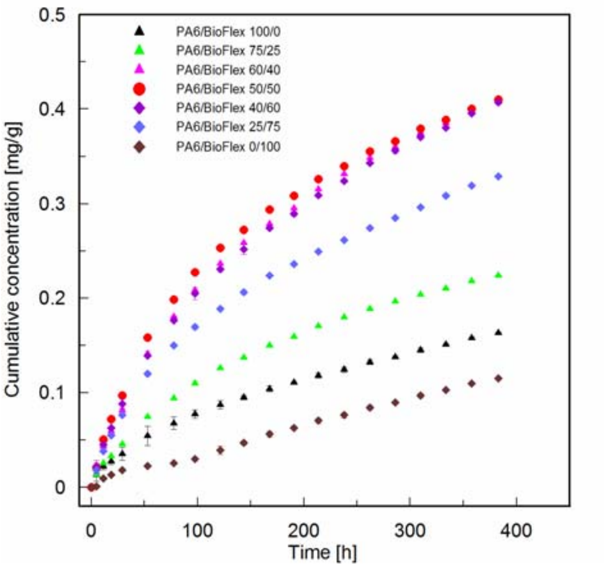

Figure 2: Release profile of tris(4-(dimethylamino)phenyl)methylium chloride into physiological solution.

The results show the significant effect of morphological arrangements of the polymer blends on release behaviour (example for distilled water shown in Figure 2) of the incorporated bioactive compounds. The effect of release medium was also found to be significant. In addition, evaluation according Equation 1 brings relevant release characteristics allowing a comparison of the process for various blends as well as release medium.

APPLICATION OF THE DSC, TG AND DMTA ANALYSIS FOR THE STUDY OF FUNCTIONAL PROPERTIES OF POLYURETHANE- RUBBER COMPOSITES OBTAINED FROM WASTE MATERIALS

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INTRODUCTION

One possible way of rubber waste management is to brake up the waste rubber and to use the obtained fine rubber, rubber granulate or rubber dust as a valuable additive to raw materials for production of composites made from rubber and different elastomers e.g polyurethane glues.

EXPERIMENTAL

Samples of polyurethane-rubber composites, of defined contents, were used for the analysis. At the first stage, polyurethane glues were received from the mixture of Recypol®201 and Recypol®601 polyols (obtained by chemical recycling of polyurethane foam) and MDI (4,4' diphenylmethane diisocyanate) used in excess. Then, the rubber-polyurethane composites from polyurethane glues (obtained at the first stage) and granulated rubber with the grain size between 1.5 and 2.0 mm, received from waste car tires, were obtained. The composites were placed in forms under the 2 MPa load and held at temperature of 363 K for 90 min. In order to determine the glass transition temperature the polyurethane-rubber composites samples were studied using DSC (Perkin Elmer PYRIS). Composite samples weighing from 15 to 20 mg were heated at a heating rate equal to 293 K in a nitrogen atmosphere at temperatures ranging from 123 K to 273 K. The analysis of the DMTA in the DMA Q800 apparatus of TA Instruments were subjected. Measurements were carried out at the temperature range from 123 K to 323 K at a heating rate equal to 2 K/min with the bending frequency range from 1 to 150 Hz.

RESULTS

Two glass transition temperatures were determined for polyurethane-rubber composites and polyurethane glues and one glass transition temperature of the rubber granulates. An increase of glass transition temperature of composites with the increase of the isocyanate index of the used polyurethane glues was observed. This can be associated with the possible reaction of diisocyanate with rubber granulate. The analysis of the DMTA spectra allowed us to determine the glass transition temperature Tg and the course of the relaxation processes in the composites. The analysis of the changes in the storage module E' and loss module E" as a function of temperature enabled the calculation of the activation energy for relaxation processes of various polyurethane glues and polyurethane-rubber composites. The thermogravimetric analyses of rubber-polyurethane composites, granulated rubber and polyurethane glues were carried out by means of the PYRIS device by Perkin Elmer. Measurements were made within the temperature range between 298 K and 1173 K, with the heating rate of 20 K min^{-1}, 40 K min^{-1}, 80 K min^{-1}, and with nitrogen as carrier gas.
Stability of composites made from polyurethane glues and granulated rubber was estimated on the basis of thermogravimetric measurements of apparent activation energy of their thermo-degradation process. On the basis of obtained results, one can conclude that the values of apparent activation energies of composites destruction for polyurethane glues increase along with a raise in isocyanate and polyol Recypol$^{®}$201 contents in glues.

CONCLUSIONS

The application of the DSC, DMTA and TG analysis for the study of functional properties of polyurethane-rubber composites obtained from waste material (the application of Recypol$^{®}$201 and Recypol$^{®}$601, received in the processes of glycolysis of used polyurethane foams, as an ingredient of polyurethane glue and granulated rubber from used tires car) allows us to confirm that the obtained composites were stable with good mechanical properties, that was also the subject of our previous works.

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DEVELOPMENT OF MWCNT/CARBON FIBER REINFORCED EPOXY MATRIX COMPOSITES FOR AERONAUTICAL APPLICATIONS

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Introduction The increasing demands of the aerospace industry require the development of novel structural materials. Besides the mechanical properties one of the main requirements towards airframe materials is electrical conductivity. When lightning strikes an airplane the current has to be evenly distributed in the structure, otherwise the localized damage can lead to catastrophic failure. Nowadays in most airplane hulls a metal web is integrated into the composite structure to enhance its electric conductivity. The aim of our research was to develop a novel CNT/carbon fiber/nanofiber reinforced material with high electrical conductivity and suitable mechanical properties, which is capable of effectively distributing the electrical current without installing a heavy metal net into the composite.

Materials and methods Baytubes C150HP (Bayer, Germany) multiwalled carbon nanotubes have been selected as nanosized reinforcement in the composites based on their high electrical conductivity. As matrix MR 3012 (Ipox Chemicals, Hungary) aliphatic epoxy resin was used with MH 3111 (Ipox Chemicals, Hungary) hardener (mixing weight ratio: 100:116). The system is suitable for prepreg applications.

The MWCNTs were dispersed in the epoxy component by a masterbatch method, developed for low viscosity resins utilizing a three roll mill [1] in 0, 0.1, 0.3, 0.5 and 1 weight% proportions. Hybrid composite laminates consisting of 4 layers of unidirectional carbon weave in [0/90/0/90] layer sequence were prepared by vacuum bagged hand layup. The laminates have been cured at 80°C for 8 hours.

The conductivity of the specimens has been investigated by two methods. In the first method was surface resistivity measurement according to IEC 60093 performed using an Iteco Gigalab digital megaohmmeter with cylindrical electrodes (Ø63 mm, and 4 mm thickness). The second method was resistivity measurement in a four electrode setup using four gold plated electrodes placed linearly in 20 mm separation and an Agilent 4338B milliohmmeter.

Results and discussion The results of the tests provided promising results. The surface resistivity tests showed that the surface resistivity of each sample was below the lower threshold of the megaohmmeter (1 kΩ) so the samples were electrically conductive. The results of the four-pin resistivity measurements are presented in Table 1.

Table 1 Specific resistivity of the samples acquired from four-pin resistivity measurements

Sample	Specific resistivity (Ωcm)	Conductivity (S/cm)
0 wt% MWCNT	351.85	0.0280
0.1 wt% MWCNT	7.71	1.9684
0.3 wt% MWCNT	72.22	0.0280
0.5 wt% MWCNT	2.13	0.4836
1 wt% MWCNT	10.91	0.1168

Conclusions The results of both electric conductivity tests are promising. The MWCNT filling of the matrix of the conventional composite caused two orders of magnitude increase in the conductivity thanks to the conductive MWCNT network in the matrix.

Acknowledgement This work is connected to the scientific program of the "Development of quality-oriented and harmonized R+D+I strategy and functional model at BME" project supported by the New Széchenyi Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and by the Hungarian Scientific Research Fund (OTKA NN82462). The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Clean Sky Joint Technology Initiative under grant agreement n° 270599, and n° 298090.

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CHARACTERIZATION OF TERNARY MIXTURES PA-6 / SEBS-*g*-MA OR PVB FILM / NANOFILLERS

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This work presents a study of blends polyamide-6 (PA-6)/SEBS-g-MA or PVB film, with and without addition of nanofillers: two sodium smectite clays (Laponite RD and CloisiteNa$^+$), and nano-sized fumed silica. To mixtures composed by 60 wt.% of PA-6, 40 wt.% of SEBS-*g*-MA or PVB film, 5 wt.% of filler were added. The mixtures were characterized by mechanical tests (tensile and impact strength), and morphological analysis (scanning electron and optical microscopy).

Figure 1 presents the notched Izod impact strength of the blends with and without clay or silica addition. It can be seen from Figure 1 that the notched Izod impact strength increases when the PVB film or the SEBS are added to PA-6. The blends containing clay or silica also present an improvement in the impact strength values. In particular, the PA-6/PVB blends containing Laponite or CloisiteNa$^+$ shown an abrupt increase in impact, reaching values of 1166 J/m. Figure 2 shows the Young's modulus of the samples. The results show that the PA-6/PVB film or PA-6/SEBS-*g*-MA blends present reduction in modulus values. A reduction in this property is a common observation in rubber toughened polymers because of the lower strength and modulus of the dispersed phase[1,2]. Surprisingly, the addition of nanofiller, mainly CloisiteNa$^+$, recovers the rigidity of the blends. Moreover, the microscopical observations show that the presence of nanofiller stabilizes the morphology of the blends: the droplets are homogeneously dispersed within the matrix, and the size of the disperse phase is reduced.

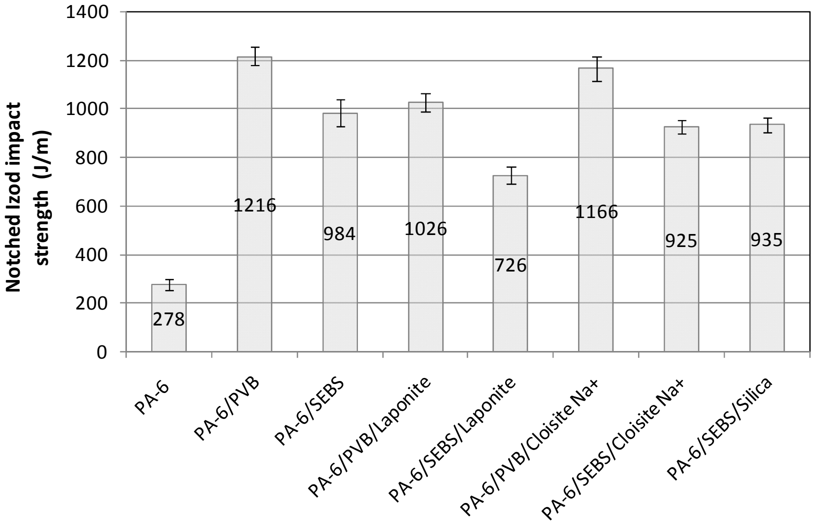

Figure 1. Izod Impact Strength of the blends with and without addition of nanofillers.

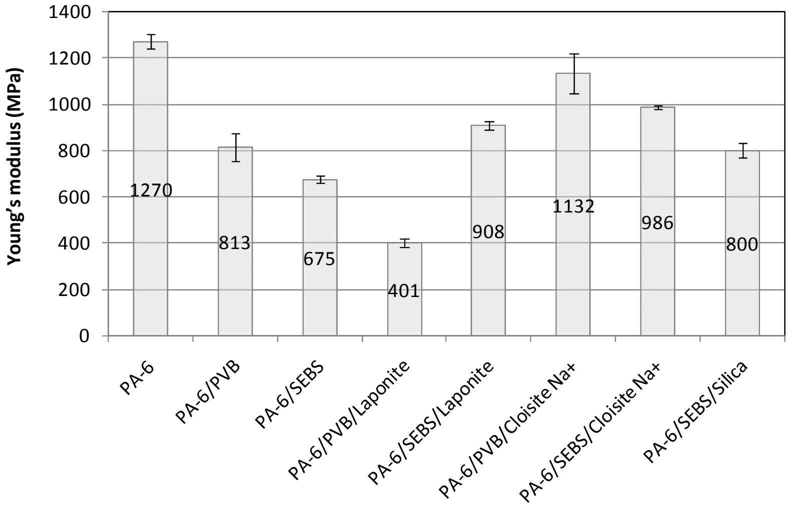

Figure 2. Young's modulus of the blends.

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RHEOLOGICAL PROPERTIES IN PROCESSING AND MORPHOLOGICAL STRUCTURE OF COMPATIBILIZED PP/HDPE BLENDS

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Blends of polypropylene (PP) and high density polyethylene (HDPE) with and without ethylene-propylene–diene terpolymer (EPDM) as compatibilizer were prepared by a twin screw extruder. The EPDM was added to PP/HDPE blends at two levels (5 and 7 phr). Rheological properties in processing were followed during preparation of samples in twin screw extruder. Extrusion capacity (or output) (Q), torque (TQ) and back-pressure (p) were recorded and apparent viscosity was determined by TQ/Q and p/Q ratios. Morphology was determined by scanning electron microscope (SEM). Ultrathin sections of the samples were observed by the scanning transmission electron microscopy (STEM). The results of rheological properties in processing (Figure 1.) showed higher viscosity value of pure PP, compared to pure HDPE. Blending of HDPE and PP decreased TQ/Q and p/Q values, so that the PP/HDPE blends had viscosity between the values of pure homopolymers. In PP-rich blends (PP/HDPE 80/20), the addition of the compatibilizer EPDM slightly decreased TQ/Q values. The decrease was more expressed at higher EPDM addition. The p/Q ratio value was just slightly increased by a higher amount of EPDM. In the HDPE-rich blend (PP/HDPE 40/60) addition of the compatibilizer EPDM had no influence on the apparent viscosity (TQ/Q and p/Q). SEM micrographs showed quite good compatibility in the PP/HDPE blends; interface adhesion seems to be sufficient even without the addition of the compatibilizer. PP/HDPE 80/20 blend revealed two-phase structure where the HDPE particles were dispersed in the PP matrix. The particle size in the blends did not change significantly by the addition of compatibilizer

EPDM. Morphological difference between the PP/HDPE blends, with 5 or 7 phr of EPDM is very small.

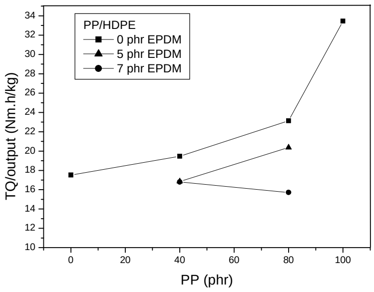

Figure 1. Processing parameters (TQ/Q) of PP, HDPE and PP/HDPE blends

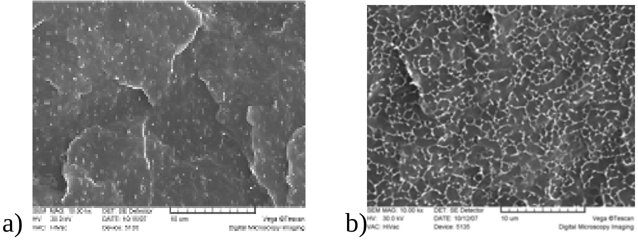

Figure 2. SEM micrographs of PP/HDPE/EPDM blends: a) 80/20/7 and b) 40/60/7

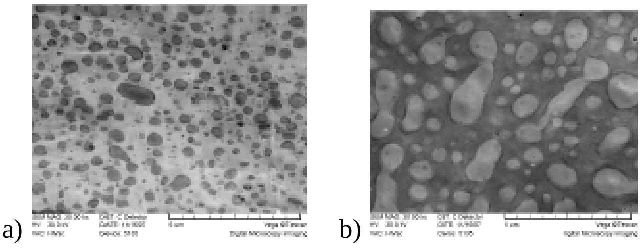

Figure 3. STEM micrographs of PP/HDPE/EPDM blends: a) 80/20/7 and b) 40/60/7

In the PP/HDPE/EPDM 80/20/7 blends core-shell structure[1] is observed (Figure 2 a), where the HDPE particles were enveloped by EPDM. The blends PP/HDPE 40/60 (both non-compatibilized and compatibilized with EPDM) tend to be co-continuous (Figure 2 b). Localization of EPDM at the interphase was confirmed by the STEM (Figure 3.). The size of the HDPE particles in the PP/HDPE/EPDM 80/20/7 blend is smaller than the size of the PP particles in the PP/HDPE/EPDM 40/60/7 blend, as a result of higher viscosity of PP. It can be concluded that the compatibilizer EPDM did not change significantly the rheological properties in the processing nor the morphology of the PP/HDPE blends.

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EFFECT OF UV-IRRADIATION ON POLY(ACRYLIC ACID)/SILVER NANOCOMPOSITES

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Introduction

Poly(acrylic acid), PAA, is polyelectrolyte braoadly applied in practice owing to its advantageous physicochemical properties in solution and in solid state, for example, the high ability to water sorption, reversible changes of chain conformation, sample volume and swelling degree[1]. The important feature of PAA is its solubility in water and low cyto-toxicity. Particularly interesting is PAA capability to formation of charge transfer complexes with transition metal salts or other polymers[1-3]. The objective of this work was to synthesize of PAA/silver nanocomposites and to investigate theirs spectroscopic and photochemical properties. Mercaptosuccinic acid was chosen as stabilizer of Ag nanoparticles because it is non-toxic substance with metal chelating properties used in pharmacy as antidote for heavy metal poisoning.

Methods

Monomer (acrylic acid, AA) was purified by distillation under reduced pressure. PAA has been polymerized in aqueous solution at 50 - 70°C in the of 30% hydrogen peroxide as initiator.

Ag nanoparticle has been obtained by modified method[4] based on the reduction of $AgNO_3$ by $NaBH_4$ in the presence of mercaptosuccinic acid (MSA) as stabilizer. The blend composed of 5%(wt) Ag/MSA and 95%(wt)PAA was prepared by solution mixing and film casting.

The samples were exposed to high pressure mercury vapor lamp in solution or in solid state in air atmosphere at room temperature. The lamp emitted polychromatic radiation (λ = 248-578 nm). The maximal times of exposure were: 25 hours for studies in solutions and 10 hours for studies in solid state. The samples were analysed directly after irradiation to avoid the post-effects.

FTIR spectra of PAA/Ag/MSA and PAA films before and after UV-irradiation were obtained using FTIR Genesis II (Mattson, USA) spectrophotometer. UV-Vis spectra of solutions were recorded using UV-1601PC spectrophotometer (Shimadzu, Japan).

Results and Discussion

Pure PAA in solution practically does not absorb above 210 nm but UV-irradiation leads to systematic increase of absorbance without formation any particular band. The spectrum of Ag nanoparticles stabilized by MSA shows absorption in range of 250-500 nm with clear maximum at 420 nm. This band, shifted to 391 nm in spectrum of PAA/Ag/MSA, is typical for Ag plasmon.

UV-irradiation of PAA/Ag/MSA causes increase of absorbance in whole range but the position of band attributed to Ag plasmon is not changed. Similar effect is observed in spectra of Ag/MSA solutions (without polymer).

FT-IR spectra show the characteristic structure of PAA. The hydroxyl and carbonyl bands were applied for monitoring the chemical changes occurring in UV-irradiated samples. It was found that observed relative changes in integral intensities of C=O and OH are somewhat lower in PAA/Ag/MSA than those in pure PAA.

Conclusions

UV-Vis spectroscopy confirms the presence of silver nanoparticles in PAA solid composite and in aqueous solution. They are stable upon UV-irradiation in studied system (PAA/Ag/MSA).

FTIR spectroscopy proves that pure PAA undergoes systematic degradation during UV-action but its photostablility is slightly enhanced in composites with nanosilver.

PAA/Ag/MSA composites, as antibacterial materials, can find pharmaceutical or medical applications.

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Effect of electron beam on CNTs

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Introduction. Since their discovery in 1991, carbon nanotubes (CNTs) have generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties. This combination of properties makes them ideal candidates as advanced filler materials in composites, in particular for polymeric systems. For some specific applications, the polymeric product has to be subjected to treatment with energetic radiations, like electron beam during sterilization, and it becomes important to know how polymer but also how fillers respond to those treatments. Polymers usually subjected to these treatments have been studied in detail for more than a decade [1]. For CNTs most properties depend sensitively on the number, diameter and helicity of their shells so on their structure. Several works [2] reported the manipulation of nanotubes structure in several experiments, e.g., by functionalizing CNT chemically, loading tubes mechanically (straining, bending, or breaking), cutting them irradiating with electrons or ions. Electron irradiation is a powerful tool to manipulate structures locally because atoms can be displaced by collisions with high energy electrons while oxidation of tubes is useful for their following fictionalization.

In this project different kind of CNTs were subjected to oxidation and electron beam irradiation and the effects of the treatment were studied with several characterization techniques.

Experimental._The carbon nanotubes listed below in order of perfection have been used to test the effect of e-beam irradiation.

- αCNT, commercial MWCNT, produced by NanoCarbon Technologies Co., Japan.
- εCNT, commercial SWCNT, produced by Thomas Swan & Co Ltd., Consett, Country Durham, United Kingdom.
- δCNT, experimental MWCNT grew by Department of Materials Science and Engineering, Meijo University, Tempaku-ku, Nagoya, Japan.
- γCNT, experimental MWCNT grew by the Carbon Group of Polytechnic of Torino, Torino Italy.

CNTs were subjected to oxidation treatments following the procedure made up in our laboratory in order to obtain a certain degree of oxidation without too many damages for the tubes structure. The oxidative treatment utilized is the following: 200 mg of CNT were heated at 60°C in 100 ml of 20% HNO_3 aqueous solution for 6 h. The suspension was sonicated in a water bath (Bandelin Sonorex Super 10P, 35 kHz) for 24 hours.

The irradiation treatment has been performed in the industrial plant of Bioster Spa, Seriate, Bergamo, Italy. Electrons were accelerated to an energy of 10 MeV ($1.602*10^{-13}$ J), the beam was continuous with a power of 20 kW.Samples, oxidized or not, in form of powder, inserted in plastic bag with thickness lower than the penetration depth, were irradiated in three cycles of 33 kGy of absorbed dose. The total absorbed dose of about 100 kGy corresponding to 100 J/kg.

Characterization – The morphology of original CNT and treated ones was studied recording images with a ZEISS SUPRA™ 40 FESEM and a JEOL 3010-UHR TEM. Thermal degradation was measured on approx. 10 mg sample in a TGA Q 500 balance, TA Inc., with alumina pan in a 70 cm^3/min nitrogen flow and with a 10°C/min heating ramp from room temperature up to 900°C. Thermo-oxidation was determined in the same way in a 70 cm^3/min air flow. A micro Raman RamanScope (Renishaw), with a Ar^+ laser excitation wavelength of 514.5 nm and the power 30 mW, was used for the characterization of the structural order.

Results and Discussion. Nanotubes at room temperature are damaged severely and irreversibly when irradiated with electrons of energies above a critical threshold due to the accumulation of radiation damage. In CNT, the collision of an energetic particle with a carbon atom will result in displacement of the atom, i.e. formation of a vacancy (single- or multi-vacancy) and a number of primary knock-on atoms which, if their energy is high, leave the tube or displace other atoms in the CNT. This is verified with TEM and FESEM images (fig.1) where CNTs show a different morphology due to erosion of external wall with the exposition of the inner shells, net fracture of tubes etc. Also oxidation promotes the modification of outer shells of tube, with removal of part of them and the deposition of a carbonaceous layer.

Raman and TGA measures (table 1) are useful to determine respectively the extent of the defects in carbon nanotubes by the ratio of the D and G band intensities (I_D/I_G) and the presence of contaminants (purity) together with their thermal stability. The intensity of the D band is proportional with lattice defect and the degradative process temperature can be correlated with the presence of defects, either of the pristine material or after any treatment (i.e. the less defects, the higher temperature).

CNT defects, if present, are concentrated on the outer shells, so the effect of these treatments which act on these walls could be double: in perfect tubes (αCNT and εCNT), the removal of part of outer shell, increases the defectiveness while for defective tubes it increases the perfection taking away the faulty parts of them. Data confirm that the treatments done increase the defectiveness (increasing the I_D/I_G ratio and the TGA residue and decreasing the temperature at which the rate of degradation is higher, indicating a less stability) of the perfect tubes while for defective tubes the effect is completely the opposite

Conclusions. In this work different kinds of nanotubes were subjected to irradiation and oxidation. These treatments increase the defectiveness of perfect CNT while decrease the concentration of defect of less perfect ones, because of defect are present above all on their surface which is the zone where treatments are effective.

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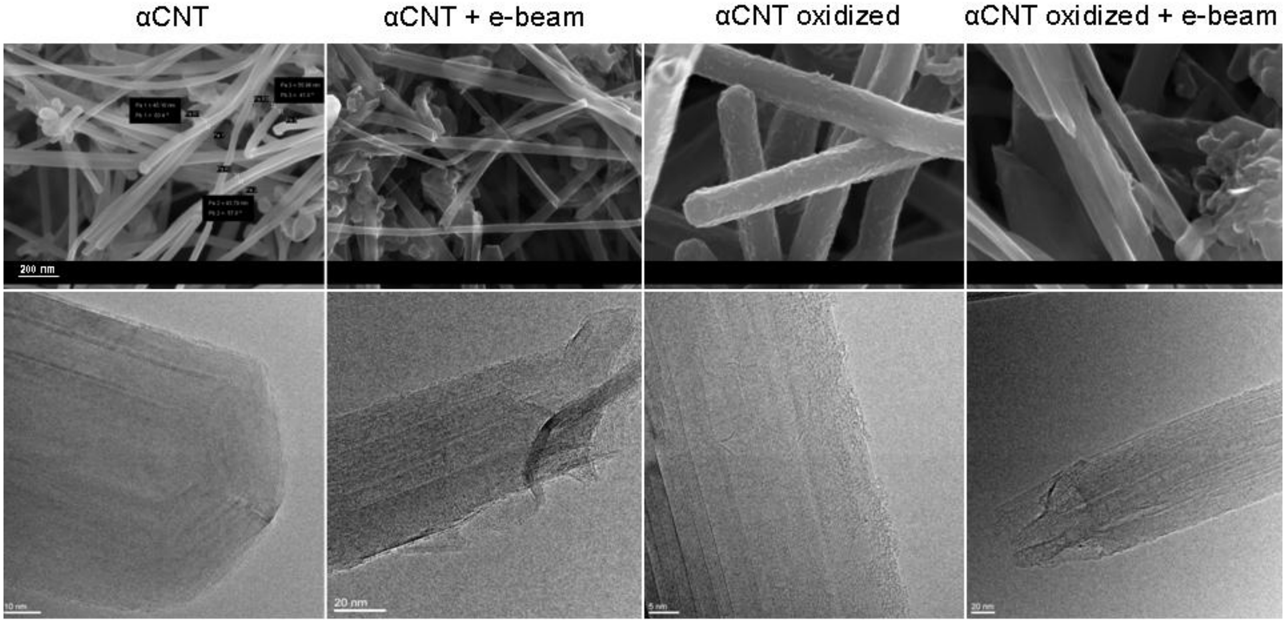

Fig. 1 Examples of FESEM (first row) and TEM (second row) images of pristine and treated αCNT.

	Raman I_D/I_G				TGA residue at 900°C [wt%]				TGA T_{max} [°C]			
	αCNT	δCNT	γCNT	εCNT	αCNT	δCNT	γCNT	εCNT	αCNT	δCNT	γCNT	εCNT
Pristine	0.111	1.343	0.747	$1.81*10^{-4}$	2.8	22.7	6.3	4.4	803	551	520	570
Oxidized	0.115	1.060	0.692	0.372	4.8	13.6	4.9	5.3	662	594	548	571
Irradiated	0.151	0.996	0.610	0.361	2.8	18.0	1.6	5.8	750	520	554	577
Oxidized and irradiated	0.104	1.176	0.603	0.212	4.8	12.3	4.6	4.4	793	597	551	573

Table 1 Raman and TGA data of pristine and treated CNT.

POLYMERIZATION METHOD OF FORMATION BITUMEN-POLYMERIC BLENDS

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Oil bitumens being used everywhere in practice for asphalt concrete production not always provide the necessary operational characteristics for a road asphalt covering. It is possible to increase the quality of a paving by using composite binding materials on the basis of bitumen, for example, polymer-bitumen materials. Two approaches exist to receive polymer-bitumen materials: combination of ready polymer with bitumen or polymerization of the corresponding monomers in bitumen. Each of these approaches has its advantages and shortcomings. One of shortcomings of the first approach is a limited number of the polymers compatible to bitumen. Polymerization of vinyl monomers in bitumen allows expanding essentially quantity polymer-bitumen materials.

In this work we present the results of research of radical polymerization of styrene, methyl- and butyl methacrylates in the medium of oil bitumen for the purpose of an assessment of influence of bitumen, as reactionary medium, on radical polymerization of vinyl monomers.

The usage of oil bitumen as a reactionary medium for polymerization of styrene results in conditions, both material, and thermal initiation, as in the atmosphere, and argon. As a whole speeds of reaction in the medium of oil bitumen are lower than those of block styrene polymerization. Received by thermal polymerization in the medium of oil bitumen samples of polystyrene are characterized by the low molecular masses which does not depend on duration of polymerization and rather narrow molecular and mass distribution. The received results specify that oil bitumen is a quite effective transmitter of chains during thermal polymerization of styrene.

In the conditions of material initiation with use of peroxide t-butyl process of radical polymerization of styrene in oil bitumen, it is accompanied by the induction period which duration decreases with increase in concentration of monomer in the reactionary medium. Values of speeds of polymerization of styrene in oil bitumen are essential below similar parameter to modeling system toluene – styrene in identical conditions. As well as in thermal polymerization, values of molecular mass of the polystyrene received in the presence of peroxide t-butyl, don't depend on duration of reaction and don't exceed 15000. However in the initiated polymerization with distinction in molecular mass of the polymers received in oil bitumen and in toluene, they are not so considerable.

Other type of the used monomers, is ether of methacrylic acid – methyl- and butyl methacrylates served. As well as in case of styrene, acid – methyl- and butyl methacrylates polymerization in oil bitumen proceeds with the induction period which is absent at polymerization in toluene. However, unlike styrene and butyl methacrylate, limiting conversion at methyl methacrylate polymerization in bitumen comes nearer to that of reaction in the medium of toluene. For both methacrylates speed of polymerization in the medium of oil bitumen is lower, than in toluene. Distinctive feature of polymerization in oil bitumen methacrylates is receiving polymers with higher molecular masses, rather than with styrene. Moreover, molecular masses polymethylmethacrylate, received in toluene and bitumen under other identical conditions of synthesis, differ slightly.

Thus, after having analyzed the results of radical polymerization of the considered vinyl monomers it is possible to conclude that oil bitumen as medium for polymerization is in many respects similar to usual organic liquids, but possesses poorly expressed inhibit action.

Polymerization approach of combination of polymeric connections with bitumen allows to receive composites with a wide range of ratios of components on a basis, even, polymers incompatible with oil bitumen. It promotes essential expansion as set polymer-bitumen materials, and to a range of their physico-mechanical and operational characteristics, and, therefore, expansion of area of practical use of similar composite materials.

TETRAZOLE-CONTAINING PAIRED POLYMERS

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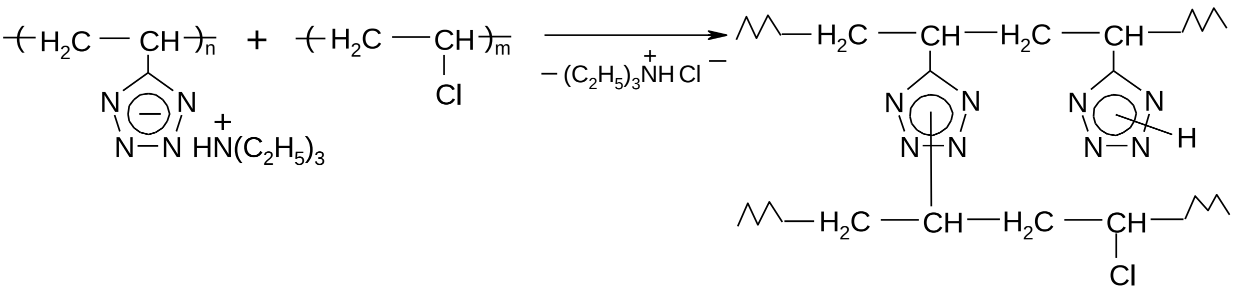
The paired polymer is the system constructed of two (or more) heterogeneous macromolecules by their chemical structures. They are chemical bonded between themselves, as a result, of reactions of functional groups, situated in recapitulative units of every macromolecule. The presence of functional groups capable to chemical reaction with each other, revealing covalent bonds, is an obligatory condition to form paired polymers. The chemical reactions between two polymers are well known and attractive as a modification method of high molecular compounds, realizing, so-called, forced mix of polymers. The present paper demonstrates possibility of alkylation reaction of the tetrazole cycle by halogen containing compounds in the base presence, to realize compelled mix of two unmixed polymers: poly-5-vinyltetrazole (PVT) and polyvinylchloride (PVC).



At low summary concentration of polymers (< 0.5 g/dl), the reaction system stays homogeneous and mobile during all over the process. The educed product from the reaction mixture is a paired polymer PVT-PVC. Both homopolymers come quantitatively into the reaction between themselves, therefore component ratio in the paired polymer corresponds to the initial ratio of PVT:PVC. However, the conversion degree θ in the reaction between PVT and PVC is not higher than 3-5 mol.% and does not depend on the quantity of added into the system base. The formation of the paired polymer from PVT and PVC stipulates the change of properties in comparison with initial homopolymers. Ionogeneous character of PVT is transmitted to a paired polymer, which is able to swell in alkali water solution with hydrogel formation. The reaction process between PVT and PVC at higher summary concentration of the polymers (>5 g/dl) is accompanied by gelatination of the reactive mass. Flowability-loss time by the system depends on many parameters: initial ratio of polymers, quantity of TEA taken into reaction and temperature. The increase of reagent concentration leads to the formation of the paired polymer swelling in DMF. Probably, it is the result of conversion degree increase at the reaction between PVT with PVC up to θ = 10-14%. At high polymer concentrations the participation of PVC monomer fragments is probable not only in alkylation reaction of tetrazole cycles but also is in the reaction of HCl molecular elimination.

Owing to the contents of PVT ionogeneous macromolecules in the structure, the paired polymers swell in in alkali water solution forming opalescent hydrogel. On its turn, a paired polymer with higher content of PVC macromolecules is able to limited swelling in THF, which is a solvent for PVC and sedimentary for PVT. Thermal stability of the paired polymers practically doesn`t differ from initial PVT and PVC homopolymers: the temperature of decomposition is 220-225 ^{o}C. The process of thermal decomposition is accompanied by considerable exothermic effect, conditioned by destruction of tetrazole cycles. In spite of the fact, that mixtures of PVT with PVC in DMF make transparent solutions without visible signs of phase division, it is impossible to obtain homogeneous films from mechanical mixtures of the mentioned polymers an account of component incompatibility. PVT, itself, does not possess film forming properties. Paired polymers make films: homogeneity of them grows depend on the reaction length between the polymers, according increase of conversion degree θ. In conclusion one should note, that owing to high complexing ability of PVT, the films from the paired polymers can be doped by ions of the wide number of metals.

THERMAL AND CHEMICAL CHARACTERIZATION OF NEW RUBBER ADDITIVIES FROM RENEWABLE RESOUCES

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Introduction

The development of new rubber formulations, with properties that meets high performance, drives to a constant search for high precision information about each component of the recipe. When, due to the needs of a specific application, the artifact must be made of high performance elastomers, one must be even more careful in the choice of the ingredients. This work is about the characterization of rubber additives from renewable resources, which will replace some which are not, like zinc oxide, aromatic oil and fillers. The new additives were obtained from soybean, wheat and sugar cane and characterized by granulometry, absorption atomic spectroscopy (AAS), elemental analysis (CHN), TGA and FTIR.

Results and Discussion

The FTIR was used to verify the chemical structure of the renewable source raw materials. Figure 1a presents the FTIR spectrum for MDECR. For this sample, the peaks around 3200cm^{-1} are related to the OH group axial deformation and the intramolecular hydrogen. Another peak at 2895cm^{-1} is related to the CH_2 and CH_3 groups axial deformation. At 1642cm^{-1} there is a peak related to the C=O axial deformation vibration. The peak at 1594cm^{-1} is related to the COO^- stretch and at 768cm^{-1} is related to the asymmetric angular deformation in the plane or twisting (methylenes rocking) [1], demonstrating a typical zinc carboxilate structure with the presence of stearic acid, thus confirming TGA analysis. The MDCO spectrum at Figure 1b presented peaks around 3305cm^{-1} related to the OH group axial deformation and to intramolecular hydrogen, around 2919cm^{-1} related to the C-H (CH_2 e CH_3) axial deformation, around 164cm^{-1} related to the C=O axial deformation vibration. At 1443cm^{-1} are the CH_2 and CH_3 angular deformations and at 1003cm^{-1} thr c-o axial deformation [1]. For it consists in MDCO, a filler derived from cereals, it was observed in this sprectrum the typical structure of cellulose [2,3] thus confirming the TGA analysis. For the MD600 spectrum, figure 1c presented peaks around 2925cm^{-1} related do the CH_2 and CH_3 axial deformations, at 1744cm^{-1} related to the C=O axial deformation vibrations, at 1467cm^{-1} related to the CH_2 and CH_3 angular deformation, at 1166cm^{-1} related to the C-O asymmetric axial deformation and the peak at 719cm^{-1} is related to the asymmetric angular deformation in the plane or twisting (methylene rocking) demonstrating that it consists in a typical soybean oil structure [1,2,3].

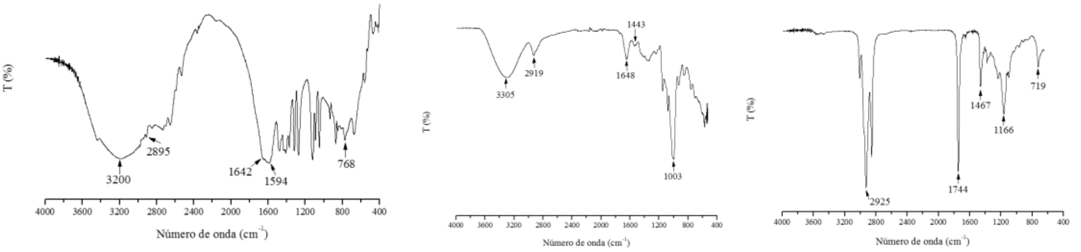

Figura 1: (a)FTIR spectrum for MDECR, (b) FTIR spectrum for MDCO and (c) FTIR spectrum for MD600.

Atomic absorption spectrometry was performed in order to determine the zinc content in the process activator – MDECR – derived from sugar cane. The analysis demonstrated that the sample has a 25,6% zinco content and 0,3% calcium content. In the elementar analysis of carbon, hydrogen and nitrogen (CHN) for compounds of plant origin and from renewable sources it was obtained minimal formulas being MDERC ($C_3H_50_5$), MDCO (CH_2O) and MD600 ($C_9H_{15}O$).

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CHARACTERIZATION OF RUBBER COMPOUNDS CONTAINING ADDITIVES FROM RENEWABLE SOURCES

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Introduction

The study of elastomeric compounds has become frequent, mainly using compounds of renewable sources for these products have lower impact on the environment [1,2]. In the present study, two compounds of renewable sources were used in an elastomeric formulation with technological application in automotive profiles. It was used a soybean oil (MD600) as plasticizing agent and a vulcanization activator (MDECR) derived from sugar cane. The technical performance through physico-mechanical analysis was evaluated. The results of the eco-friendly rubber compounds were compared to a standard formulation prepared with classic additives used in rubber industry. It was obtained, through the characterization of the rubber compounds, similar results of properties in comparison to the standard formulation and it was possible to reduce the traditional oil plasticizing and the zinc content in the composites.

Methods

A Shore A Teclock durometer model GS709 was used to measure hardness according to ASTM D 2240-05. Tensile and tear strength tests were performed in an EMIC DL-3000 instrument, according to ASTM D 412-06a and ASTM D 624-00, respectively. The tests were carried out after 40 h of conditioning the specimens at 23°C ± 2°C and a relative humidity of 50% ± 5%.

Results and Discussion

The Figure 1a presents the results of tensile strength test for the standard formulation and for the samples with MDECR.

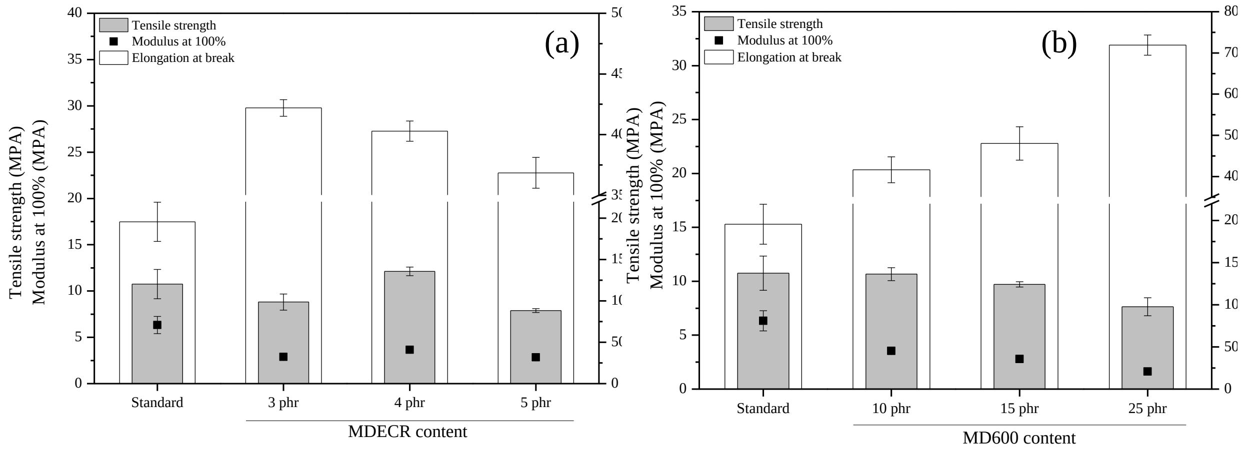

Figure 1: Tensile strength, modulus at 100% and elongation at break for standard formulation and for the samples with (a) MDECR and (b) MD600.

The tensile strength was close to the standard formulation with the incorporation of 4 phr of MDECR. The elongation at break shows an increase with the increase of the MDECR content. For the modulus at 100%, all samples presented reduced of this property [4].

The Figure 1b presents the results of tensile strength test for the samples with MD600. By increasing the content of the MD600 in the samples, there is a decrease in the values of tensile strength, except for the addition of 10 phr of MD600 that was close to the standard formulation. For the elongation at break, all samples showed an increase with the incorporation of the MD600 attributed to the greater spacing and mobility of the elastomer chains [3]. For the modulus at 100%, all samples with MD600 presented a reduction of this property.

Conclusions

The results showed that the samples can be obtained in less time of vulcanization with a reduction of 33% and 60% in the oil plasticizer and zinc content, respectively.

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ELECTRICAL CONDUCTIVITY OF HIGHLY OPEN-CELL POLYHIPE SOLID FOAM REINFORCED BY MULTIWALL CARBON NANOTUBE (MWCNT)

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Poly(styrene-co-divinylbenzene)/ single wall carbon nanotube poly(St/DVB)/SWCNT polyHIPE nanocomposite foams were synthesized via emulsion templating using a nonionic/anionic/cationic three-component surfactant system, i.e. Span20/ dodecylbenzene sulfonic acid/ ceryltrimethylammonium bromide. Adding a non-polymerizable porogenic solvent, i.e. toluene, into the continuous organic phase of high internal phase emulsion (HIPE) increased considerably the foam specific surface area at about 340 m^2/g. Figure 1 shows the SEM micrographs of the neat and SWCNT-reinforced polyHIPE foams. The mean cell size of the foam decreases as the SWCNT concentration in the aqueous pahse of the HIPE increases. The presence of SWCNT as a cosurfactant resulted in higher stability of the HIPE, and thereby produced polyHIPE foam with lower cell size. In fact, the probable adsorption of SWCNTs at the interface between the organic continuous and aqueous disperse phases prevents the Ostwald-ripening phenomenon [1].

Figure 2 shows the compression stress-strain curves of the composite foams compared to the polyHIPE foam without any reinforcement. The stress-strain curve of the polyHIPEs consists of three regions, a linear stress-strain region, a stress-plateau region, and a densification region showing an increase in stress, which is a characteristic of the open-celled polymer foams. The addition of 0.4 wt% SWNT to the polyHIPE considerably increased the compression Yang’s modulus and crush strength about 135% and 85 %, respectively. The incorporation of SWCNTs into the foam copolymer matrix increased significantly the compression properties. The synthesized composite foam with improved mechanical properties and relative high surface area can be used as a polymeric host to prepare ICP (Intrinsically conducting polymers)-based sensors [1]. However, the incorporation of various MWCNT levels increased the electrical conductivity of poly(St/DVB)/SWCNT polyHIPE nanocomposite foam on some extent.

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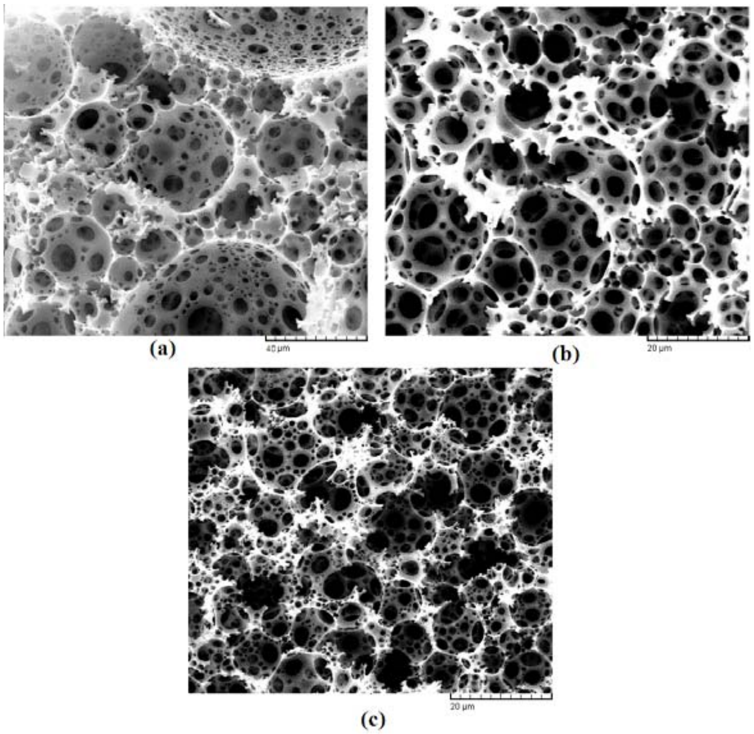

Figure 1. SEM micrographs of the polyHIPE foams reinforced by various SWCNT levels: (a) 0, (b) 0.1, and (c) 0.4

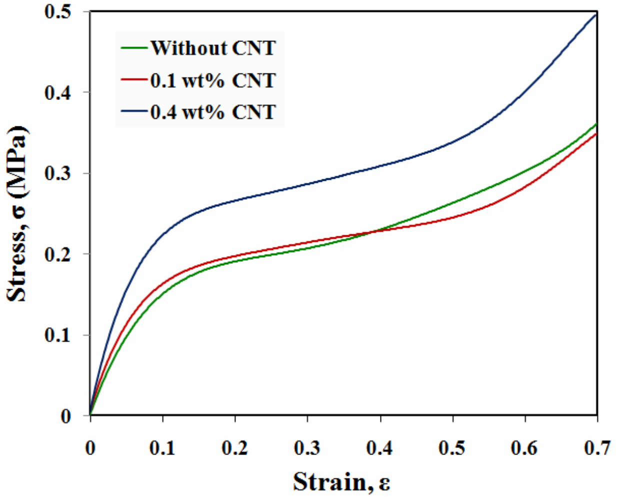

Figure 2. Stress-strain curves of the polyHIPE foams reinforced with various SWCNT levels.

ON THE INTER-CONVERSION BETWEEN VISCOELASTIC MATERIAL FUNCTIONS OF POLYCARBONATE

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Amorphous polymers show a time dependent response to an external solicitation. The time dependent response is usually measured in terms of shear response, whereas the bulk response is a more difficult to measure. In the framework of linear viscoelasticity at least two viscoelastic functions are needed in order to evaluate the mechanical behavior of viscoelastic amorphous polymers. Often the one of viscoelastic function is available in terms of creep compliance and the other one is available in terms of relaxation modulus: a reliable procedure for the inter-conversion is needed. Here the inter-conversions between relaxation moduli and creep compliances are described and a numerical method for the inter-conversion is presented. It is shown that the numerical solution lays on the analytical one and it is also less time consuming.

POLYMER DEGRADATION AND STABILIZATION

Full Abstracts of Oral Presentations

(PHOTO)OXIDATIVE DEGRADATION AND STABILIZATION OF FLAME RETARDED POLYMERS

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Flame retarded polymers are mainly used in long-term applications, therefore the role of stabilizers is decisive as many flame retardants influence the oxidative and photo-oxidative stability of polymers directly through acceleration of the degradation process or indirectly by interacting with antioxidants and light stabilizers. Whereas the behaviour of brominated flame retardants is well understood, the impact of halogen free flame retardants on the (photo)oxidation of polymers is only investigated in very few examples. However, phosphorus and nitrogen based flame retardants seem to influence the (photo)oxidative stability of polymers less than brominated compounds and they show no or less antagonism with hindered amine light stabilizers. Some recently developed flame retardants combine even flame retardancy and light stabilizer functionality.

Furthermore, many flame retardants act as a typical polymer filler, whereas it is known that filler interactions with stabilizers influence the overall stability of the polymer. This effect is even more critical if nano-sized materials are used. Adjustment of stabilization of plastics containing fillers either used for mechanical reasons or as flame retardant is necessary to achieve sufficient long-term properties. Filler deactivators and metal deactivators can play a decisive role in this respect.

Challenges of the (photo)oxidative stabilization of flame-retarded polymers are reviewed with regard to the components and mutual interactions with focus on halogen free flame retardants. Processing and long-term thermal stabilization of flame retarded polymers are discussed and strategies of improving the light stability of flame retarded polymers are provided. Additionally, the specific requirements of the stabilization of nanocomposites as potential flame retardant components are covered.

POLYMER OXIDATION AND ITS IMPACT ON MATERIALS PERFORMANCE AND LIFETIME PREDICTION: AN OVERVIEW

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This presentation offers an overview on the various aspects of oxidative degradation and lifetime prediction of polymers. We intend to address this topic in a broad manner, allowing us to provide some guidance and a generational perspective for new researchers. We also hope to successfully link applied and fundamental research trends that we have witnessed developing over the years with some ongoing activities in this area. It is not possible to condense all of "oxidative polymer degradation" into a 40 minute talk due to the broadness of the field as well as the depth of many excellent researchers who contribute to this area, as seen by countless original papers. Instead, we will focus initially on a few key trends that could provide a framework for the type of physical polymer chemistry approaches that have made a significant difference in our collective understanding of oxidatively-driven polymer degradation. This will be documented with highlights from the behavior of a few specific materials.

Oxygen will degrade polymers; it is just an issue of time, our performance expectations and how individual properties may change, that determines whether we should care about it or whether it may even be favorable. In some intances, for example accelerated environmental degradation, oxidative degradation is a desirable material breakdown avenue. Regardless of material requirements we must understand the interaction between oxygen and polymers. We will therefore review the following key aspects: Our basic understanding of thermo-oxidative degradation principles and potential countermeasures, approaches towards the measurement of oxidation rates, benefits of degradation kinetic modeling and how oxidation reactions depend on temperature. Examples will show how knowledge of oxidation sensitivity and its temperature dependence can be translated into a basic framework for oxidation extent with time. When coupled with concurrent material performance demands, and hence what matters from an application point of view, this may then yield guidance for material lifetimes. It is important to establish useful material property correlations with the underlying level of degradation. This is one of the most challenging tasks in comprehensive aging assessments, as reliable and predictable ‘aging’ cannot be expected to occur simply in matter of a few weeks (consider the example of wine). Relevant thermo-oxidative aging for lifetime prediction requires patience (i.e. sustained research funding) and an angle on temperature effects and mechanistic variations in the development of bulk property degradation. Ideally, multiple temperatures should be studied with extended aging times at low temperatures and comprehensive ‘aged-oxidized’ material characterization, together with a clear definition of performance criteria.

From a material point of view, this discussion will provide a perspective on generic behaviors in the thermal oxidative degradation of elastomers in comparison with polyolefins and then focus on epoxy and composite materials. This allows for an opportunity to touch on some of our latest trends in the oxidative aging of thermo-set materials. It offers an excellent example how the interplay between comprehensive experimental approaches, degradation modeling and data extraction using numerical methods can yield an understanding of highly complex material behaviors; initially at least with a perspective of polymer oxidation. We will review the current trends in experimental requirements and modeling approaches to gain a solid understanding of the underlying processes in such challenging polymers followed by a few comments on how this could be used for lifetime prediction and establishing performance limits.

Acknowledgments
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Photochemical Stability of Materials for Organic Photovoltaics

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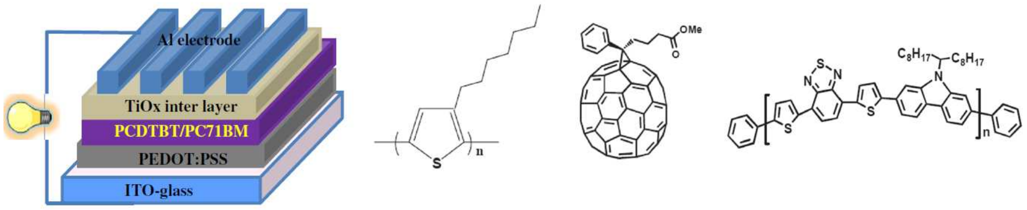
Polymer-fullerene-based donor–acceptor blended bulk hetero- junction (BHJ) solar cells have specific major advantages; for instance, they can be embedded in large-area devices through an efficient, low-cost manufacturing process that involves roll-to-roll methods. Polymer solar cells are now expected to have an innovative impact on developments in the electronics industry, particularly on account of flexibility, light weight, and easy processibility. Moreover, the efficiency of the device has been significantly improved and studied in many ways for several decades through extensive research.

Although the reported device efficiencies are already close to fulfilling some of the requirements of commercial applications, the short life span of polymer- based solar cells is still an obstacle to their commercialization. Because the polymer-based electronic device is seriously vulnerable to UV-visible light, high temperatures, air, water vapor, the photo-thermal stability of semiconducting polymer is essential for investigating the degradation mechanism of a BHJ active layer.



(left) A schematic of a polymer solar cell with a PCDTBT/$PC_{70}BM$ BHJ; (right) Molecular structures of photovoltaic materials (P3HT, PCDTBT, and $PC_{70}BM$).

In this communication, we report the physical and chemical degradation behaviors of active layers based on the current state of the art P3HT (poly(3-hexylthiophene)):$PC_{60}BM$ ([6,6]-phenyl-C_{60}-butyric acid methyl ester).

A new class of push-pull polymers combined with a fullerene derivative have enabled organic photovoltaic efficiencies approaching 10%. One such polymer is PCDTBT (poly[*N*-9”-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole). We present the long-term stability of PCDTBT, and PCDTBT in BHJ composites with the $PC_{70}BM$ fullerene derivative ([6,6]-phenyl C_{70}-butyric acid methyl ester).

The last part of the presentation reports part of an inter-laboratory collaboration to study the stability of seven distinct sets of state-of-the-art polymer solar cells. We present the stability data and detailed characterization of devices submitted to accelerated full sun simulation. Cells were submitted for destructive testing to analyze the BHJs. New insights in the variety of mechanisms by which polymer solar cells degrade are presented.

ADVANCES IN FIRE RETARDANT POLYMER MATERIALS

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Key Words : Fire retardants, Polymer combustion, Cone calorimeter, Time to ignition

ABSTRACT

Fire and flame retardants have been used so far as synonyms to indicate polymer additives which should reduce polymers fire risk (probability of fire occurrence) and fire hazard (fire consequences to people and property). In a fire, these additives role is that of increasing time to flashover above time required for people to escape from the fire scene and/or to allow for extinguishing means intervention.

Flame propagation was mostly involved in the research work carried out in this area in the past, whereas little attention has been devoted to the ignition step. However, time to ignition accounts for a significant part of the overall time to flashover, since the polymer material is accidentally exposed to a heating source. On the other hand, temperatures involved in the pre-ignition polymer thermal volatilisation and hence its rate, are lower than when flame is established, making thus easier contrasting processes that supply combustible volatiles to the gas phase prior to ignition occurrence.

The polymer degradation scenario before and after ignition is very different e.g. being respectively aerobic or very much oxygen depleted. Furthermore, after ignition, heat from volatiles combustion adds to that from the ignition source, affecting polymer heating rate. Since polymers thermal decomposition may be strongly affected by the degradation scenario, a detailed knowledge of physical/chemical evolution of polymers in the pre-ignition step is necessary to develop a successful strategy to delay ignition.

It would thus be convenient to define **flame retardants**, those additives which delay ignition and **fire retardants** those which slow down combustion/flame propagation.

In this work, thermal evolution of the polymer surface exposed to radiant heat in the Cone Calorimeter was monitored by thermocouples measuring surface and bottom temperature of exposed specimens as shown in figure 1 in which time delays due to polymer melting and volatiles flux growing to reach flammability limits, are shown

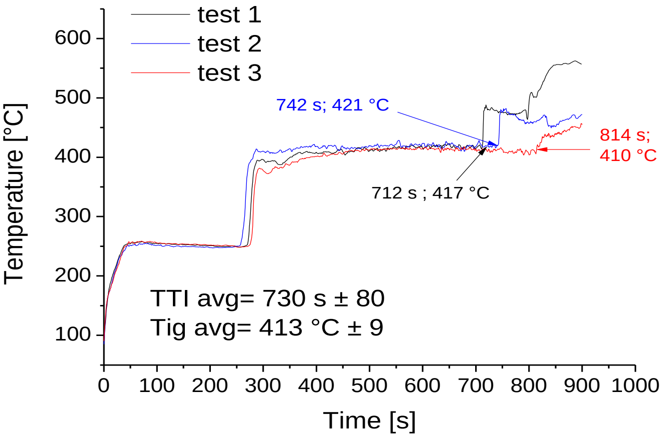

Figure 1. Surface temperature-time plot: PET copolymer exposed to 25 kW/m^2.

Physical polymer modifications were visually observed as shown in Figure 2 where build-up of surface char and bulk voids due to bulk volatilisation can be seen.

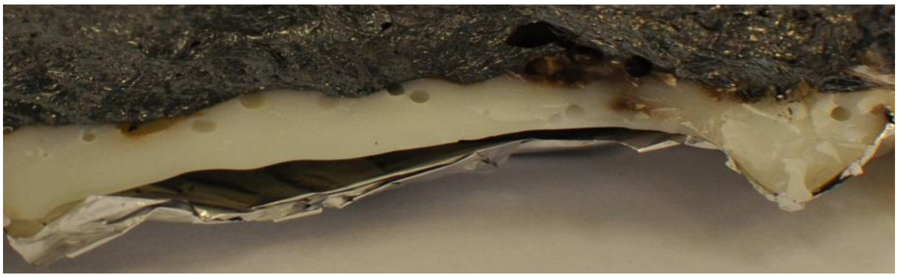

Figure 2. Polyamide 6 at ignition time on exposure to 25 kW/m^2.

Chemical polymer evolution on heating before ignition occurs was studied by infrared spectroscopy as shown in figure 3.

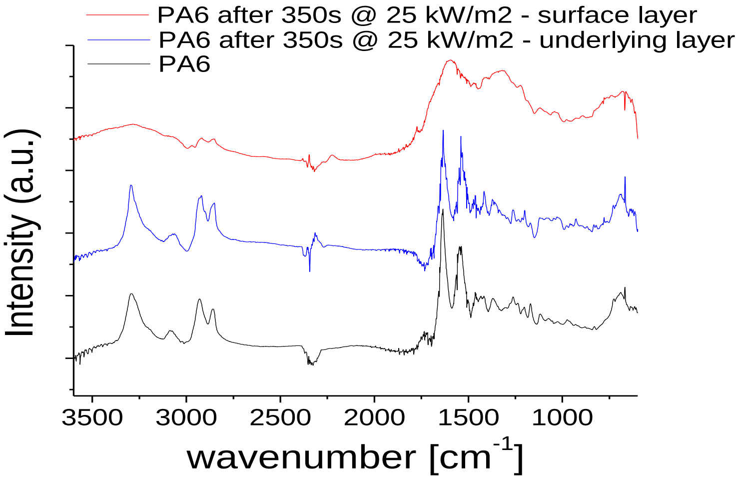

Figure 3. Infrared spectra of surface and bulk Polyamide 6 at ignition time (350s)on exposure at 25 kW/m^2, compared to original sample.

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STABILITY OF GAMMA IRRADIATED PVC FORMULATIONS WITH CROSSLINKING DENSITY ENHANCEMENT BY USING TRANSFER AGENTS

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Abstract

Gamma irradiated PVC has a very low reaction yield, so the use of a crosslinking agent is needed. TMPTMA is a trifunctional additive commonly used for such purpose. During irradiation TMPTMA suffers homopolymerization before any crosslinking reaction occurs. In this work we have added 3 transfer agents to PVC formulations (mercaptoethanol-ME, dodecylmercaptane-DDM, bencyltriphenyl phosphonium chloride-CBF) in order to reduce TMPTMA homopolymerization reaction, enhancing crosslinking density of the PVC network. Gel percentage and crosslinkg densities are reported for PVC formulations, as well as Mechanical (DMA) and spectroscopic (FTIR) evaluations. Stability has been evaluated by HCl evolution and Activation energies (Ea) for dehyrdrochlorination measured by a TGA-Arrhenius method.

Introduction

Irradiated PVC has been widely studied due its cost and versatility as in electrical wire and cable coating. On the other hand, high energy radiation has an important role in several chemical processes, like polymerization and graft reactions; however, the main reaction observed during polymer irradiation is crosslinking. For PVC, addition of a crosslinking agent as trimethylolpropane trimethacrylate (TMPTMA) is needed to improve networking PVC chains. Moreover, during first stages of irradiation TMPTMA suffers homopolymerization, affecting crosslinking density[1-3].

The use of transfer agents is widely known to have control in growing chains in order to get a polymer with specific molecular weight. Any kind of chemicals, including the own solvent could behave as a transfer agent, especially if they include sulphur in their structures[4]. Mercaptides, are transfer agents widely used; the ones involving n-dodecyl and the mercaptoethanol has been studied by several authors as agents for high temperatures, they have enough sensibility to react with double bonds, and been intensively used in reactions with acrylics[5,6]. In this work, we used three different transfer agents and TMPTMA to study their effect in the crosslinked density of PVC formulations.

Methods

An industrial PVC K=72 was used to prepare typical plasticized formulations. The polyfunctional TMPTMA, obtained from Sartomer, and a synergistic mixture of Ca/Zn stereates (2/1 % w) stabilizers were added, both industrial grade. Three transfer agents were also added: mercaptoethanol (ME), dodecylmercaptide (DDM) and bencyltriphenylphosphonium chloride (CBF). Other components (filler, plasticizer and co-stabilizer) were also industrial grade.

Samples were initially mixed in a roller mill at 150ºC, with an initial roller separation of 0.5 mm and steadily increased until 1.5 mm in a time period of 3 minutes. After milling, the final samples were prepared in a hot press PHI mod. Q230, to make plates with a 2 mm thickness following two steps: 1 minute hot press at 180ºC and 15 Tons and 5 minutes in cold press at 20 Tons. Plates were cut into final probes of 1/2 x 1/8 x 5 in.

The gamma treatment was carried out in an industrial irradiator with a ^{60}Co source under oxidative conditions and a dose rate of 12.4 kGy/h. Final dose was around 75 kGy. Characterization of irradiated samples consisted in gel percentage, spectroscopic studies with FTIR, mechanical using DMA, HCl evolution and Activation energy (Ea) to degradation by TGA. Flory-Rehner equation was used to calculate crosslinking density when sample was kept under THF during 48 h and then dried during 24 h at 50ºC for obtaining soak and dried weights of samples.

Results

FTIR spectra (Figure 1) show a growing band in the 3400 cm^{-1} region corresponding to peroxide formation and carbonyls in 1720 cm^{-1} as a consequence of irradiation and presence of oxidation in the material. PVC added with transfer agents have less oxidation comparing with the blank.

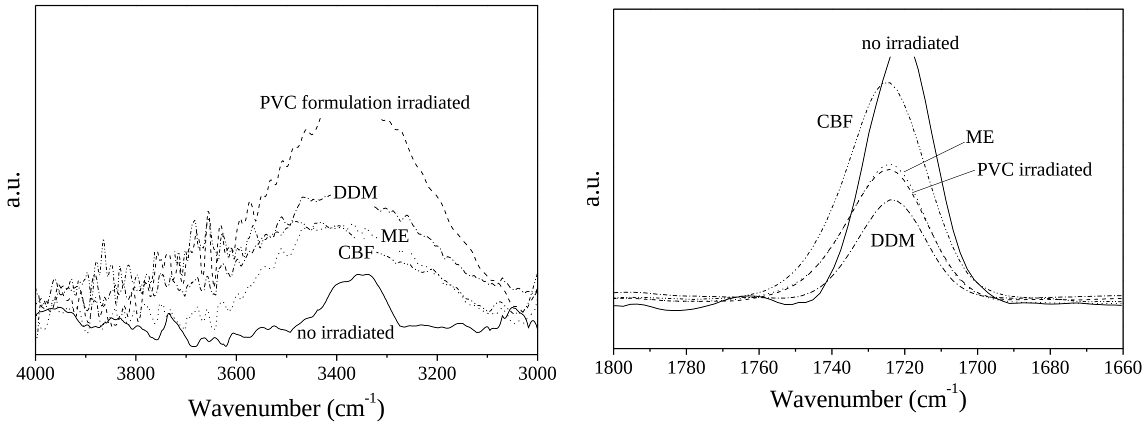

Figure 1. Peroxides and carbonyls in FTIR for different gamma irradiated PVC formulations.

Table 1 show the results obtained for gel percentage, crosslinking density and mechanical behaviour from DMA tests; although there are no significant changes in crosslinking density, the effect in storage modulus is important.

Table 1. % Gel and density crosslinking for PVC formulations irradiated with gamma.

Formulations	*% Gel*	*Crosslinking Density (mol/m^3)*	*Storage modulus at 35°C (MPa)*
Ca/Zn	20	44.34	152.6
Ca/Zn-ME	30	46.66	158.8
Ca/Zn-DDM	33	46.71	189.6
Ca/Zn-CBF	8	37.77	131.2

Finally, thermal sensitization was measured with HCl evolution and activation energy (Ea) by TGA and Arrhenius equation (Figure 2).

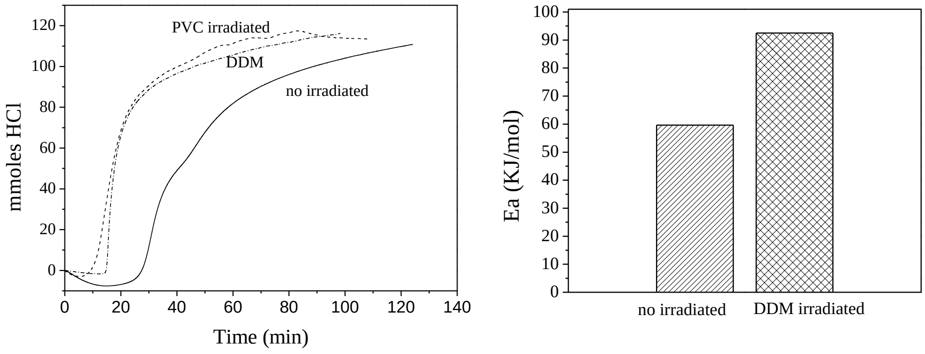

Figure 2. HCl evolution and Ea to degradation for PVC samples.

Discussion

Growing bands at peroxide and carbonyl regions is consequence of irradiation under oxidative conditions, although the initial values could be an effect of the preparation (processing) step. However, PVC formulated with transfer agents shows noticeable lower levels of oxidation, comparing with blank PVC formulations. The latter suggests that crosslinking is occurring through oxi and peroxi radicals.

Gel formation in the polymer is an evidence of crosslinking reactions among the chains of PVC, however crosslinking density values give direct information about the effect of transfer agents on such reactions. CBF is apparently less efficient and it is believed to be the consequence of an inhibition effect from stabilizers and pentaerythritol (co-stabilizer). Even though the changes in density values are not very significative, they are having an important impact over mechanical properties.

Finally, addition of transfer agents and irradiation affect behaviour in sensitization to thermal degradation; differences between both dynamic (TGA) and static (HCl evolution) temperature measurements are clearly seen. PVC+DDM degrades easily as measured statically but in contradiction needs high energy to activate degradation when measured by TGA. The latter indicates that stability measurements have to be taken with care and decided according to final use of materials.

Conclusion

Transfer agents are having control on the homopolimerization of TMPTMA and induce crosslinking reactions through oxidation functionality. Mechanical properties and thermal stability have changes for the plasticized PVC formulations and DDM shows to be better enhancement over the rest of transfer agents evaluated.

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POST-IRRADIATION OXIDATION OF POLYPROPYLENE.

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The high energy irradiation process has recently assumed increasing importance as sterilization process for polymeric materials used in the medical field. Among these, the PP is widely used. The process of radiation-induced oxidation of e-beam irradiated UHMWPE has been recently investigated[1]. The present study aims to verify if the mechanisms observed there may be also translated to isotactic, syndiotactic and atactic PP.

The irradiation process induces homolytic bond scissions in the crystalline and amorphous phase. Most of the radical pairs formed rearrange with formation of hydrogen and a double bond. The H° radicals, being of minimum size and having therefore some mobility, can migrate from the radical pair and, for extraction of an H ° from a polymeric chain, lead to the formation of a second polymeric macroradicals and H_2. These macroradicals, in the amorphous phase, in the presence of oxygen, decay in short time, while in the crystalline phase possess longer lifetimes.

At room temperature, the alkyl macroradicals can be transferred from the crystalline to the amorphous phase[2], at a rate depending on the size of the crystallites, and react with the species present there (oxygen, chain imperfections and stabilizers, if any). The oxidation process takes place in the solid state and, consequently, the morphological structure and steric hindrance acquire a fundamental importance. The oxidation cascade is due essentially to macroradicals formed in the crystalline phase. Figure 1 shows the kinetics of formation of hydroperoxides and related ketones in isotactic PP e-beam irradiated at 100 kGy. The rate of oxidation at room temperature decreases quickly with time and after one hundred hours approaches zero.

Therefore the existence of a termination reaction, involving two radical species, must be hypothesized. A reaction between the alkyl macroradicals, that migrate along the polymer chains, and the peroxy macroradicals fixed on the polymer chain seems to be the most reliable hypothesis.

The addition of vitamin E does not prevent completely the reaction with oxygen, but reduces its efficiency, the reaction with the additive being in competition with oxidation. The remarkable efficiency of vitamin E is due to the possibility of introducing a further termination reaction of the oxidation process.

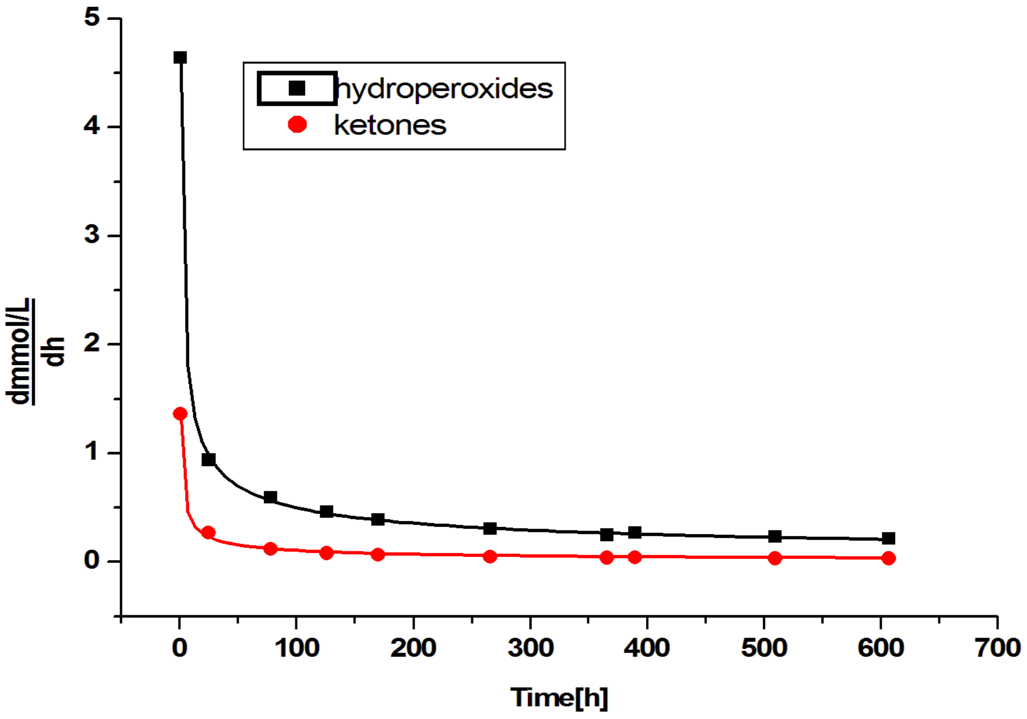

Figure 1. Oxidation rate of isotactic PP irradiated at 100 kGy

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LIGHT-INDUCED DEGRADATION OF POLYSACCHARIDES: FROM THE MODIFICATION OF THE CHEMICAL STRUCTURE TO THOSE OF THE NANOMECHANICAL PROPERTIES

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The ageing of polymeric materials provokes dramatic modifications of the chemical structure of the macromolecules and induces a loss of the polymer engineering properties. For that reason, it is absolutely necessary to correlate changes in the chemical structure to changes in the properties. The modifications of the chemical structure result from several processes: rearrangement, fixation of oxygen, chain scission and cross-linking reactions. The main objective was to give evidence of the consequences of photochemical reactions on the macroscopic properties of the polymer and to qualitatively and quantitatively confirm the direct relationship between the modifications of the chemical structure and the modifications of the properties.

In this study, we analysed the consequences of photo-ageing in the presence and in the absence of oxygen on majors Polysaccharides: cellulose ether/acetate/nitrate, chitosan... We realised roughness and stiffness measurements by AFM in combination with the use of other techniques, such as infrared and UV visible spectroscopies, gel fraction, SEC, micro-Hardness, DMTA... This set of attractive complementary techniques allows us to propose a new mechanism of degradation for each king of cellulose derivatives. In order to quantify degradation, mechanical analyses were done and it confirms that that the cross-linking reaction is ,in the most case, the predominant route.

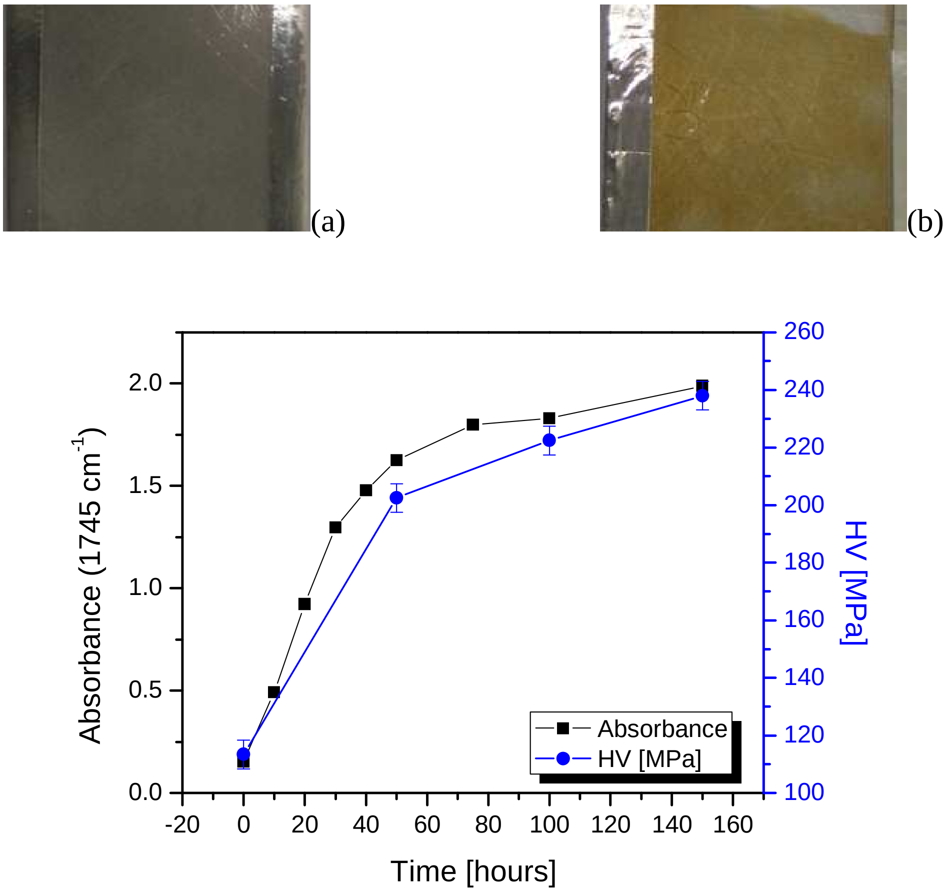

Figure 1. Bottom: Δmicro-Hardness (■) and conversion rate of the CO groups at 1740 cm^{-1} (●) versus exposure time. Top: image of the cellulose nitrate before(a) and after (b) 100 hours of irradiation, the right picture presents an important yellowing and the formation of cracks.

Then, for a better understanding, quantitative correlations were made between the main relevant criteria of degradation, from the chemical structure to the mechanical properties. The most outstanding result obtained is the quantitative correlation between the modification of the chemical structure and the variation of the physical properties at each scale of analysis.

PHYSICOCHEMICAL AND MECHANICAL IMPACTS OF ACCELERATED PHOTO-AGEING ON POLYCARBONATE CD-R SUBSTRATES

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Polycarbonate (PC) is a ductile polymer used in many industrial sectors such as automotive, medical or electronics [1]. Among these applications, PC is also used as a substrate for CD-R manufacturing [1]. Accelerated photo-ageing of PC in oxidative conditions (λ>290nm) is known to lead to chains scissions [2]. However, these modifications can not explain the formation of cracks and the global loss of PC ductility during irradiation. The aim of this study was to identify the molecular origin of this polymer embrittlement.

Mechanical, thermal and spectroscopic analyses were performed on irradiated PC samples in order to correlate the evolution of the chemical structure to the variations in the functional properties. Nano-hardness values were determined from indentation experiments performed by atomic force microscopy (AFM). The glass transition temperature was measured at a nanometric scale by AFM thermal analysis (Vita mode).

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The glass transition temperature was measured at the surface of PC under photooxidation (Figure 1) to understand the macromolecular changes involved in these mechanical evolutions. The decrease in nano-Tg observed for short irradiation periods reflects an increase in molecular mobility. This change in mobility can be attributed to scissions of the macromolecular “backbone”, which is consistent with the known photo-oxidation mechanism [2]. For longer irradiation periods, the increase in nano-Tg suggests a drop in molecular mobility, which can only be explained by cross-linking reactions.

Spectroscopic analyses were performed to characterize the chemical evolutions.

The correlation of the chemical analysis with the evolution of the mechanical properties of PC highlighted both chain cleavages and cross-linking reactions. This correlation allowed us to form a more complete photo-oxidation mechanism, which can explain the loss of polycarbonate ductility observed during photo-ageing. A new reaction pathway, which corresponds to a cross-linking reaction route, was added to the current photo-oxidation mechanism.

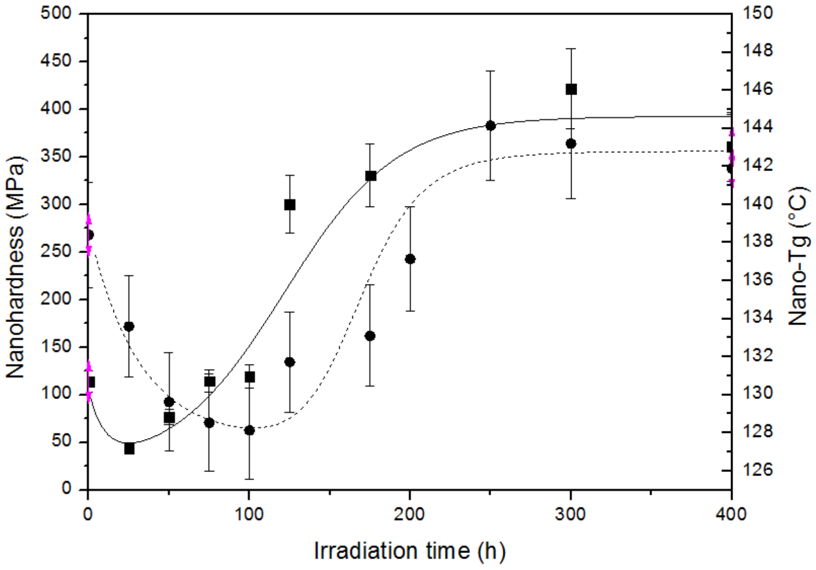

Figure 1: Nanohardness (■) and nano-Tg (●) evolution of polycarbonate substrate during irradiation

NATURAL ANTI-OXIDANT ADDITIVES FOR BIO-DEGRADABLE POLYMERS

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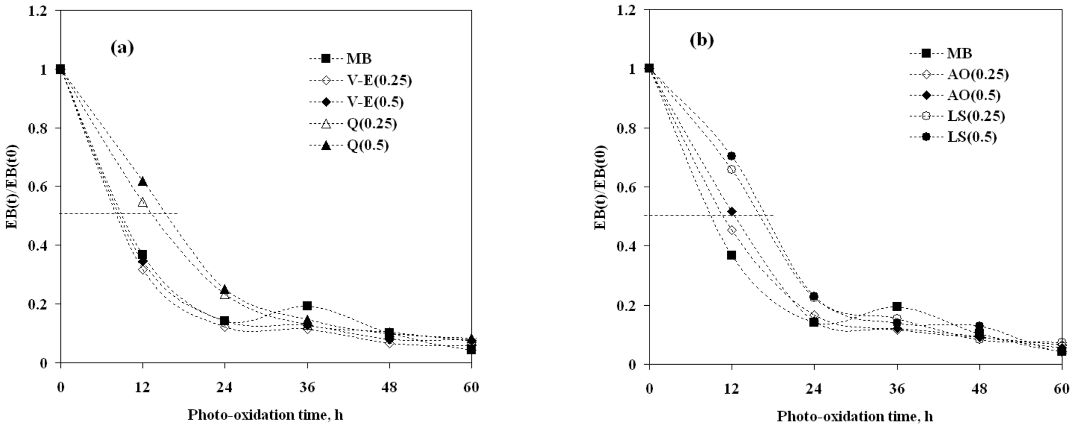
In the last years the introduction of large amount of biodegradable polymers in many conventional applications is a very important tool in environmental-friendly management of the polymers. The applications of the biodegradable polymers in the agricultural field as covering film, mulching film, packaging,etc are a very promising and challenging issue[1-2]. Commercial starch-based biodegradable polymer, i.e. a new Mater-Bi® (MB), was additivated with natural stabilizers as tocopherol and quercetin in order to formulate biodegradable film for outdoor applications free by synthetic compound and with good photo-oxidation stability. Moreover, the photo-oxidation behavior of these MB films was compared to the behavior of MB films loaded with synthetic anti-oxidant and light stabilizer systems. In Figure 1, the dimensionless elongation at break (EB) of all the investigated films, subjected to the accelerated weathering as a function of the exposure time are reported. All dimensionless values were calculated by dividing the values of EB at a given exposure time by the EB value measured before photo-oxidation. Adding natural anti-oxidant, as α-tocopherol (Vitamin E) at both 0.25 and 0.5 wt% does not change the trend of the dimensionless elongation at break, see Figure 1 (a), while, a benefit effect can be noticed by adding the flavonoid system, i.e. quercetin at both low and high concentrations, especially at short exposure times. The decays of the dimensionless elongation at break at long exposure times for unstabilized MB film and stabilized films using natural (see Figure 1 (a)) and synthetic stabilizers (see Figure 1 (b)) are very similar. At short exposure time the synthetic anti-oxidant and even more the light stabilizer are able to slow down the loss of the MB film ductility's. The trends of the dimensioless tensile strenght and elastic modulus (not reported) confirm the observed trend for EB.

Mechanical and spectroscopical results suggest that the quercetin additivated MB film shows similar behavior to the MB film additivated with the same amount of synthetic light stabilizer, which is suitable for outdoor greenhouse agricultural applications. Both natural and synthetic anti-oxidant systems are not able to prevent the formation of radicals and consequently to slow down the photo-degradation of the MB films. Finally, the quencetin compound seems to work better the vitamin E and the improvement in the photo-oxidation behavior of the biodegradable film are very similar to these obtained using synthetic light stabilizer.



(a) (b)

Figure 1. Dimensionless elongational at break of Mater-Bi® film and MB additivated (a) with natural stabilizing systems and (b) with synthetic stabilizing systems

Using same natural and synthetic stabilizers for stabilization of the bio-polyester film, as PLA film, do not give similar results. In particular, the stabilized PLA films show reduced durability than the unstabilized PLA film. This unexpected result could be understood considering the ability of the stabilizing molecules to plasticize the matrix and consequently, to improve the oxygen propagation into the bio-polyester matrix.

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Ricerca prot. RBFR10DCS7_003. Ricerca prot. RBFR10DCS7_003.

INFLUENCE OF ADDITIVES ON POLYOLEFINS' DEGRADATION STUDIED BY INFRARED SPECTROSCOPY

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Degradation of polypropylene (PP), polyethylene and poly(ethylene-co-norbornene) stabilized by set of hindered amine stabilizers was followed by infrared spectroscopy to study changes in the molecular structure of the materials. The attenuated total reflectance technique was used to obtain spectral series during the photooxidation experiment. Relative occurrence of the oxidation products in the material was determined. Additionally, the statistical method, factor analysis, was applied on the sets of measured spectra to clarify degradation process in the dependence on the chosen commodity polymer and stabilizer. The evaluation of ATR FTIR experiment is illustrated on the PP samples in presented text.

After weathering, the spectra of all PP samples exhibit similar changes, typical of material oxidation. Three new bands were found. The complex peak in carbonyl region with maximum located at 1717 cm^{-1} in the case of irradiated and at 1735 cm^{-1} in the case of non-irradiated surface, broad band with maximum about 1150 cm^{-1} and weak band at about 3350 cm^{-1}. In both spectra the carbonyl band has a pronounced shoulder at 1650 cm^{-1}, which is better defined in the spectrum taken on non-irradiated surface.

A deconvolution of the carbonyl peak showed four main absorbing bands composing the spectrum. Their maxima are at 1652 (vibration of vinyl group), 1716 (carbonyl vibration in carboxylic acid and ketones), 1745 (ester carbonyl vibration) and 1764 cm^{-1} (vibration of γ-lactones) in the spectrum of the irradiated side.[1] The additional band at 3350 cm^{-1} is typical of –OH vibrations in carboxylic acid, the broad band at about 1150 cm^{-1} is connected with vibration of C–O–O group.

The relative intensities of the bands are dependent on the set of additives and WOM exposition time. The tool which can be used to compare the course of degradation in different materials is factor analysis. The factor analysis substitutes the original series of *n* experimental spectra by their equivalent orthonormal base of vectors. The vectors of the orthonormal base are called “subspectra” S_j. The statistical importance of each subspectrum is expressed by the set of singular numbers w_j.[2] The second subspectrum S_2 should indicate the main changes in the samples’ spectra and the interpretation of the subspectrum S_2 leads to understanding of the main degradation process occurring in the sample. The main advantage of the factor analysis is the possibility to distinguish independent degradation processes in the material and follow the various degradation processes in time.

Further, the evaluation of the singular numbers w_2 and w_3 than indicates the relative intensity of the degradation process (Tab 1). The higher value w_2 in proportion to w_1 signifies higher amount of the arising oxidation products in the whole course of the degradation process.

Tab: Singular values w_j, poypropylen, A- irradiateded, B – non/irradiated site of the sample

additives	**Tinuvin®770**		**Tinuvin®123**		**Chimasorb®119**	
time [day]	**124**		**143**		**112**	
	A	*B*	*A*	*B*	*A*	*B*
w_1	14.613	15.390	14.605	13.754	15.435	14.979
w_2	0.648	0.654	0.816	0.510	**2.539**	**0.676**
w_3	0.516	0.469	0.488	0.295	0.714	0.428
additives	**Tinuvin®116**		**Tinuvin®371**		**none**	
time [day]	**112**		**112**		**112**	
	A	*B*	*A*	*B*	*A*	*B*
w_1	14.593	14.817	14.817	15.016	16.251	14.769
w_2	0.743	0.531	0.531	0.592	**2.840**	**2.155**
w_3	0.374	0.406	0.406	0.378	0.674	0.374

The values w_2 in the table confirm the effectiveness of the used stabilizers. The only exception is Chimasorb 119. The degradation of PP with this stabilizer is then the significantly lower on the non-irradiated site in comparison to the nonstabilized PP.

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FIELD-DEPLOYABLE FTIR FOR PAINT DEGRADATION ANALYSIS

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Fourier transform infrared spectroscopy (FTIR) is a widely-used technique for the analysis of polymer degradation. However, until recently, this powerful analysis method was restricted to the laboratory. With the development of portable FTIR spectrometers, new opportunities have arisen to measure polymer degradation in the field. One of the most common polymer-based materials encountered in our lives is paint, with its degradation having consequences for structural failure due to processes such as corrosion. In this light, we have used field-deployable FTIR for the analysis of paint degradation. From our studies in this area, we have been able to examine the nature of the chemical breakdown of polymer binders in paints. Results from these studies will be presented along with the technological challenges of moving from the laboratory to the field.

With the new opportunities presented by portable FTIR spectrometers, also come new challenges. One of the main challenges that has arisen is maintaining optimal spectrometer/sample alignment throughout spectral acquisitions. In the laboratory, obtaining useful spectra with ‘good’ signal-to-noise is usually a simple matter of increasing the scan time. In the field, however, increasing the scan time to obtain better signal-to-noise may not be such a simple solution. With handheld, portable spectrometers, the operator must maintain optimal spectrometer/sample alignment throughout the acquisition of a spectrum. In our experience with paints, spectra with ‘good’ signal-to-noise are only achievable with scan times of 60 seconds, or greater (see Figure 1). The limit to which an operator can maintain the optimal spectrometer/sample alignment is often hampered by sample point position and spectrometer weight and is around 30 seconds.

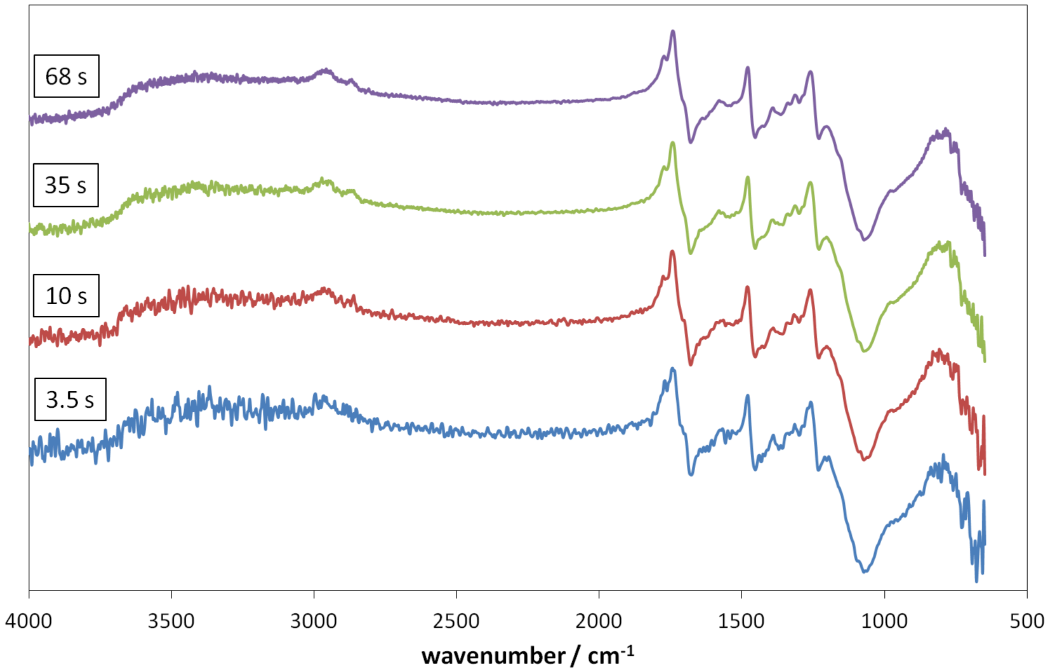

Figure 1 This Figure shows the effect of scan time on signal-to-noise for spectra collected from a polyurethane-based paint using an A2 Exoscan portable FTIR spectrometer equipped with a 45° specular reflectance sampling accessory. The spectra were collected from the same position on the same paint sample, only the scan time was changed. The spectra roughly show an improvement in signal-to-noise that is proportional to the square root of the scan time due to the random nature of the noise[1] in this case.

Therefore, to overcome the scan time limitations of handheld analysis, spectrometer holding and alignment systems have been developed. Werner and Ackerman[2] have designed a simple hook system for supporting a portable FTIR spectrometer during analysis. Their system requires connection of the hook to a substrate; however, this is not always possible in the field. Therefore, we have taken a different approach and built a standalone holding and alignment system for sample surfaces of any angle and a substrate-supported holding and alignment system for flat, level sample surfaces. These systems have allowed for the collection of better quality spectra, which will ultimately lead to more robust analyses.

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SENSITIVE LUMINESCENCE TECHNIQUES TO ASSESS POLYMER DEGRADATION

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Methods for estimating the progress of oxidative polymer degradation have traditionally involved the measurement of mechanical and macromolecular properties coupled with determination of functional groups, such as carbonyls, ketones and esters in the polymer chain by FTIR spectroscopy. These studies have demonstrated that the useful lifetime of a polymer does not extend much beyond the end of the oxidation induction period, so lifetime determination requires sensitive methods for studying the incipient degradation at short times where the rate of oxidation approaches zero.

The sensitive and complementary techniques we have employed are chemiluminescence (CL) and profluorescent nitroxides (PFN). We have previously demonstrated the sensitivity of these methods for monitoring the induction period of polypropylene oxidation.[1-3] In the PFN method the production of carbon-centred radicals can be measured in the induction period. There are two main methods for switching on fluorescence in PFNs: radical reactions (Figure 1), and redox reactions (Figure 2).

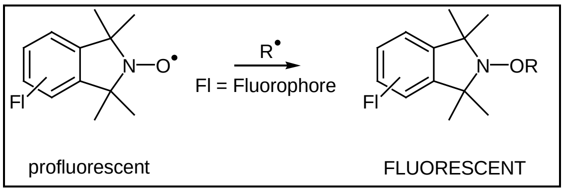

Figure 1: Switching on of PFN fluorescence by trapping an alkyl radical R·

This provides challenges in applications to epoxy resins and polyurethanes where the cure chemistry and catalysis may involve redox reactions. It also limits the use of PFNs where there are transition metal pro-oxidants present in high concentration (as in oxo-degradable polyolefins).

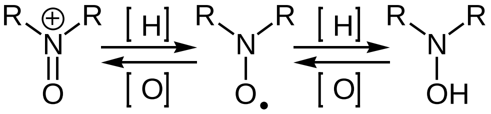

Figure 2: One-electron redox reactions of nitroxides

In that case CL is still the method of choice. An interesting example has been our experience with *cis*-polyisoprene when in contact with a polyolefin containing transition metals. Rapid degradation occurred which was able to spread infectiously through several layers of the polyolefin below where the *cis*-polyisoprene layer had been placed. Figure 3 shows a CL profile from LLDPE alone and then with the addition of cobalt carboxylate and then polyisoprene.

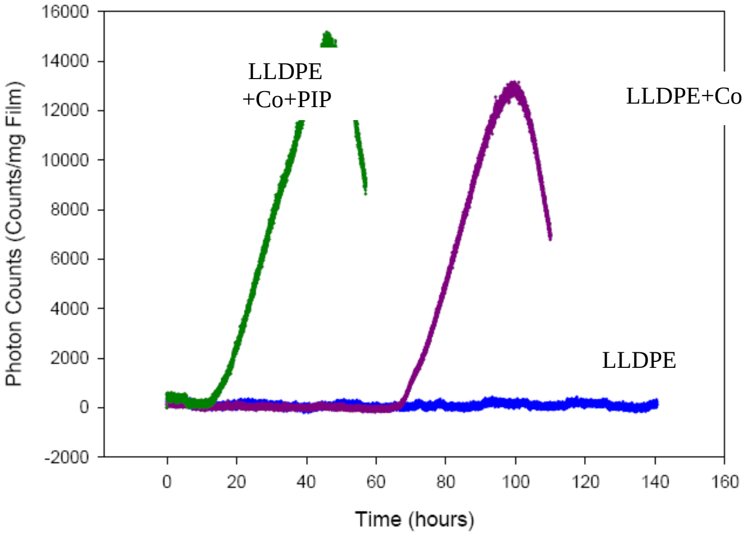

Figure 3: CL profiles from LLDPE in presence of Co^{2+} and polyisoprene (PIP).

One particular feature of both CL and PFN methods is their ready adaptation for imaging of oxidation in space and time so the infectious spreading of oxidation can be mapped.

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STUDY OF RATCHETING PHENOMENON AND INTERNAL STRESSES IN A HIGH-DENSITY POLYETHYLENE THANKS TO FLUORESCENCE SPECTROSCOPY

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High-Density Polyethylene (HDPE) is one of most used polymers in industry thanks to its beneficial properties, and its processing's low cost. That's why HDPE is employed in new industrial sectors, involving new mechanical solicitations and so new degradation mechanisms. One of them is ratcheting phenomenon, taking place during asymmetrical cyclic loading. This phenomenon generally results to stress-strain redistribution at different scales. The aim of this work is to measure internal stress thanks to fluorescent spectroscopy during these asymmetrical cyclic loads in the case of a semi-crystalline polymer. The internal stresses evolution is considered to discuss ratcheting behaviour and proposed physical base on cyclic behaviour.

The polymer adopted in this study is HDPE with crystallinity rate equal to 70 %. To allow extrinsic fluorescence, we select the Rhodamine 101 laser dye (Rh101). This laser dye insert preferentially in amorphous phase, between macromolecular chains, without reaction with them.

Ratcheting experiments were conducted at room temperature with a micro-tensile testing coupled with a fluorescence spectrometer, enabling to perform *in-situ* fluorescence spectroscopy during mechanical testing. All specimens were subjected to cyclic test at the same loading rate during the same time with $[\sigma_m ; \sigma_a]$, where σ_m is the mean stress and σ_a is the stress amplitude defined like $(\sigma_{max} - \sigma_{min})/2$. Simultaneously, fluorescent emission wavelength of Rh101 is recorded. As a matter of fact, the extrinsic fluorescence is function of the environment around the dye molecule. So, stress state modifications involve changes in polymer microstructure, changing the emission wavelength of Rhodamine. A link between this evolution of fluorescence emission wavelength and mechanical behaviour has been established, more particularly between emission wavelength and internal stresses developed during cyclic test in HDPE amorphous phase.

During tests, sinusoidal strain evolution with time is recorded, varying between ε_{max} and ε_{min}. So, ratcheting strain and strain amplitude can be determined respectively from $(\sigma_{max} + \sigma_{min})/2$ and $(\sigma_{max} - \sigma_{min})/2$. Strain amplitude doesn't vary very much according to time. However an increase of ε_a with increase of parameters values is observed whatsoever cyclic test conditions (σ_a or σ_m constant). Concerning ratcheting strain, two regimes of evolution can be distinguished. Similarly, an increase of ε_r with increase of parameters values is shown under σ_m constant or σ_a constant.

Moreover, internal stress in amorphous phase present two regimes, like ratcheting strain during time whatsoever cyclic test conditions (σ_m or σ_a constant). It is worth noting that internal stress and ratcheting strain present the same evolution as well as their respective rate. In order to compare internal stress evolution with ratcheting strain, $d\sigma_{ia}/d\varepsilon_r$ versus ε_r is calculated for all couples $[\sigma_m ; \sigma_a]$. The presence of one or two peaks can be observed which highlight a change in regime. Moreover, for each couples, critical ratcheting strain ε_{rc} can be determined which is the maximum of the first peak. We can join up ε_{rc} to change in regime observed on ratcheting strain experiment.

Ratcheting tests, using *in situ* extrinsic fluorescence spectroscopy, have provided information concerning relationship between ratcheting phenomena and internal stresses evolution in amorphous phase. Moreover the predominance of mean stress parameter on amplitude stress parameter in ratcheting strain has shown, even if σ_a play a sizeable function. It is worth noting that extrinsic fluorescence spectroscopy seems to be a very sensitive method to investigate the internal stresses developed in semi crystalline materials during fatigue test.

CHEMICAL DEGRADATION OF POLYETHYLENE IN CONTACT WITH CHLORINE, DIFFUSION LIMITED OXIDATION ASPECTS

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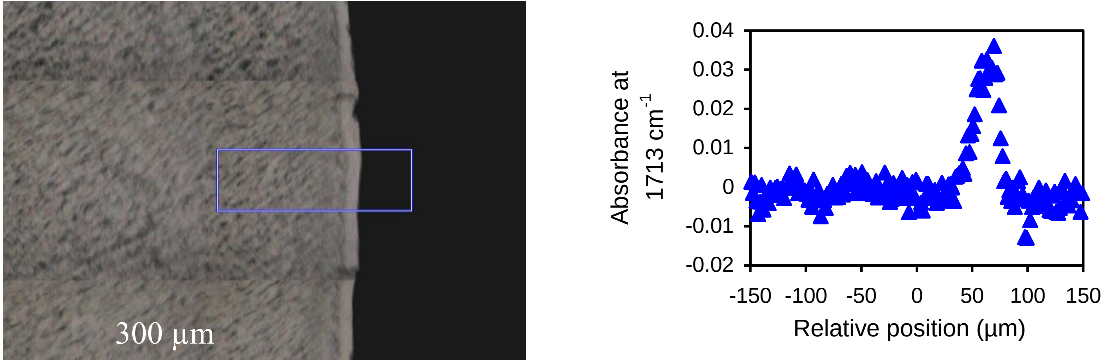
High density polyethylene (HDPE) is a semi-crystalline polymer widely used for drinking water supply. A good microbiological quality of the distributed water is ensured by adding disinfectants such as chlorine dioxide ClO_2 or chlorine Cl_2. However, these disinfectants have the potential to initiate oxidation processes. Indeed, under specific operational conditions (chlorine concentration, pressure and temperature), long-term contact with water containing chlorine is known to lead to degradation effects such as pipe inner surface embrittlement.

In order to accelerate the ageing, two approaches have previously been used. The first approach consists of increasing the temperature of the water containing the chlorine [1]. The second approach consists in increasing the chlorine concentration up while keeping the immersion temperature close to room temperature [2]. For thick samples, a gradient of degradation from the surface in contact with chlorine solution should be observed due to the diffusion of species like chlorine and oxygen.

Carbonyl profiles as a function of time of exposure for several chlorine concentrations are assessed using different tools as ATR-FTIR imaging. An example of carbonyl cartography by ATR-FTIR imaging is shown in Figure 1. The thick sample has been exposed during 333 days in contact of 70 ppm chlorine solution at 40°C. Thanks to optical microscopy, a brittle layer with cracks of 50 μm thick appears clearly. In a same time, FTIR mapping by following carbonyl absorbance at 1713 cm^{-1} put in evidence an oxidized layer having a thickness close to 50 μm. As a result, brittle layer thickness which can initiate pipe failure can be assessed precisely by FTIR mapping during exposure. Figure 2 shows oxidized layer thickness changes as a function of time exposure for three exposure conditions: oxidized layer increases linearly with time and the corresponding slope is proportional to chore concentration. These results will be discussed according to a diffusion limited oxidation modeling.



(a) (b)

Figure 1: a) section of a thick sample exposed during 333 days in contact with a 70 ppm chlorine solution at 40°C, observed by optical microscopy (the blue rectangle corresponds to the analyzed zone by FTIR mapping) b) Carbonyl absorbance through the section in the blue rectangle.

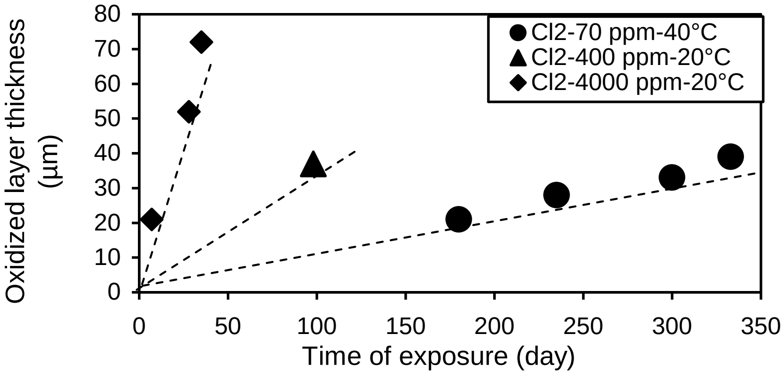


Figure 2: Oxidized layer thickness as a function of exposure time for three exposure conditions.

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CORROSION OF PLASTIC PIPES AFTER LONG TERM USE OF CHLORINE DIOXIDE DISINFECTION

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Chlorine dioxide is becoming more and more popular as a disinfectant; partly due to its advantage over chlorine is its efficiency in Legionella prevention. Since chlorine dioxide generators are relatively simple and cost-effective to use and maintain, hospitals, hotels, and other facilities where there is an increased risk of Legionnaires' disease in the water pipe systems are now equipped with their own chlorine dioxide generators.
This paper presents the results from both laboratory investigations of UHMWPE (Ultra High Molecular Weight Polyethylene) exposed to chlorine dioxide and an investigation of polypropylene pipes used in a number of hospitals using chlorine dioxide generators. The pipes had been used for up to 10 years. Some of the pipes had failed and some had been used successfully without failure. All the pipes were found to be attacked by the chlorine dioxide but the pipes that had failed showed signs of low quality with regards to processing.

Chlorine dioxide has an unpaired electron but is not regarded as being reactive enough to abstract a hydrogen from a hydrocarbon.[1, 2] There have been a number of alternative mechanisms proposed for how chlorine dioxide changes the rate of oxidative degradation.[3] Figure 1 shows FTIR scans of an unstabilised UHMWPE sample oxidised in air at 120°C for 20 hours and one which had been exposed to 100 mg/l chlorine dioxide at 50°C for 7 days after reaction with NO-gas to mark the hydroperoxides. As can be seen in the figure the oxidation products are about the same in the two samples. The effect of the chlorine dioxide is thus the same as an increased temperature.

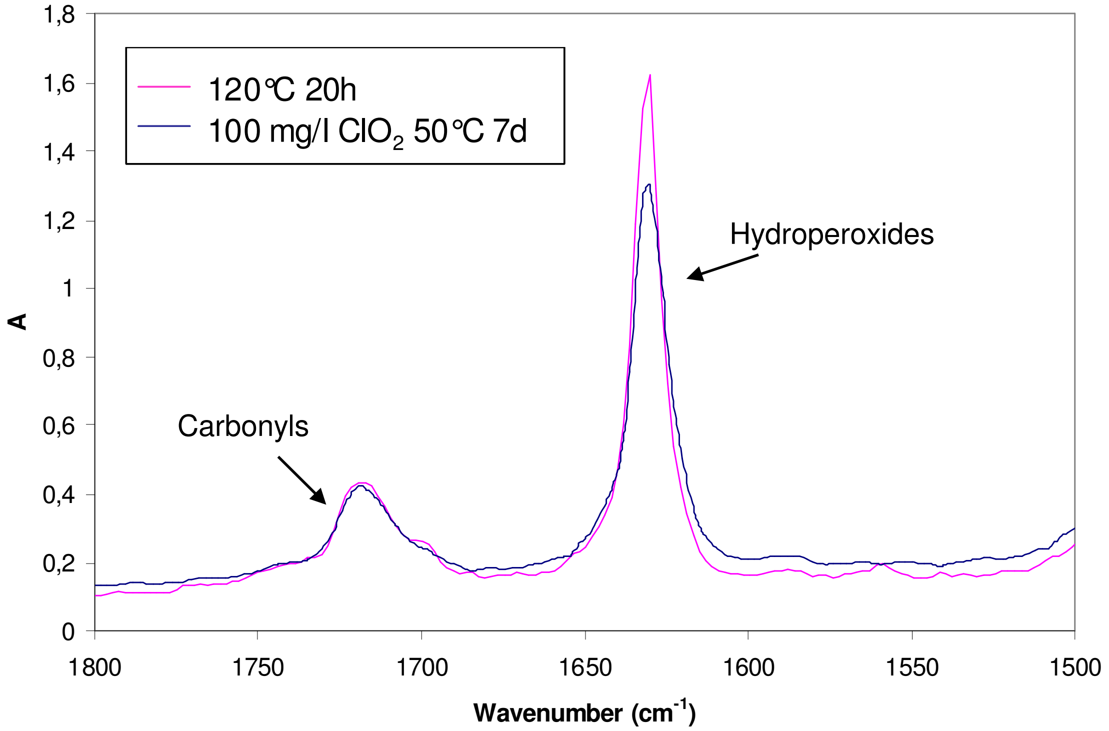

Figure 1. Unstabilised UHMWPE exposed in air at 120℃ for 20 hours and to 100 mg/l ClO_2 for 7 days at 50℃. The reaction products are almost identical (carbonyls at 1720 cm^{-1} and hydroperoxides after NO reaction at 1630 cm^{-1}).

Chlorine dioxide is known to react with hydrogen peroxide

$$2\,ClO_2 + HOOH \rightarrow 2HClO_2 + O_2 \qquad (I)$$

It can thus most probably also react with polymeric hydroperoxides

$$ClO_2 + ROOH \rightarrow RO_2^{\cdot} + HClO_2 \qquad (II)$$

Reaction II will thus also be a chain branching reaction just as thermal degradation of hydroperoxides and is proposed to be the reason for the accelerated rate of oxidative degradation in chlorine dioxide.

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PHYSICOCHEMICAL BEHAVIOR OF AGED PVC INSULATED CABLE

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Introduction

PVC insulated cables still remain operated in EDF nuclear power plants. Studies have been initiated to characterize the aging state of internal sheath PVC insulated cables and predict their life time.

Electrical tests have shown sometimes a decrease of insulation resistance but a dielectric strength good enough to withstand the voltage. Physicochemical analyses have been done to characterize the insulation material: infrared micro-spectroscopy, differential scanning calorimetry and thermo-mechanical analysis.

Results

Infrared microspectroscopy in the Attenuated Total Reflection (ATR) mode was used to scan the material versus the thickness. Figure 1 shows the 3D plot of the spectra obtained.

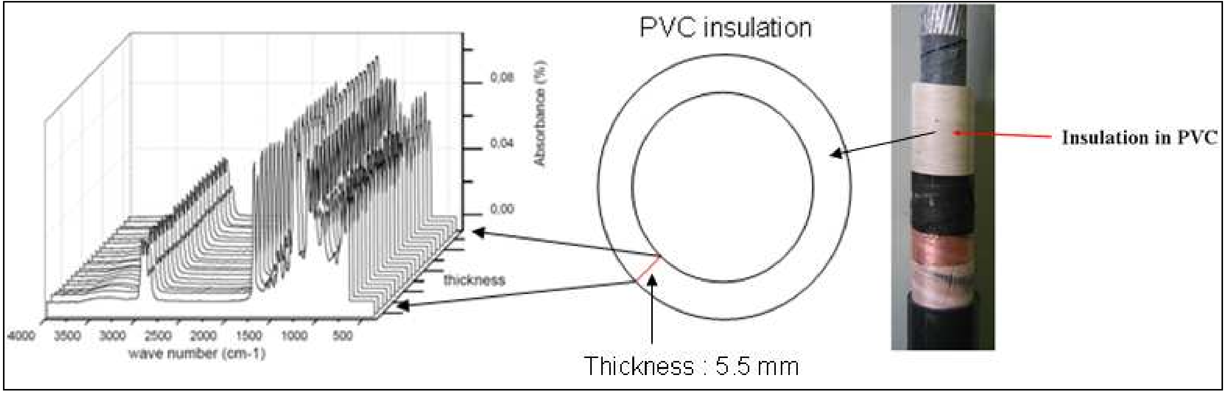

Figure 1 : IR spectra of PVC insulation versus the thickness

The most important vibrationals bands detected are the bands at 1750 cm^{-1}, and 1600 cm^{-1} assigned to the C=O and C–O stretch vibrations of the ester function of the phthalate plasticizer[1]. These bands are present with the same intensity through the thickness of the sample probed. It means that no change in the composition of the PVC can be detected. Thus migration of the plasticizer does not seem to be an aging phenomenon to consider.

DSC characterizations have allowed us to evidence the working temperature of the cables. Figure 2 shows the thermograms obtained after two identical successive heat treatments:

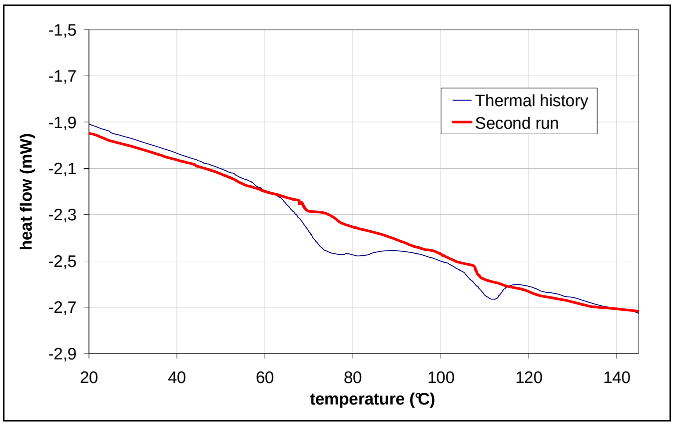

Figure 2: DSC thermograms of PVC sample after two thermal treatments

As they disappear after the second run, the endothermic peaks are a proof of the thermal history of the cable. The first one at about 70°C is in agreement with the theoretical working temperature. The second one at about 110°C is unexpected and we can assume that it may be due to a temporary overheating of the cable.

TMA has shown variations of thermo-mechanical properties along aging with a decrease of the expansion coefficient. Creation of carbon double-bounds by a dehydrochlorination process is suspected to lead to this evolution.

Conclusion

The study of aged PVC coming from cable insulation concerned with a resistivity decrease shows that this decrease is not due to a loss of the plasticizers. As the working temperatures determined by DSC are compatible with the dehydrochlorination aging phenomena[2,3], this hypothesis has to be further investigated. Thermo Mechanical Analysis is a way to link it to the physicochemical behaviour of the PVC insulated cable

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INVESTIGATION ON FLAME RETARDANCY AND ANTIDRIPPING OF NOVEL INTUMESCENT FLAME RETARDANT TOWARDS A TRADITIONAL ONE ON POLYPROPYLENE

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The main goal of this work is to investigate the effectiveness of novel phosphorous-nitrogen intumescent flame retardant (IFR) on the flame retardancy of polypropylene at incorporation level below the standard amount (25-30 wt.%[1-3]) required for intumescent flame retardants. Furthermore, the flame retardancy performance of this novel intumescent flame retardant was compared with that of traditional IFR, such as Exolit AP760.

Experimental

Polypropylene (Mopen HP500N-trademark) supplied by Basell. An intumescent additive combination comprising poly(2,4-piperazinyl-6-morpholinyl-1,3,5,-triazine, abbrev. MMP Triazine HF) and ammonium polyphosphate (abbrev. APP), (MCA®Intumescent system HF7525-trademark, abbrev. IS1) supplied by MCA Technologies GmbH. Exolit AP760-trademark (abbrev. IS2) supplied by Clariant. Pentaerythritol (Charmor PM15-trademark, abbrev. PER) supplied by Perstorp. All the PP/IS composites (PP/10 wt.-% IS1, PP/15 wt.-% IS1 and PP/20 wt.-% IS1), with the exception of the PP/20 wt.-% IS2 composite, were prepared via direct melt compounding using a Leistritz ZSE 18 HP co-rotating twin screw extruder. The PP/20 wt.% IS2 composite was prepared with an internal Rheomix-Brabender OHG 47055 mixer.

The UL-94 vertical burning (UL94-V), the limiting oxygen index (LOI) and cone calorimeter tests were carried out in accordance with ASTM D 3801-00, UNI EN ISO 4589-2 and ISO-5660-1 standard procedures. Thermogravimetric (TG) analyses were performed using a Q 500 Thermal Analyzer at a heating rate of 10 ^{o}C · min $^{-1}$ from 50 ^{o}C to 800 ^{o}C under nitrogen flow.

Results and discussion

The UL-94 V Flammability ratings provide an indication of material’s ability to extinguish a flame once ignited. The results (Table 1) revealed that the addition of 20 wt.-% of IS1 into neat PP is enough to reach V-0 rating (short burn without dripping). In contrast, IS2 at the same concentration level of IS1 did not pass the UL94 V rating (the test specimen is completely burnt up to the sample holding clamp; Fig. 1 digital pictures taken during the UL-94 V test).

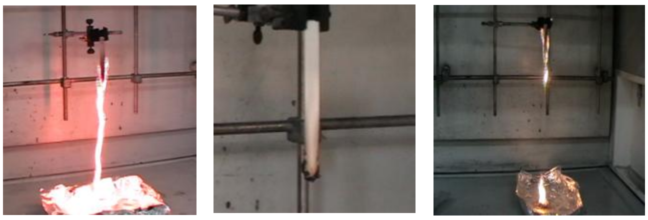
The LOI testing allows to measure the minimum oxygen concentration needed for the self-sustained combustion of polymeric material. A higher increase of the oxygen concentration for ignition was also found with the addition of novel intumescent flame retardant than traditional one to neat PP (Table 1).

The combustion behavior of the PP/IS composites was investigated by means of cone calorimeter under a heat flux of 35 kW/m^2 and the fire response parameters measured are reported in Table 1. As a general conclusion, novel intumescent flame retardant showed better flame retardancy performance than the traditional one pointing out that the intumescent char formed resists oxidation better; this aspect was confirmed also by the thermogravimetry analysis, in other words we investigated the synergistic effect between APP and PPM Triazine HF (IS1) as well as APP and PER (IS2) during their pyrolysis by comparing the experimental TG curves of the mixtures with the calculated ones. It is worthy to note that (Fig 2), although the char residue at 500 ^{o}C (char formation) is almost the same for both types of IS, however at 800 ^{o}C (char degradation) for the APP-PPM Triazine HF mixture is substantially increased (48%) in comparison with that of the APP-PER mixture (18%) pointing out the higher oxidation stability of the char. Based on the final char yield it can be assumed that the synergistic effectiveness is better for APP-MMP Triazine HF mixture than APP-PER mixture.

In the light of the aforementioned findings, we concluded that, the novel intumescent flame retardant is more suitable for flame retardancy of polypropylene towards to traditional one at just 20 wt.% loading.

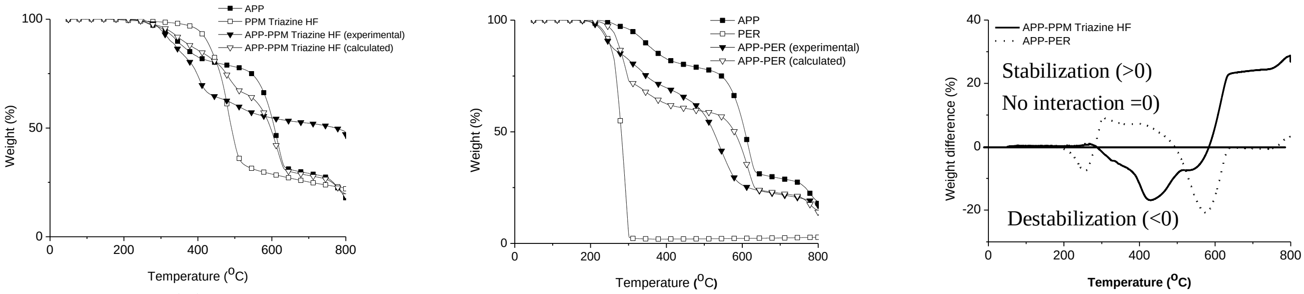
Table 1. Cone calorimeter data of neat PP and the PP/IS composites at kW/m^2.

Sample	UL-94V	LOI	TTI ± σ (s)	PHRR± σ (kW·m^{-2})	FIGRA± σ (kW·m^{-2}·s^{1})	FPI± σ (s·kW^{-1}·m^{2})	THR± σ (MJ· m^{-2})	ASEA± σ (m^{2}·kg^{-1})	TSR ± σ (m^{2}·m^{-2})
neat PP	Unclassified	19	62±9	1221±28	3.35±0.13	0.05±0.01	265±16	604±27	3144±135
PP/10IS1	Unclassified	26	44±1	313±12	1.21±0.05	0.16±0.02	235±5	638±29	3305±139
PP/15IS1	Unclassified	29	45±2	148±18	0.46±0.07	0.31±0.03	191±9	399±96	1985±567
PP/20IS1	V-0	31	43±4	115±8	0.24±0.06	0.38±0.05	153±42	313±8	1309±346
PP/20IS2	Unclassified	24	35	136 ±15	2.26±0.16	0.27±0.03	167±16	540±116	2332±392



(a) **(b)** **(c)**

Fig.1.UL-94V of (a) neat PP, (b) PP/20IS1 and (c) PP/20IS2



(a) **(b)** **(c)**

Fig.2. (a) Experimental TG curves under nitrogen atmosphere of APP, MMP Triazine HF, APP-MMP Triazine HF mixture and calculated curve obtained for this mixture, (b) Experimental TG curves under nitrogen atmosphere of APP, PER, APP-PER mixture and calculated curve obtained for this mixture and (c) curves of the weight difference between APP-MMP Triazine HF experimental and calculated and APP-PER experimental and calculated.

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DEVELOPMENT OF FLAME RETARDED NATURAL-FIBRE-REINFORCED EPOXY RESIN COMPOSITES

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Introduction

Epoxy resins are extensively used in various industrial application fields, for example as adhesives, surface coatings, laminates and matrix materials. Despite their exceptional characteristics, such as good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistant properties, their flammability still represents a limit in structural applications. Recently, there has been an increasing interest to use natural fibres instead of man-made fibres in many fields including composite materials. As biofibres are flammable, contrarily to artificial ones, an efficient flame retardant method needs to be developed to improve the applicability of natural-fibre-reinforced composites.

Materials and methods

Hemp-fabric-reinforced (surface mass: 580 g/m^2, received from the Institute of Natural Fibres and Medicinal Plants, Poznan, Poland) epoxy resin composites were prepared and flame retarded. The epoxy resin matrix consisted of a pentaerythritol-based epoxy component type ipox MR 3016 applied with a cycloaliphatic diamine curing agent (ipox MH 3122) supplied by ipox chemicals Kft., (Hungary). A recently synthesized phosphorus-containing amine-type curing agent (TEDAP) was applied as flame retardant[1]. Fabrics were surface-treated in two ways: by the thermotex procedure[2] and by a reactive modification with an aminosilane type coupling agent (Geniosil GF-9, Wacker Chemie AG, Germany). The flammability properties were characterized by mass loss type cone calorimeter, LOI and UL-94 tests while the mechanical performance was investigated by tensile and falling weight impact tests.

Results and discussion

The surface treatment decreased the flammability of the hemp fabrics significantly, the peak of heat release rate (pHRR) was reduced to the fifth of the original and also the epoxy resin composites made with them had increased Limiting Oxygen Index (LOI) values. However, to reach the V-0 rating in UL-94 test, the flame retardancy of the matrix was also necessary. When not more than 80% of the commercial curing agent was replaced with TEDAP, a significant (>70%) decrease was achieved in the pHRR while the LOI value increased from 21 to 31.

Concerning the tensile properties, the best results were achieved by the application of thermotex-treated fabrics in flame retarded matrix: an improvement of 90% in the tensile strength and 50% in the modulus could be reached, while the shock resistance could be increased by more than one order of magnitude.

Conclusions

In this work, novel hemp-fabric-reinforced epoxy resin composites were prepared and flame retarded by the application of surface-treated hemp fabrics and a reactive flame retardant. A synergetic effect could be observed between the two types of FR both in mechanical and flammability properties.

Acknowledgement

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FIRE BEHAVIOR OF ETHYLENE VINYL ACETATE/KAOLINITE COMPOSITES

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Kaolinite is a dioctahedral aluminosilicate, which is built with a tetrahedral SiO_4 and an octahedral $AlO_4(OH)_2$ sheets bonded together by oxygen atoms[1]. It is widely used as paper filler and coating pigment. At the best of our knowledge, kaolinite is not widely used in polymer industry and few studies have concerned its use in polymers. Therefore, in this study, the flame retardant effect of kaolinite in ethylene vinyl acetate copolymer (EVA) was studied and compared with an alumina trihydrate (ATH).
Compositions were extruded and injection molded. Specimens were tested in cone calorimeter, microcalorimeter (PCFC) and TGA. Also, viscosity measurements were conducted.

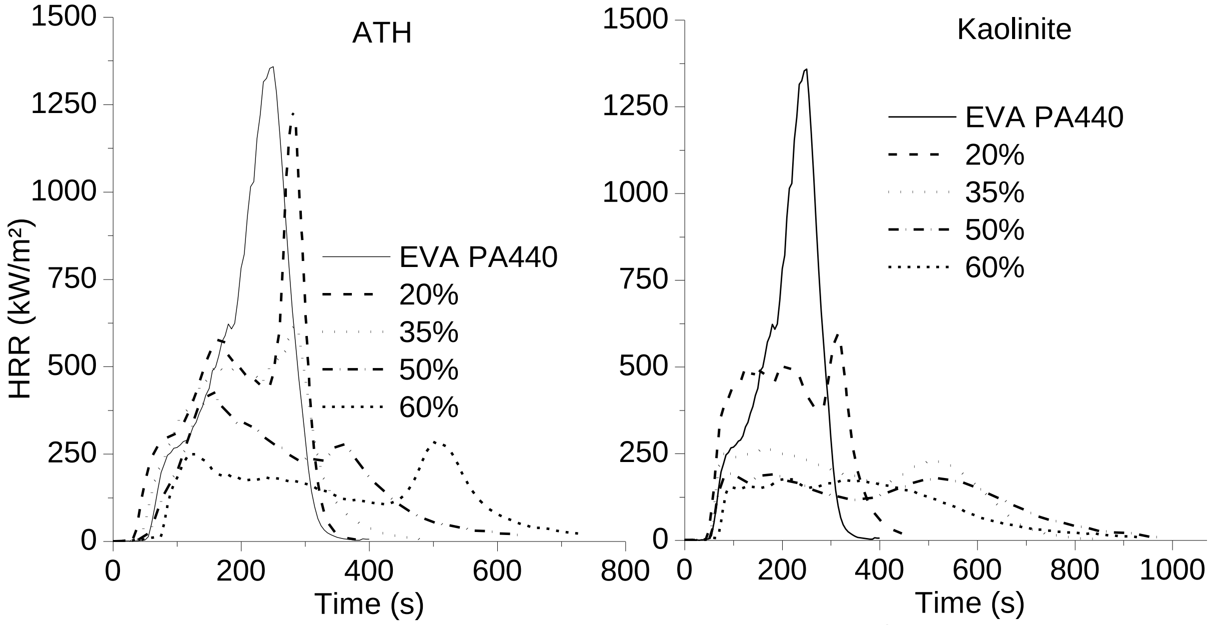

Fig. 1. Cone calorimeter results at 50 kW*m^{-2}.

The addition of ATH or Kaolinite to the polymer strongly decreases value of pHRR (Fig. 1). The results obtained shows that the weight percentage of ATH must be at least 50 wt. % in order to reach an improvement in fire retardancy in terms of pHRR. When kaolinite is used, even with 35 wt. % the pHRR is largely reduced. Furthermore, it was observed during tests that kaolin forms a protective layer on the surface of the samples, which could insulate the material. This behavior could reduce the transfer of the degradation products to the flame allowing radical recombination reactions[2] and improve time to ignition (TTI). In addition, a slightly intumescent behavior was observed.

Viscosity measurements showed an improved viscosity for kaolinite/EVA composites that could explain the intumescence observed. Also, it seems that pHRR is dependent on the viscosity of the composites, particularly to the rate of η”/η’ (Fig. 2). It should be noted that the increase of this parameter in kaolinite/EVA composites is obvious, that could lead to the improved fire behavior observed.

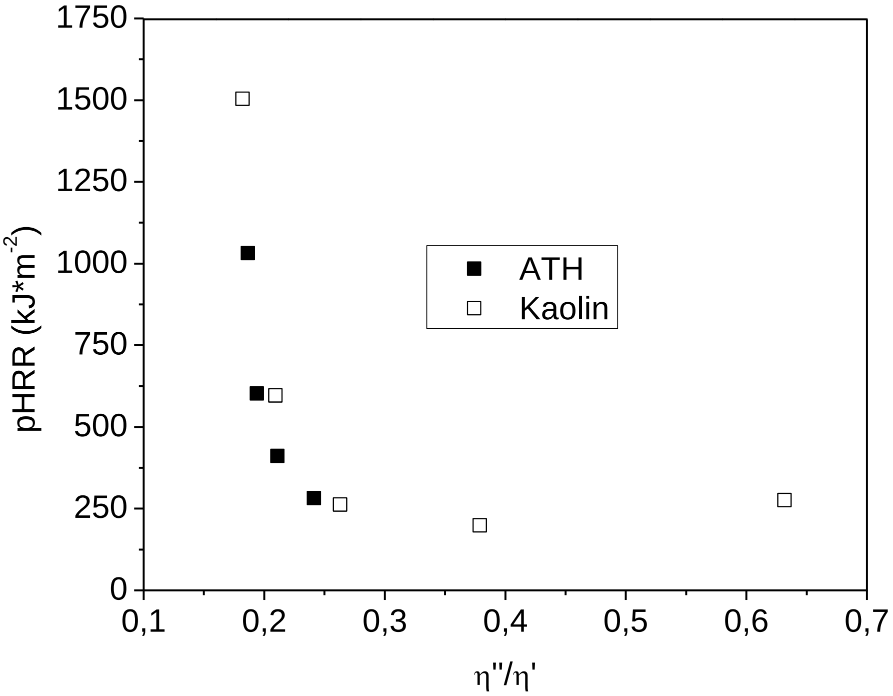

Fig.2. Rheological measurements of composites at 0.15 Hz. (Dynamical mode at 160°C).

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LAYER BY LAYER ASSEMBLY OF NANOARCHITECTURES FOR ENHANCING THE FLAME RETARDANCY OF PET AND PET-COTTON FABRICS

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In the recent years the Layer by Layer technique has arisen great interest in many research fields, concerning the enhancement of oxygen barrier properties, the building up of conductive thin films and the obtainment of substrates with antibacterial and antireflective properties and electrical conductive coatings [1]. This technique, which falls in the category of self-assembled coatings, was firstly discovered by Iler in 1966 [2]. Decades later, LbL was thoroughly studied by Decher who proposed a practical method for the deposition [3].

Nowadays, it has been reviewed several times and widely exploited for obtaining a multimaterial assembly, without any particular chemical modification: the specific controlled surface interactions achieved in between the deposited layers allow to either improve the physico-chemical properties of the substrates or to build surface-based devices.

In its simplest application, LbL requires an alternate immersion of the substrate in oppositely charged polyelectrolyte solutions/nanoparticle suspensions, thus giving rise to a structure of positively and negatively charged layers piled up on the substrate surface.

Because of the possibility to obtain organic or hybrid organic-inorganic nanoarchitectures on different substrates, LbL has recently opened up the way for achieving flame retardancy for fibres and fabrics. In this scenario, our study focuses on the possibility to enhance the thermal stability and flame retardancy of polyester and polyester-cotton blends [4-7].

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NEW FACTOR IN MECHANISM OF FIRE RETARDANCY: SYNERGISM OF FIBRES WITH INTUMESCENT FLAME RETARDANTS

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Introduction

The flame retardant mechanism of an intumescent flame retardant (IFR) system is already comprehensively reviewed in the literature[1,2]. Accordingly, at least 15-20 wt% IFR is needed in order to achieve acceptable level of flame retardancy in polyolefins, however even 25-35 wt% of IFR is also generally used. Several chemical substances have been studied as synergetic effect additives when combined with IFR system, thus the needed amount of IFR could be somewhat, but not drastically, lowered. However, the beneficial influence of a physical phenomenon on the effectiveness of the IFR system has not been discussed in the literature, yet. Recently, the authors observed significant synergistic effect between highly oriented polymer fibres and IFR system and utilized successfully in multilayer polypropylene (PP) self-reinforced composites (SRCs).

Materials and methods

The flammability and mechanical properties of multilayer SRCs (with a nominal reinforcement of 45 wt%) comprising highly stretched PP fabrics (T-PPT-181, Stradom S.A.) and IFR (Exolit AP766, Clariant Ltd.) loaded matrix layers, prepared by film stacking method[3], were compared to unreinforced PP compounds with the same IFR content. For evaluating the role of molecular orientation on the flame retardant effectiveness of the IFR system, PP SRCs of identical compositions but with pre-heat-treated (i.e. relaxed) reinforcing PP fabrics were prepared and comprehensively examined.

Results and discussion

Significantly lower grade flammability was observed in case of SRCs than that of compounded mixtures, when concentration series with increasing IFR contents were evaluated (**Table 1**).

Table 1 Flammability characteristics of PP based compounds and SRCs

PP compound	UL-94 Classification*	LOI (vol%)	pkHRR (kW/m^2)	PP SRC	UL-94 Classification*	LOI (vol%)	pkHRR (kW/m^2)
PP-REF	HB (30.5)	18	880	**SRC-REF**	HB (33.5)	19	751
PP-IFR9	HB (22.8)	24	587	**SRC-IFR9**	V-0	26	413
PP-IFR13	HB (19.4)	27	514	**SRC-IFR13**	V-0	30	295
PP-IFR17	V-2	31	340	**SRC-IFR17**	V-0	36	227
PP-IFR21	V-0	35	222	**SRC-IFR21**	V-0	42	160

*in parenthesis the horizontal burning rates (mm/min), if measurable, are indicated

In accordance with our further experimental results, SRCs of identical compositions but comprising pre-heat-treated (i.e. relaxed) reinforcing PP fabrics represent an intermediate flammability state between the unreinforced samples and the high-performance SRCs indicating that the molecular orientation degree of the embedded PP fibres is the key factor for the observed extraordinary flame retardant performance of flame retarded SRCs. The observed beneficial effect may be attributed to a physical interaction between the expanding process of intumescent FRs and the shrinking of highly oriented tapes. It is presumed, that this system exposed to heat forms a special compact charred layer, of reduced oxygen permeability and enhanced heat barrier characteristic, on the surface of the sample. In this case the vaporization of phosphorus compounds and the gas release of the nitrogen containing foaming agent occurs in a much smaller volume, being more effective in the fire extinction (e.g. when the V-0 rating achieved by IFR content of only 9 wt% is considered), as a consequence.

Conclusion

Special synergistic effect was observed between intumescent flame retardants and highly oriented PP fabrics in multilayer SRCs. This interaction resulted in significantly improved flame retardancy, such as UL-94 V-0 classification at as low as 9 wt% of IFR additives, noticeably higher LOI values, and significantly reduced heat release rates than those of intumescent alone. The studied novel synergism promotes the possibility of cost-effective fire retardancy of high mechanical performance and recyclable SRCs.

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RADIOCHEMICAL AGING OF ATH FILLED EPDM

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EPDM elastomer, representative of current formulations of cable insulators used in reactor buildings of power plants, was elaborated by press molding into 2-3 mm thick plates at 170°C under 200 MPa during 15 minutes. EPDM elastomer was filled by 0, 33 and 100 phr of alumina trihydrate particles (ATH), surface untreated (U-ATH) or treated by a vinylsilane coupling agent (T-ATH), and crosslinked with 3phr of dicumyl peroxide. The plates were exposed to ionizing γ irradiation under different dose rates (0.1, 1 & 10kGy/h) in air at room temperature. The resulting changes in the tridimensional crosslinked structure of this elastomer were determined by different complementary analytical technics at molecular, macromolecular and macroscopic scales.

For instance, the distribution of oxidation products concentration in the sample thickness and its change versus exposure time were determined by FTIR spectrophotometry (Fig.1). The results are in accordance with our expectations: as the dose rate increases, the thickness of oxidized layer decreases while the concentration of oxidation products increases.

As another example, the changes in crosslinking density (or in concentration of elastically active chains) were determined by swelling measurements in cyclohexane at 25°C using the Flory-Rehner equation, modified by Krauss for filled samples, and were verified by mechanical spectrometry. The results indicate that a post-crosslinking process occurs in the early periods of exposure to irradiation, which is expressed by a raise in crosslinking density. Then, a chain scission process predominates over crosslinking once the crosslinking density reaches a maximum value (Fig.2). It is deduced that post-crosslinking results from addition of peroxy radicals to residual insaturations of norbornene monomer not consumed during vulcanization step.

The oxidation kinetics is practically unaffected by the presence of ATH. Swelling results only show a higher initial crosslinking density in the case of surface treated ATH, which may be attributed to chemical crosslinks at the filler/polymer interface.

The Young's modulus follows the same pattern as the crosslinking density. The elongation at break similarly shows an increase followed by a slight decline to demonstrate an acceptable correlation between different scales. In case of filled elastomers, the tensile tests show a more significant fall when the filler content increases. This last result may suggest more significant degradation at the filler/polymer interface.

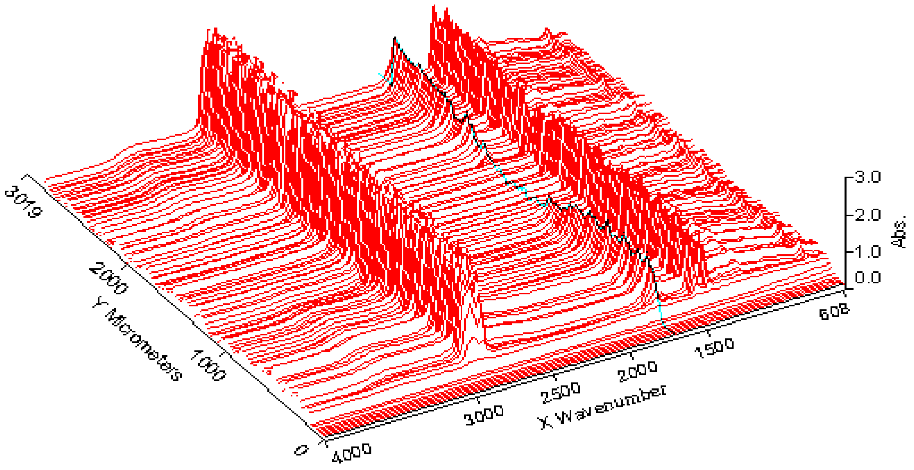

Figure.1: FTIR spectra presenting oxidation products profile for unfilled EPDM γ-irradiated for 800 hours in air under 1kGy/h dose rate

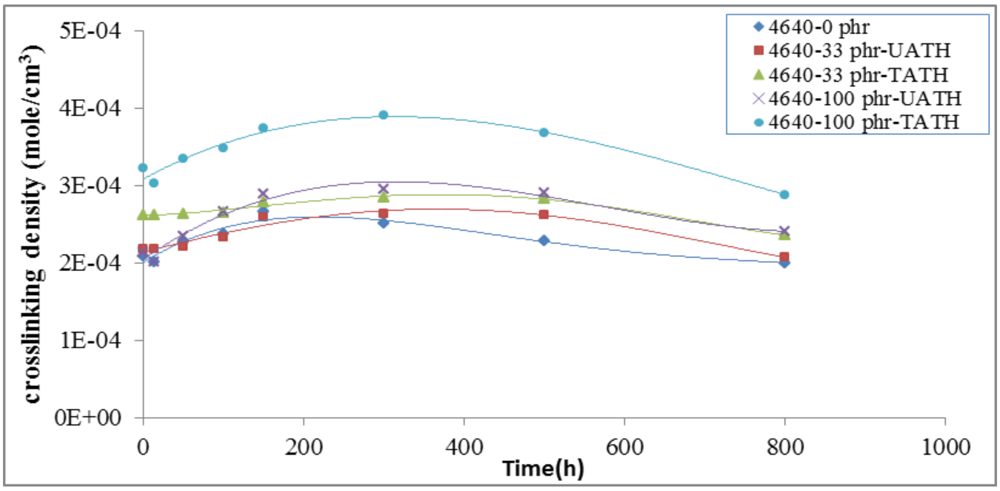

Figure.2: Evolution of crosslinking density of γ-irradiated EPDM samples under 1 kGy/h dose rate determined by swelling measurements

PHOTODEGRADATION OF LUMINESCENT ETHYLENE-VINYL ACETATE/INORGANIC PHOSPHOR COMPOSITES FOR APPLICATION AS MULTIFUNCTIONAL COATING OF ORGANIC SOLAR CELLS

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Efficiency and lifetime of organic solar cells (OSC) are two bottlenecks for their massive industrial development.

A multifunctional encapsulation could improve both efficiency and lifetime by increasing the conversion efficiency of the cell and limiting the oxygen and water diffusion toward the active layer.

In this work, photodegradation of composite films made of ethylene-vinyl acetate copolymer (EVA) and micrometric particles of luminescent strontium aluminate $SrAl_2O_4$ (SA) was studied. The targeted application of these composites is the multifunctional encapsulation of OSC.

The SA particles were doped with Eu^{2+} for obtaining a down-conversion effect resulting from the absorption of high energy UV light and then an emission of lower energy visible light at 520 nm (figure 1).

The luminescent SA material was chosen for its spectroscopic properties, permitting SA to be excited in the UV solar domain and giving a good spectral overlapping of its emission with the absorption of poly(3-hexylthiophène) (P3HT), which is a reference in the field of OSC.

Films of composites with SA amounts from 10 to 30% w/w were prepared by extrusion and pressed to obtain films of thickness at about 50µm. These samples were characterized by FTIR and UV-visible spectroscopy.

Artificial accelerated photoageing at $\lambda > 300$ nm in presence of oxygen was performed at a temperature of 60°C.

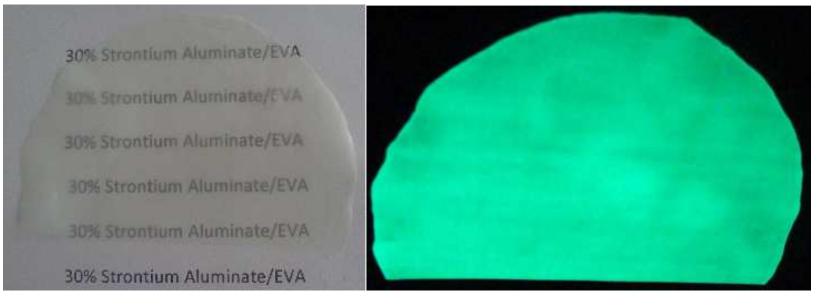

Figure 1 Composite films of EVA with 30% of SA ; in room light (left) and under UV 365 nm light (right)

The kinetics of photo oxidation of the EVA composites are shown on Figure 2. The oxidations rates of EVA composites were slightly higher than those of pristine EVA. This effect could be explained by the light scattering induced by the SA particles which increase the effective optical path in the irradiated films.

In order to check that the increase of the photooxidation rate was not coming from an increase of the local temperature caused by the absorption of the SA, we have also exposed composites of polyethylene (PE) and $CaCO_3$, this last being chemically inert and totally reflective. The same increase in the photooxidation rate was observed. This increase reflects the light scattering properties of the filler related to the size and nature of the particles. Complementary experiments on the role played by the size and shape of the filler are on-going.

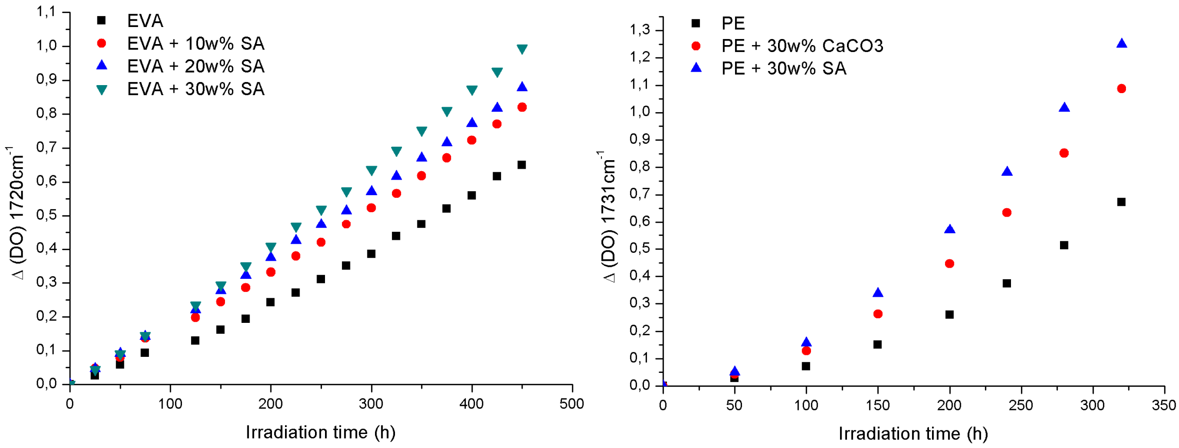

Figure 2 Variations of absorbance as a function of irradiation time : at 1720 cm^{-1} for EVA composites films with 0, 10, 20, 30% of SA (left) ; and at $1731cm^{-1}$ for PE composites films with 0, 30% of SA and CaCO3 (right).

PHOSPHORUS POLYESTERS AS HALOGEN-FREE POLYMERIC FLAME RETARDANTS IN POLY(BUTYLENE TEREPHTHALATE) – INFLUENCE OF THE CHEMICAL STRUCTURE

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Halogen-free flame retardancy of poly(butylene terephthalate) (PBT) is at present mainly achieved using low-molecular-weight additives.[1] These additives often suffer from drawbacks, such as deterioration of the mechanical properties of the polymer. Polymeric flame retardants are a promising approach to overcome these drawbacks. Three phosphorus polyesters with altered chemical environment of the phosphorus (**Fig. 1**) are investigated as potential halogen-free flame retardants for poly(butylene terephthalate).

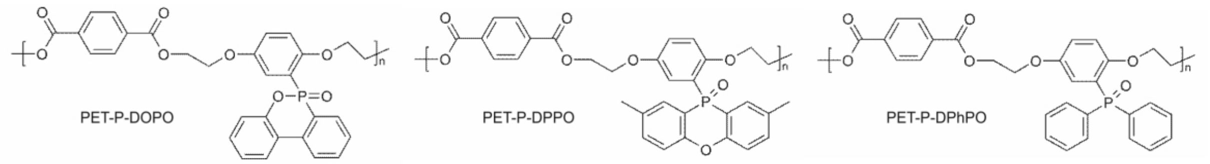

Figure 1. Chemical structures of the phosphorus polyesters.

The outstanding fire properties of the neat PET-P-DOPO as flame retarded polyester material itself and as polymeric flame retardant additive in PBT were reported recently.[2, 3] PET-P-DPPO and PET-P-DPhPO were additionally synthesized[4] to investigate the influence of the chemical environment of the phosphorus on decomposition mechanisms and fire behavior. Deep insights into structure-property relationships provide the basis for optimizing a flame retardant for a given application.

All three phosphorus polyesters formed strongly intumescent residues under forced-flaming conditions in the cone calorimeter (**Fig. 2**). Three flame-retardancy mechanisms including flame inhibition, charring, and a protection effect of intumescent char are simultaneously active in all three phosphorus polyesters leading to decreased fire risk. Flame inhibition was similarly strong in the three phosphorus polyesters despite their different structure. The amount of residue formed clearly depended on the structure of the polyester. PET-P-DPhPO (phosphine oxide structure, non-bridged phenyl rings) yielded less residue (27 wt.%) than PET-P-DOPO and PET-P-DPPO. The first step in the formation of char is cross-linking.[5] Therefore, PET-P-DPPO with its bridged phenyl rings formed more residue (33 wt.%) than PET-P-DPhPO. PET-P-DOPO formed a high residue (40 wt.%) because of its bridged phenyl rings and because of using phosphinate instead of phosphine oxide.[6]

Figure 2. Intumescent fire residues of PET-P-DOPO, PET-P-DPPO, and PET-P-DPhPO (from left to right) obtained with an irradiation of 50 kW/m² in the cone calorimeter.

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NEW HYBRID HALOGEN FREE FLAME RETARDANT

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Compounds containing chlorine or bromine atoms in the structure have ben used as flame retardants for many decades. However, polymers which are modified by that kind of flame retardants emit toxic gases during the combustion. These gases are more hazardous to health than the fire itself. In recent years particular attention was paid to melamine or its derivatives, especially the salts of melamine as flame retardants. One of the halogen-free flame retardant is melamine phosphate (FM). It is prepared by reacting melamine with phosphoric acid. The aim of this work was the developing of the methods of the modification of silicate layer-tabular mineral (SL-TM) using salts of melamine, i.e. melamine phosphate or melamine polyphosphate (PFM). The modified mineral was used as flame retardant to thermoplastic polymers.

The main objective of this work were researches concerning of the methods of the modification of silicate layer-tabular mineral using the salts of melamine, i.e. melamine phosphate or melamine polyphosphate.

Modification was confirmed using IR spectroscopy and thermogravimetric analysis. Also, the scanning electron microscopy of the modified salts was made.

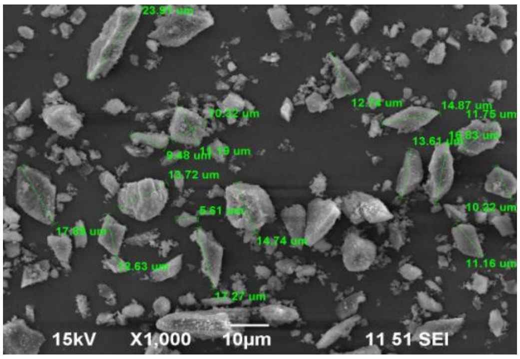

Fig.1 SEM of FM modified by 40 % by weight of SL-TM

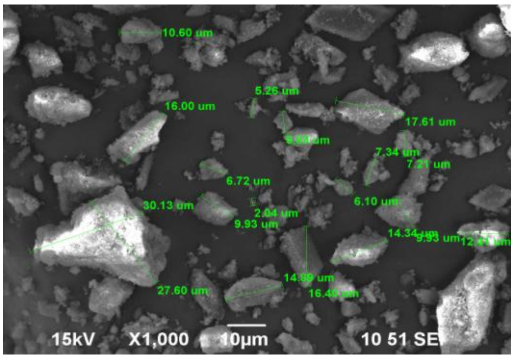

Fig. 2 SEM of PFM modified by 40 % by weight of SL-TM

The obtained salts of melamine were introduced, in the amount of 10 and 15 percent by weight, into the selected thermoplastic polymers, i.e. polyethylene (PE), polypropylene (PP) and polyamide 6 (PA6) using twin screw extruder. Than the test samples were made and oxygen index was limited and mechanical properties were examined.

In the case of polyethylene and polypropylene the value of the oxygen index increased. But in case of polyamide 6 values remains unchanged. The thermogravimetric analysis of the modified polymers was made. In the case of PP the influence of the flame retardant on the thermoresistance of the sample is observed. It is visible that at the same temperature the loss of the mass of the sample with a filler is smaller than the control sample. So, the same loss of the mass of the filled sample is reached at a higher temperature than the sample without the filler

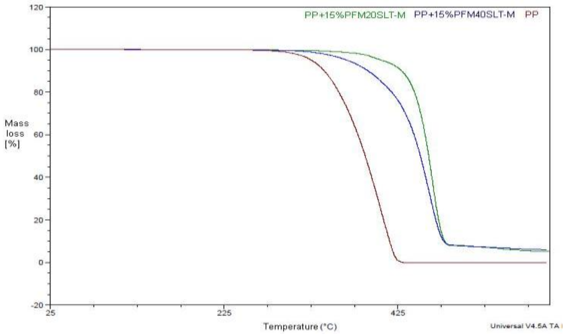

Fig. 3 Comparison of TG curves of pure PP and PP filled by melamine polyphosphate modified by 20 and 40 % by weight SL-TM.

The modification of salts of melamine by silicate layer-tabular mineral had a positive effect on the mechanical properties of thermoplastic polymers which were filled with modified salts of melamine.

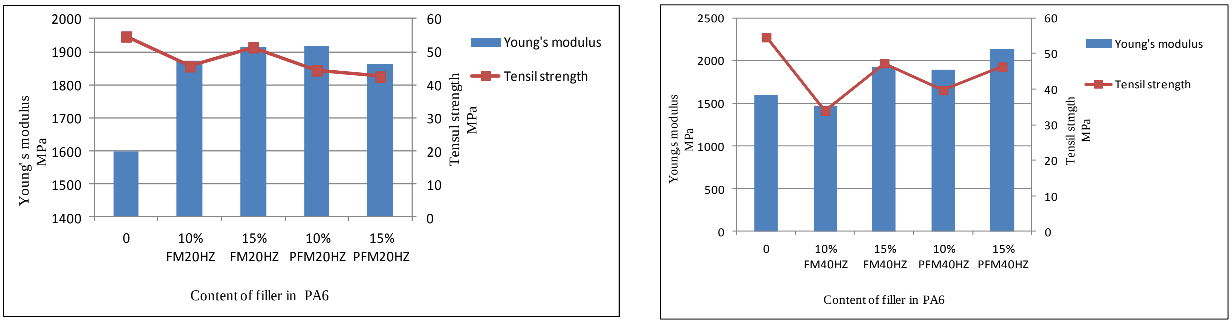

Fig. 4 Dependence of Young's modulus and tensile strength on quantity and kind of filler in PA 6.

As shown on the drawings the calcinations of melamine phosphate (modified by 20 percent by weight of SLT-M) to melamine polyphosphate and introducing it into the plastic caused increase of Young's modulus and the modulus of elasticity. On the other hand, tensile and bending strength remains unchanged or slightly decreased. So, rigid materials with unchanged strength and better thermal resistance are obtained.

PHOSPHINIC ACID FUNCTIONALIZED POLYETHYLENE IMINE (HPEI) – A NOVEL FLAME RETARDANT AGENT FOR GLASS REINFORCED POLYBUTYLENE TEREPHTALATE

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Introduction

Glass fiber-reinforced Poly(Butylene Terephthalate) (GF-PBT) is a thermoplastic widely used for electrical and electronic devices. Since it is easily flammable, it has to be flame retarded to comply with fire standards[1]. The objective of this study is to synthesize a novel flame retardant agent for GF-PBT: a phosphinic acid functionalized hyperbranched-polyethylene imine (HPEI). This approach was motivated by the P/N synergism widely reported in the field of flame retardancy[2] and by the high nitrogen content of HPEI. Fire performances of the material will be evaluated using standardized fire tests (UL94, Limiting Oxygen Index, cone calorimeter).

Materials and Methods

The phosphinic acid functionalized hyperbranched-polyethylene imine (fHPEI – Figure 1) was obtained from a reaction between hyperbranched polyethylene imine (Lupasol WF from BASF) and oxophospholane oxide (Exolit PE110 from Clariant). The reaction was carried out in CH_3Cl at 60°C for 6h. The reaction products were then precipitated in diethyl ether and used after drying.

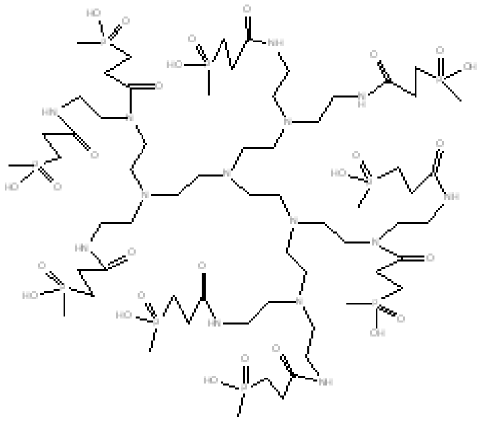

Figure 1. Phosphinic acid functionalized polyethylene imine (f-HPEI)

The flame retardant additive (fHPEI) was incorporated to PBT/GF using a micro-compounder from DSM Xplore (3min, 250°C, 80 rpm). UL-94 classification was obtained on sheets (130x12.7x 0.8cm^3) according to the conditions of the standard test (ASTM D 3801). Limiting Oxygen Index (LOI) was carried out according to ISO4589 on barrels (10x10x0.3cm^3). Mass Loss Calorimeter was carried out on samples (10x10x0.3cm^3) following the procedure defined in ASTM E 906 at an external heat flux of 35 kW/m² (mild fire scenario).

Results and Discussion

Table 1 presents the flame retardant properties of PBT/GF including 20 and 30wt-% fHPEI. It is observed that the addition of fHPEI in PBT/GF leads to an increase in the flame retardant properties. The LOI increases from 19vol.-% for PBT/GF to 27vol.-% when 30wt.-% additives are incorporated in the PBT/GF matrix. This latters material achieves V0 classification at UL94 test whereas at 20wt.-% only V2 classification is obtained. Those results also show that at 20wt% of fHPEI in PBT/GF lead to a 61% decrease of the peak of Heat Release Rate (pHRR) as compared to PBT/GF whereas the time to ignition decreases. The total heat release (THR) is also sharply reduced when fHPEI is used as flame retardant in PBT/GF.

Table 1. Flame retardant properties of PBT/GF and PBT/GF/fHPEI

	LOI vol.-%	UL94 rating	PHRR (kW/m²)	TTI (s)	THR (MJ/m²)
PBT+25%GF	19	NC	400	62	52.8
PBT+25%GF+20%f-HPEI	23	V2	154	39	34.6
PBT+25%GF+30%f-HPEI	27	V0	-	-	-

Conclusion

A novel flame retardant additive (phosphinic acid functionalized hyperbranched-polyethylene imine) was successfully synthesized. Its efficiency as flame retardant additive in reinforced PBT was demonstrated using various standardized fire tests.

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SOL-GEL TREATMENTS FOR ENHANCING FLAME RETARDANCY OF COTTON

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Recently, fatal accidents caused by the burning of fabrics have remarkably motivated both the academic and the industrial research to study and produce smart textiles with flame retardant properties. The combustion behavior of fabrics is very complex and depends on their nature and characteristics. In particular, although cotton is known to be the most common natural fiber used for several applications (wearing apparel, upholstery, furniture, mattresses, bed-lines...), it is also a highly combustible fiber, as well as its blends with polyester. Several flame retardant additives, such as halogen derivatives or phosphorus-based compounds have been used, notwithstanding their possible adverse effects on the environment. For this reason, among the alternative procedures, the use of the sol-gel technique is becoming a relatively novel process in the textile field for conferring flame retardancy and thermal stability. The treatment of fabric surfaces by means of a sol–gel process from a solution has been described as an encouraging approach, since it can lead to the formation of hybrid organic–inorganic coatings at or near room temperature.

Sol-gel processes are based on two steps involving hydrolysis and condensation reactions starting from (semi)metal alkoxides, like tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide.

In this context, a detailed investigation on the possibility of obtaining the formation of silica architectures (particles, coatings) on cotton fabrics has been carried out by using the sol-gel technique. The effect of different process parameters such as silica precursor type, silica precursor:water molar ratio and drying conditions (namely, temperature and time) has been thoroughly investigated, aiming to optimize the sol-gel procedure applied to cotton textiles. Cone calorimetry tests have been exploited in order to assess the fire resistance of the treated fabrics; in addition, the thermal stability of the obtained products has been evaluated by thermogravimetric analyses, performed both in nitrogen and air. The coating durability to different washing programs has been studied as well [1, 2].

Furthermore, the possibility to utilize joint or synergistic effects between the obtained silica phases and commercial phosphorus-based flame retardants has been explored [3]. Very recently, the role of several silica precursors, which differ as far as their structure is concerned (i.e. number and type of hydrolysable groups, presence of aromatic rings), has also been investigated [4].

Alternatively to silica-based coatings (derived from tetraethylortho-silicate), it has been demonstrated that interesting oxidic phases can be deposited on cotton fabrics starting from other alkoxides (tetraethylortho-titanate or -zirconate and aluminium isopropylate). Titania, zirconia and alumina turned out to significantly enhance the flame retardancy of cotton fabrics, although their efficiency was lower than silica [5]. In addition, the effect of such oxidic phases as efficient smoke suppressants has been studied [6].

Finally, the effect of a hybrid organic-inorganic coating obtained through a dual-cure process (i.e. a photopolymerization followed by a thermal treatment for promoting sol-gel reactions) on the thermal stability, fire resistance and combustion behavior of cotton fabrics has been assessed [7].

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EFFECT OF POLYMER MATRIX STRUCTURES ON ITS DEGRADATION AND FLAMMABILITY

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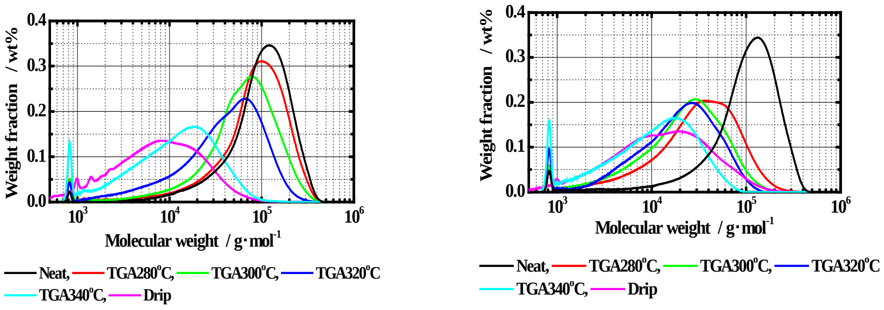
Polymeric materials are heated during 180 ^{0}C to 280 ^{0}C where the temperatures are the process in synthesis and processing. However metal oxide catalysts that we used are not reacted at that temperature and it only reacts over 350 ^{0}C. Our research clarified that changing matrix structure by adding metal oxide has effected on its flammability.

In this study, a multi calorimeter (MCM-1 manufactured by Toyo Seiki Seisaku-Sho, Ltd.) was used for vertical flame test. For the experiment, strip shaped specimen was suspended in the chamber under controlled atmosphere and heated vertically. And the samples were heated until ignition to study the flammability, whereas in a standard UL-94-V test the samples are heated for 10 sec. After the ignition the methane burner was separated from the sample to a regulated position and the experiment was conducted [1].

From our results, polymer structures were changed until the temperature rises to the combustion temperature by adding metal oxide as a catalyst. In the case of PLA with metal oxide, its flammability was controlled by microscopic and physical factor. It is not only restrained combustibility but also stop ignition and kept dripping down until the specimen completely finished. Figure 1 shows a change in molecular weight due to the thermal history of the sample were PLA neat and adding metal oxide to PLA. The molecular weight was changed before volatilization by adding a catalyst



(a) PLA neat (b) PLA/SiO_2/MgO 10 wt%

Figure 1 Distributions of molecular weight.

and combustion was also suppressed [2].

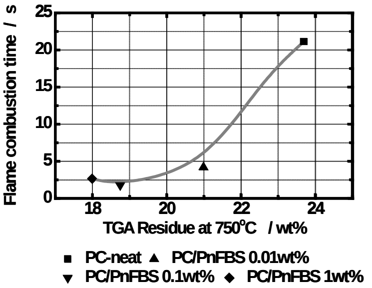
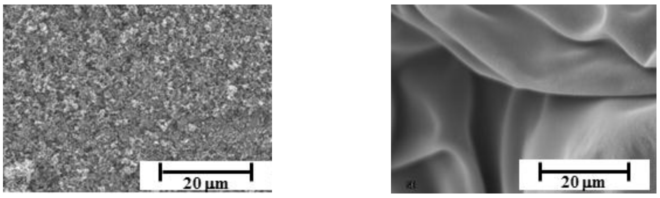


Figure 2 Flame retardancy effect by PnFBS and the relation of residue.

In the case of PC, its flammability was controlled by chemical factor such as Fries rearrangement, hydrolysis etc., and macro changes such as the surface structure until the temperature rises to the combustion temperature. The samples that contain PnFBS showed about 20% of residue formation at around 750 ^{0}C, which is less than PC-neat. Figure 2 shows that with increase in addition of PnFBS, the residue decreases. Also as the residue decreases, the total flame combustion time also decreases.

The PC surfaces after vertical flame test were observed by SEM and shown in Figure 3.The small particles and larger particles were observed in the X2000 photos on the surface of PC-neat. It show that the particles of which the ratio of carbon/hydrogen is richer because the hydrogen in the specimen, were separated from the melted PC at higher temperatures and formed the particles.



(a) PC Neat (b)PC/PnFBS 1wt%

Figure 3 Polymer surface after vertical flame test (X2000).

On the other hand, granular carbide was not found for PC/PnFBS 1 wt% and the smooth surface was observed. However the combustion of PC/PnFBS 1 wt% displayed an excellent retardancy.

Changing matrix structure has effected on its flammability. Specially, the molecular weight of polymer and modification of polymer surface structure were very affected on its flammability.

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STUDY ON THE THERMAL DEGRADATION OF A MIXTURE OF A NOVEL CAGED BICYCLIC PHOSPHATE AND AMMONIUM POLYPHOSPHATE

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Keywords: Intumescent; Trimer; APP, Thermal degradation.

In order to understand the intumescent flame retardant effect of a novel caged bicyclic phosphate (Trimer, tri (1-oxo-2,6,7-trioxa-1-phosphabicyclo [2,2,2] octane-methyl) phosphate) and ammonium polyphosphate (APP) used in intumescent coatings [1] and some polymers such as polypropylene [2], the thermal degradation of Trimer, APP and their mixture were studied.

Different degradation behavior of Trimer/APP (mass ratio of 2:1) from Trimer and APP was observed by thermogravimetric analysis (TG) shown in Fig.1. Trimer shows higher thermal stability, its first weight loss peak reached 43.2 %/min (30 % weight loss at 375 ℃), and relative main gaseous products are hydrocarbon containing compounds. The experimental TG curve of Trimer/APP, compared with the theoretically calculated one, showed lower initial degradation temperature and higher char residue at 800 ℃, demonstrating interactions of Trimer and APP during thermal degradation. Such interactions were evidenced by gaseous degradation products analyzed by TG-FTIR.

It is interesting that Trimer couldn't expand alone, but after mixed with APP expanded rapidly during about 365~420 ℃ (see Fig. 2) and with more P, O and N compounds being kept in condensed phase proved by X-ray photoelectron and spectroscopy (XPS) shown in Fig. 3. These results demonstrated the synergistic effect involving cross-linking reactions between Trimer and APP during the thermal degradation process. The synergistic main products of the char residue should be polyphosphate and its derivatives.

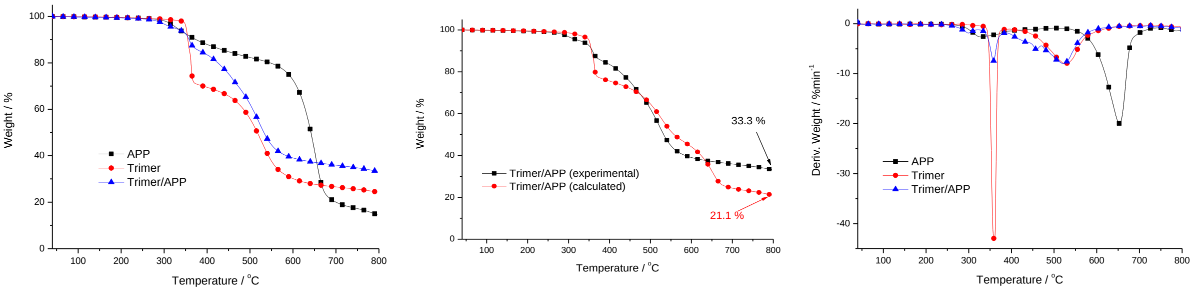

Fig. 1 TG (left and middle) and DTG (right) curves of APP, Trimer and Trimer/APP under N_2 atmosphere (20 °C/min)

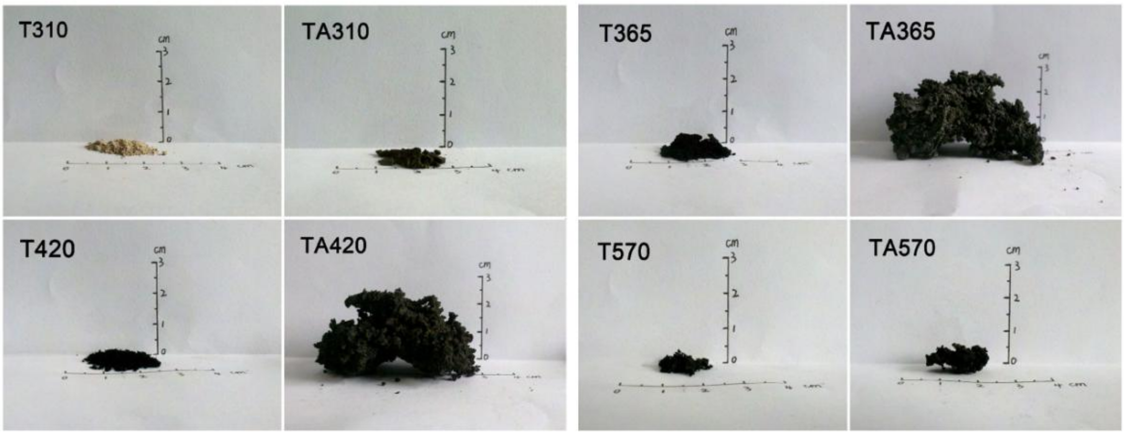

Fig. 2 Digital pictures of Trimer (T) and Trimer/APP (TA) after thermal-oxidative degradation at different temperatures

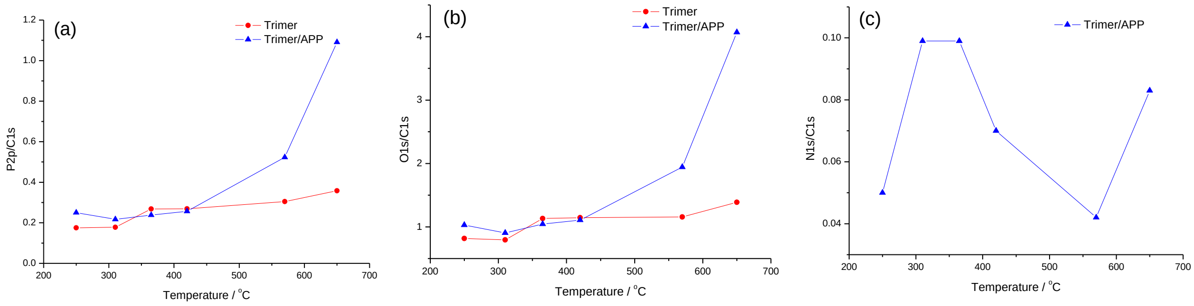

Fig. 3 Comparison of P2p/C1s (a), O1s/C1s (b) ratios of Trimer and Trimer/APP, and N1s/C1s ratio of Trimer/APP (c) with temperature increased

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STUDY OF THERMO-STABILIZATION OF BIODEGRADABLE POLYMERS DURING EXTRUSION PROCESS

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Introduction

The increasing use of plastic front of the other materials have been causing an increase of this kind of residue in landfills, dumps and even in streets and rivers due to inappropriate disposal. As an alternative to solve the environmental problem, biodegradable plastics have achieved a prominent position in the academic community and industry[1,2]. However, the population has the stigma that biodegradable polymers must be used in products of short life cycles. This project aims to study the thermo-stabilization of poly(buthylene adipate-co-terephthlate) – PBAT and poly(lactide acid) – PLA. It is hoped that the results will lead to materials with high life cycles, stable during the processing, and recyclability while maintaining its characteristic of biodegradability.

Experimental

The polymers used were poly(buthylene adipate-co-terephthlate) – PBAT and poly(lactide acid) – PLA. A processing stabilizer was used for both polymers: Tris(2,4-di-tert-butylphenyl) phosphite. To PBAT were used stabilizer concentrations of 0.1 and 0.5% (w/w) and to PLA were used 0.05 and 0.1% (w/w). The neat polymers and stabilized ones were submitted to five cycles of extrusion cycles in an extruder Haaker. Different temperatures profiles were used:

PBAT: 170 °C – 180 °C – 190 °C – 200 °C

PLA: 190 °C – 200 °C – 210 °C – 230 °C

After each cycle a quantity of the sample was collected to posterior analysis. Firstly, Melt Flow Index (MFI) analysis were done because the short time to obtain the results. After MFI analysis, Size Exclusion Chromatography (SEC) and Infrared spectroscopy (FTIR) analysis were done.

Results and discussion

The results from MFI analysis are showed on Table 1 and 2, for PBAT and PLA, respectively. The data from polymers without stabilizer show that scission reactions are the main phenomena on the degradative process. The presence of processing stabilizer was effective. Similar results were seen on SEC analysis for both polymers (see Table 3 and 4).

Table 1: MFI results (g/10min) of PBAT with and without processing stabilizer.

Extrusion cycles	*Samples*		
	neat PBAT	*PBAT + 0,1%*	*PBAT + 0,5%*
0	7,00 ± 0,13	7,30 ± 0,17	7,10 ± 0,03
1	6,98 ± 0,48	7,13 ± 0,56	6,98 ± 0,38
2	7,96 ± 0,51	7,19 ± 0,29	7,56 ± 0,39
3	8,44 ± 0,21	7,26 ± 0,47	7,73 ± 0,57
4	8,73 ± 0,29	7,74 ± 0,52	8,01 ± 0,39
5	9,29 ± 0,48	8,67 ± 0,29	8,45 ± 0,45

Table 2: MFI results (g/10min) of PLA with and without processing stabilizer.

Extrusion cycles	*Samples*		
	neat PLA	*PLA + 0,05%*	*PLA + 0,1%*
0	14.57 ± 0.76	18.71 ± 0.52	15.07 ± 0.25
1	13.57 ± 0.88	20.28 ± 0.66	16.19 ± 0.52
2	17.49 ± 0.36	25.09 ± 0.54	22.83 ± 0.29
3	20.59 ± 0.87	25.65 ± 0.48	22.89 ± 0.45
4	27.11 ± 1.00	26.05 ± 1.20	26.69 ± 0.75
5	36.76 ± 0.74	28.33 ± 2.83	29.96 ± 0.60

Table 3: Molecular weight ($\overline{M}_n$) of PBAT with and without processing stabilizer.

Extrusion cycles	*Samples*		
	neat PBAT	*PBAT + 0,1%*	*PBAT + 0,5%*
0	41350	41350	41350
1	35100	41400	42000
3	31300	42200	39350
5	37600	41400	41600

Table 2: Molecular weight ($\overline{M}_n$) of PLA with and without processing stabilizer.

Extrusion cycles	*Samples*		
	neat PLA	*PLA + 0,05%*	*PLA + 0,1%*
0	65000	65000	65000
1	66350	61300	61600
3	61400	58900	62200
5	49000	58650	56200

PBAT and PLA have carbonyl groups in its backbone. This carbonyl group is responsible to became them susceptible to microorganism attack; however, the same group became this polymer thermo-sensible. The Figure 1 and 2 show spectrum of PBAT and PLA, respectively.

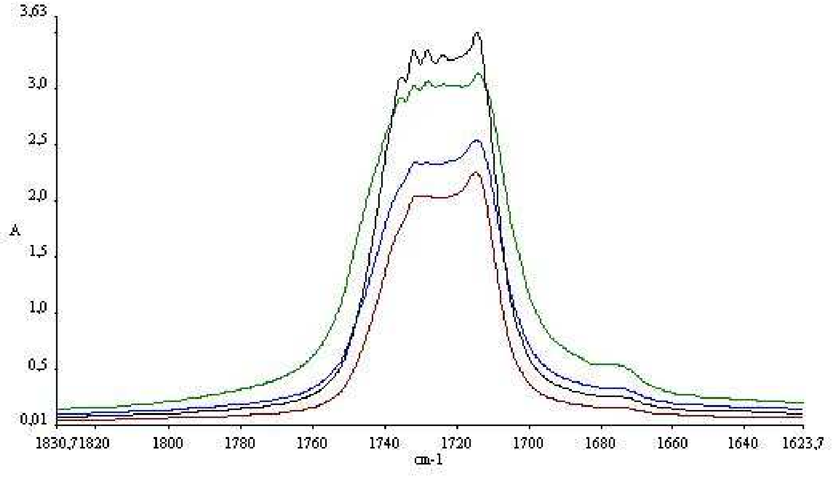

Figure 1 – Spectrum of neat PBAT (read), neat PBAT after 5 cycles (green), PBAT + 0.1% after 5 cycles (blue) and PBAT + 0.5% after 5 cycles (black).

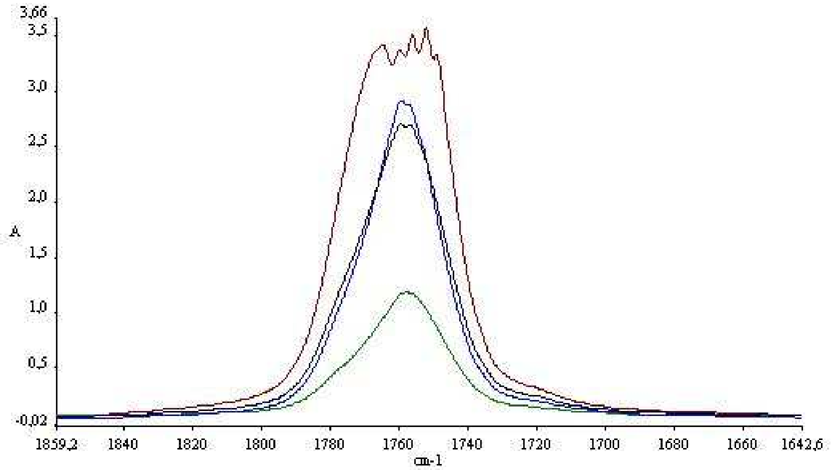

Figure 2 – Spectrum of neat PLA (read), neat PLA after 5 cycles (green), PLA + 0.05% after 5 cycles (blue) and PLA + 0.1% after 5 cycles (black).

In Figure 1 a broadening of carbonyl (C=O) peak were observed after 5 cycles for neat PBAT. The left shoulder (1790 and 1750 cm^{-1}) indicates the formation of free C=O, and the right shoulder represents the formation of a lower molecular weight ester[3]. A minor effect was observed for PBAT samples containing stabilizer. In Figure 2 a narrowing of carbonyl peak were observed for neat PLA after 5 cycles. It is confirmed that the degradation mechanism was predominantly by scission of ester linkage[4]. These scissions were suppressed by presence of processing stabilizer.

Conclusions

Similar to commodities polymers, the results show the importance of the previous study about thermo-stabilization and the correct choice of additive for a particular polymer.

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LIMITING POLY(LACTIC ACID) DEGRADATION DURING PROCESSING BY REACTIVE EXTRUSION

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As an eco-friendly material, Poly(Lactic Acid), is considered to replace traditional oil-based thermoplastics. Nevertheless PLA degradation during processing limits its use at an industrial scale. Degradation is due to several reactions including hydrolysis, oxidation and transesterification which cause chain scissions and a decrease in average molecular weight [1,2]. The loss in molecular weight can be counterbalanced by blending PLA with additives which can react with PLA end chains [3]. For instance, Pyromellitic anhydride (PMDA) is known to react with polyester such as poly(ethylene terephthalate) by reactive extrusion [4].

In this study, additives with three or four functional groups (such as ester and anhydride) have been used together with specific catalysts. Whereas anhydrides are able to react with PET during its processing without using any catalyst, the processing temperature used in order to limit PLA degradation is too low to trigger this reaction [5]. Therefore using a catalyst (titanium butoxide) was necessary in this study and its effect on PLA macromolecules has been investigated. All the reactions are performed during PLA extrusion and optimal processing conditions have been determined.

Results show that increasing the catalyst amount leads to a decrease in PLA average molecular weight. This means that chain scission occurs in presence of catalyst whereas it was not observed during pure PLA processing in this study. We also characterized how this decrease in average molar mass impacted PLA's physical properties (Fig 1).

Then, with the same catalyst amounts we investigated the effect of incorporating reactive species. We demonstrate that some additives (Fig2) allow to limit the loss in average molecular weight by promoting some chain exteion and branching.

As a conclusion this study demonstrates that favoring reactive chain extension and branching with appropriate processing conditions is an effective way to limit PLA degradation by chain scission.

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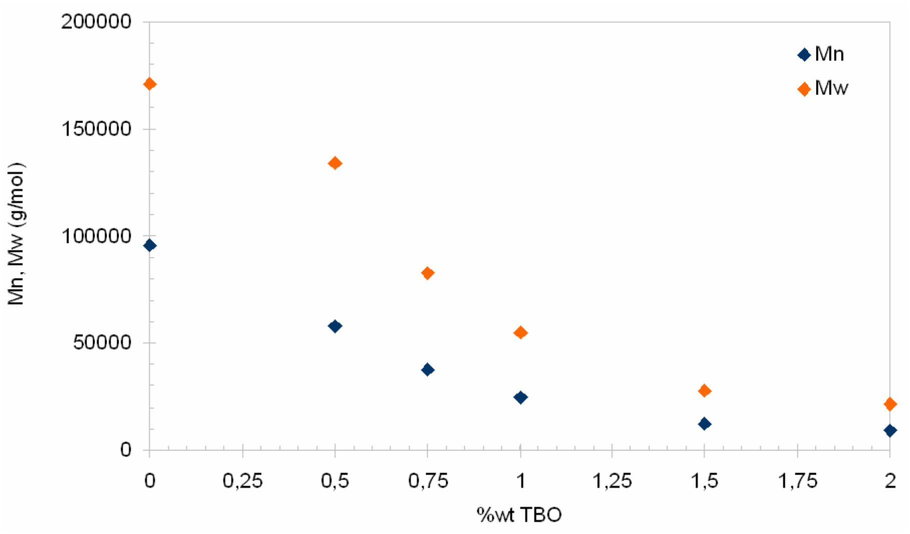

Figure 1. Average molecular weight of PLA versus catalyst amount.

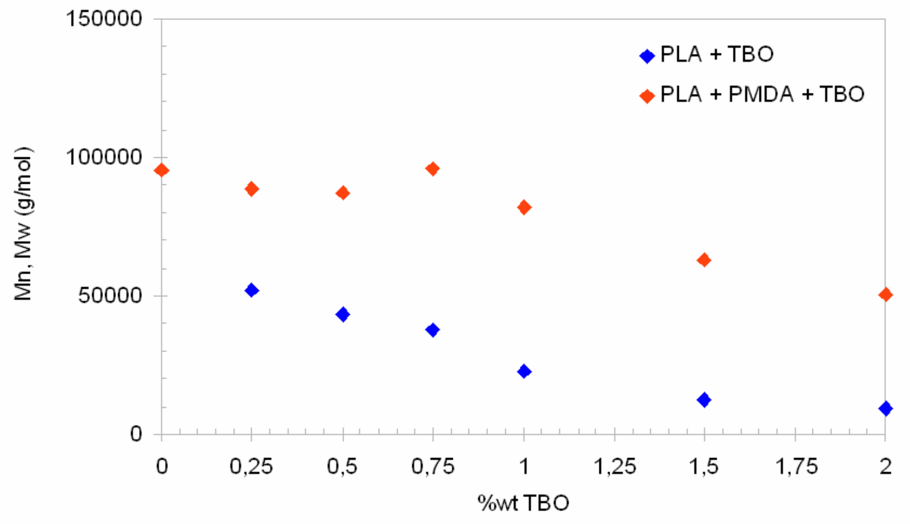

Figure 2. Average molecular weight of modified PLA with PMDA versus catalyst amount.

RELATIONSHIP BETWEEN CHEMICAL AND MECHANICAL MODIFICATION DURING OXIDATION OF CHLOROPRENE RUBBER

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The aging of polymers is commonly studied either from a chemical point of view[1,2] , by focusing on chemical reactions involved in degradation mechanisms, or from a mechanical point of view by characterizing the change in properties, such as tensile elongation at break[3]. However, there have been few successful studies[4] offering a direct link between the development of chemical changes in the material and the loss of mechanical properties over time.

In this study we focus on the thermal oxidative aging of an unfilled and unstabilized polychloroprene rubber. The ageing chemistry has been characterized using oxygen absorption and FTIR at different temperatures. At the same time, the change of the modulus during oxidation has been measured using in-situ DMA analysis on 100 micron thick films, in order to avoid any Diffusion Limited Oxidation (Figure 1).

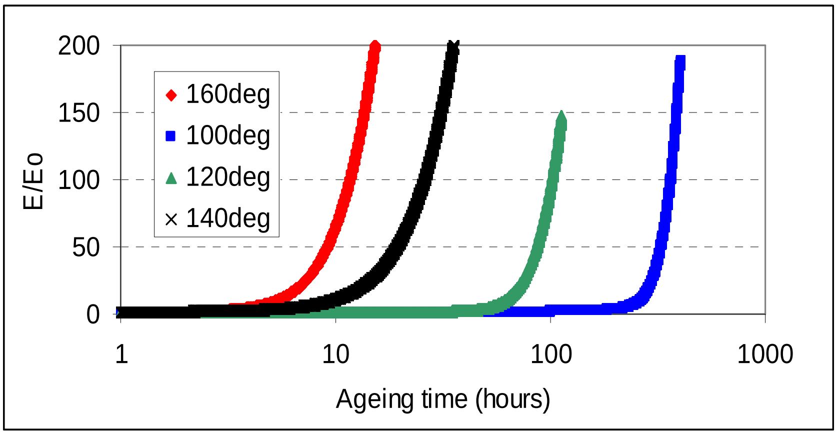

Figure 1 Evolution of the modulus on 100mic thick films as function of ageing time and temperature.

The effect of oxygen diffusion has been assessed by modulus profiling using instrumented indentation on 5mm thick samples during oxidation at 120°C (Figure 2).

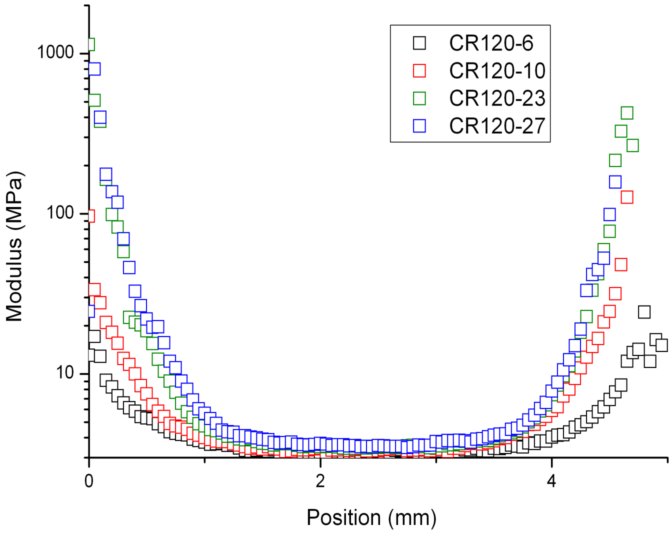

Figure 2 Modulus profile of the unfilled neoprene rubber aged at 120°C for different ageing duration in days.

Using these data, possible relationships between chemical and mechanical property changes during the oxidation of the CR are proposed and discussed.

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PRODUCTION OF POLYMERS BASED ON FURANIC DICARBOXYLIC ACID THROUGH POLYCONDENSATION REACTIONS – EFFECTS OF POLYMERIZATION CONDITIONS ON POLYMER STABILITY

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The environmental concern is leading to increasing interest in the production of polymers from renewable resources. Particularly, furanic compounds (more specifically, 2,5-furandicarboxylic acid - FDCA) constitute promising raw materials because of the structural similarity with derivatives of terephthalic acid.

Previous studies have shown that it is possible to synthesize poly(ethylene 2,5-furandicarboxylate) - PEF - successfully from FDCA and ethylene glycol[1,2,3]. However, polymerization conditions affect the final properties of the resin very significantly, including molecular weight distributions, characteristic transition temperatures, color and thermal stability. For this reason, this work evaluates the influence of reaction conditions on the thermal stability (in inert and oxidizing atmosphere) of polyesters synthesized through reaction of 2,5-furandicarboxylic acid with different diols, including ethylene glycol, 1,2-propanediol and glycerol.

PEF syntheses can be performed in three steps. First, esterification is carried out in a mixture containing the diacid (FDCA) and a mixture of diols. The reaction is conducted in slurry, at different temperatures and catalyst concentrations, under constant nitrogen flow. Nitrogen is used as a carrier gas for removal of volatiles and to keep the inert atmosphere. Then, transesterification of oligomers obtained in the first step is conducted in the melt phase in presence of catalysts under increasing vacuum. Finally, the obtained polyesters are subjected to solid state polycondensation under reduced pressure at different temperatures.

When thermograms of PEF and PET homopolymers are compared to each other (Figure 1a), it can be observed that PEF is less stable to temperature increase than PET resins obtained in the melt phase and after solid state polymerization. TGA analyses also show that the increase of the reaction temperature leads to decrease of thermal stability, while the increase of catalyst concentration leads to appearance of a point of maximum stability (Figure 1b). TGA analyses also show that the increase of the comonomer concentrations leads to decrease of thermal stability (Figures 1c and 1d).

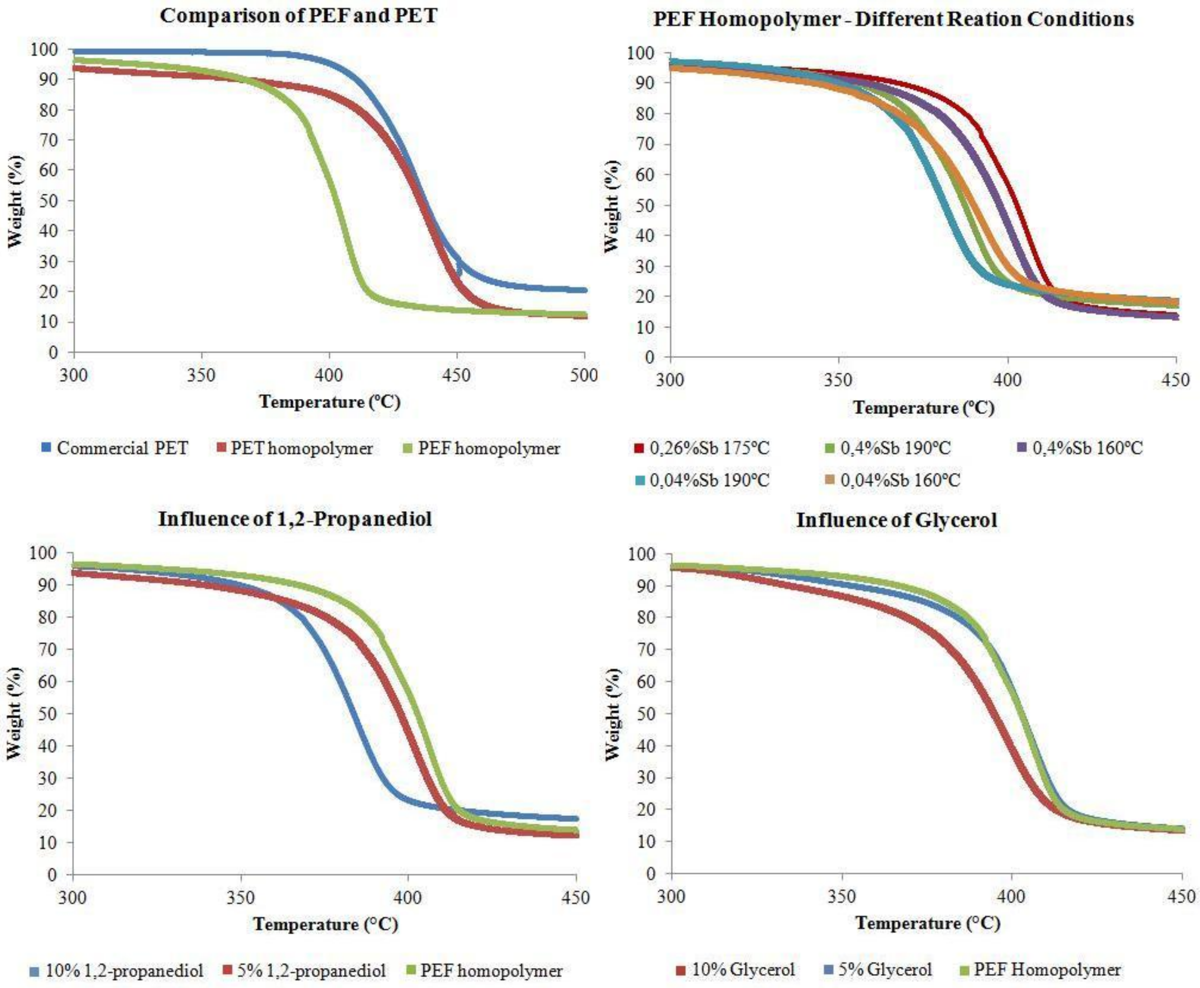

Figure 1. TGA thermograms for different PEF samples obtained under inert atmosphere.

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POLYMER OXIDATION IN GLASSY STATE

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Most of the fundamental literature on polymer oxidation deals with polyolefins and elastomers, i.e. with polymers in which the reacting rubbery phase is stirred by ample cooperative motions favoring the diffusion of radicals and the homogenization of the reactive medium. This paper deals with the oxidation glassy polymers through a discussion of orders of magnitude of initiation or termination rate constants. Data obtained for several polymers oxidized below T_g will be reviewed assuming that their oxidation is described by the following model:

$PH \rightarrow P^{\circ} + 1/2H_2$	r_i	radiochemical initiation
$\delta POOH \rightarrow \alpha P^{\circ} + \beta POO^{\circ}$	k_1	thermal initiation
$P^{\circ} + O_2 \rightarrow POO^{\circ}$	k_2	
$POO^{\circ} + PH \rightarrow POOH + P^{\circ}$	k_3	
$POO^{\circ} + POO^{\circ} \rightarrow$ inact. prod. $+ O_2$	k_6	

Radiooxidation of PEEK and PSU at ca 60°C[1,2] was monitored oxidation profile in thickness by FTIR. From a classical diffusion reaction theory, the thickness of oxidized layer can be linked to the ratio k_3^2/k_6. This was found surprisingly high for those aromatic thermostable polymers. k_3 is linked to the C-H bond dissociation energy and is thus very low so that k_6 is very low also (on the order of unity) instead of 10^5-10^8 $l\ mol^{-1}\ s^{-1}$ for PP or PE.

Polycyclopendadiene ($T_g \sim 160°C$) is a very oxidizable polymer in which maximal POOH concentration recorded by DSC coupled with specific SO_2 treatment is reached in less than 1 hour for thermal ageing at 90°C (Figure 1) and induction period for carbonyl clearly 10 or 100 times shorter than for BR[3], IR[4], PP[5] or PE[6]. Hydroperoxides analysis by DSC suggested ΔH = 200 – 1000 kJ mol^{-1}as decomposition enthalpy per mole of POOH[7] so that

$[POOH]_{max}$ ~ 1 mol l^{-1} which is for example 5 times higher than for PP in the same conditions.

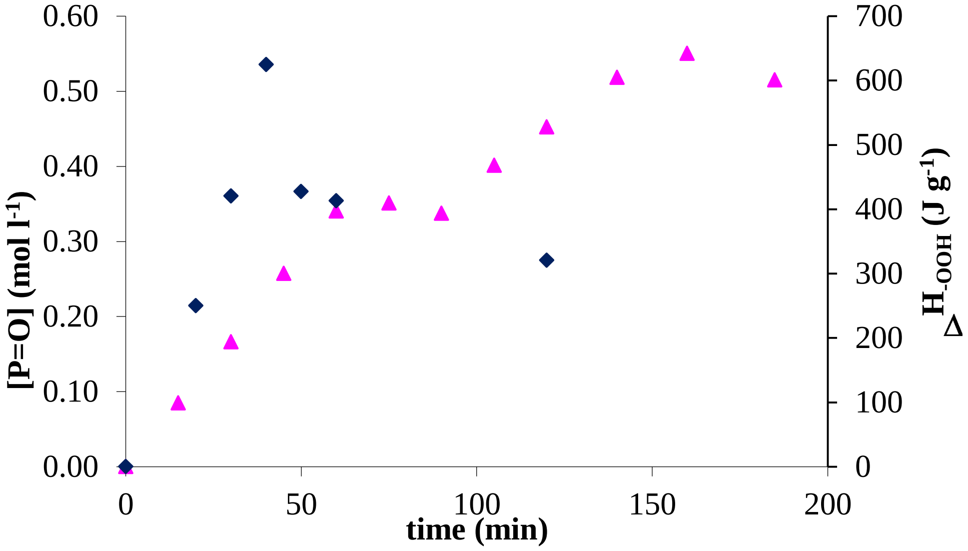

Figure 1 Carbonyl concentration and enthalpy of hydroperoxides thermal decomposition for PCPD ageing at 90°C.

The low induction period is explained by high k_1 value[8] meanwhile it is easy to show that $[POOH]_{max}$ depends on the ratio $k_3^2/(k_6.k_1)$ which suggests that k_6 is low here also.

These observations militate in favor of a control of termination kinetic by the low mobility of radicals at glassy state which is slower than expected for the bimolecular process between two radicals.

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AGEING STUDIES OF NATURAL RUBBERS USED IN SPACE APPLICATION

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Thanks to their high tensile strengths and excellent dynamic properties, natural rubber compounds are commonly used in a variety of technical applications, satellites in particular. The rubber should fulfill the space technology requirements during all the lifetime of the satellite which is of 15 years: 5 years of storage at ground and 10 years in space environment.

However, some properties such as air permeability, thermal resistance and damping capacity could be hugely modified during the lifetime of the material.

The study of these materials ageing is also essential in terms of research. The objective of this work is to investigate the ageing of natural rubber filled with carbon black particles under two kinds of stress: temperature (70°C) and vacuum (5.10^{-6} mbar).

Thermal ageing at 70°C under air (oxidative conditions) and high vacuum (non oxidative conditions) was first investigated. It was shown that the static and dynamic mechanical properties, such as for example the tensile strengths at 20 and 50% of elongation were greatly increased during oxidative ageing (Figure 1). These modifications of the material properties could be explained by an increase of the crosslinking density. This hypothesis was confirmed by swelling measurements (before and after ageing) which allowed an estimation of the crosslinking density thanks to the Flory-Rehner equation.

At the opposite, the strengths at 20 and 50% of elongation did not change during 22 days of ageing at 70°C under vacuum.

Then, the oxidation effect on the mechanical properties was studied by using Atomic Force Microscopy (AFM). Force measurements showed that the elastic modulus of aged rubber (184 days at 70°C) is higher at the surface than in the bulk. These results could be explained by the formation of a highly oxidized thin layer at the material surface during ageing. The evolution of this layer thickness during ageing was estimated thanks to AFM measurements.

In addition, Scanning Electron Microscopy observations coupled with Energy Dispersive X-ray (SEM-EDX) analyses were carried out in order to investigate the evolution of the morphology and the chemical structure of the rubber during ageing.

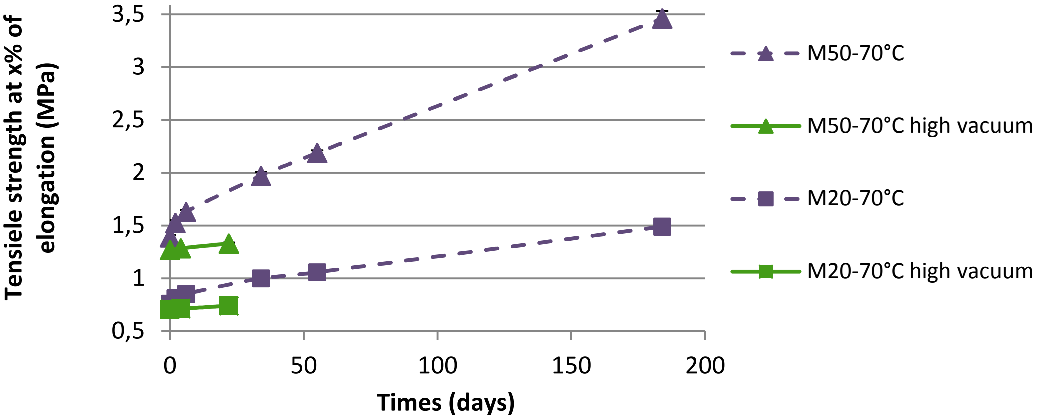

Figure 1 Variation of the tensile properties of natural rubber exposed at 70°C in air versus ageing duration.

EPDM COMPOUNDS DEGRADATION UNDER γ IRRADIATION: INFLUENCE OF COPOLYMER COMPOSITION AND FILLERS

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EPDM are copolymers (Ethylene Propylene Diene Monomer) widely used in the industrial domain for their numerous advantages: a good resistance to ozone and weather, to oxidant reagents, a strong thermal stability and a good electrical insulating property. EPDM are usually cross-linked thanks to the addition of peroxide during the material processing. Mineral fillers are commonly added to their formulation – such as ATH (Aluminium TriHydrates) – in order to reduce the production costs, improve mechanical properties and give a fire retardancy functionality.

EPDM are often employed as insulating sheath for cables, in particular for cables used in the nuclear power plants. For this application, because of their exposition to radiation, EPDM are degraded and eventually lose their electrical insulating property. The degradation of the mechanical properties has been proved to be the precursor of this modification of the electrical properties. Thus, for this reason, the lifetime prediction of EPDM is based on the evolution of the material elongation at break.

Studies have been performed on the different chemical [1, 2] and physical processes interacting during the degradation. Thus, an explanation of the evolution of the properties [1, 3] (mechanical and dielectrical) with the modification of the molecular structure and the crystalline morphology has been proposed. It was evidenced that the crystalline phase attenuates the impact of the degradation of the matrix. Besides, the influence of the fillers on the radiochemical degradation processes has been investigated. ATH fillers apparently accelerate the material degradation [4, 5].

Nevertheless, the mechanisms explaining this acceleration are unknown. Moreover, it is also difficult to dissociate this effect from a modification of the polymer/filler mechanical coupling. However, this is mandatory to understand the evolution of the strain and stress at break of the irradiated materials. Thus the present study is devoted to the following questions: what is the influence of the polymer architecture, the filler presence and the semi-crystalline microstructure on the mechanisms of the radiochemical degradation, and eventually on the evolution of the material properties at break?

Two EPDM copolymer are studied with two PE/PP ratio, thus one EPDM is amorphous and the second one initially contains 8% of cristallinity. Three filler types have been studied: 3 micron size surface treated and not treated ATH, 70 micron size ATH, and a smaller one of 300 nm. The different materials have been γ irradiated in O_2 at room temperature, at 1.2 kGy/h with different doses up to 450 kGy.

Compared to previous studies where the ENB content of the copolymer was below 2.5% (wt) the high ENB content (5wt) used in this study leads to a weaker degradation of the material under irradiation. This is explained by the presence of residual ENB which have not participated to the polymer crosslinking. A strong chemi-crystallization process is induced by irradiation in the case of the semi-crystalline matrix. Chain scissions are promoted during the irradiation: this promotes the crystallization initially inhibited by the high crosslinking degree of the studied material. Compared to previous studies, it is more difficult to evidence the impact of the filler on the degradation kinetic since this degradation is strongly perturbed by the residual ENB in the matrix. However, specific study is presently performed to characterize the possible evolution of the filler-matrix interface. In addition, a modeling approach is also developed to account for all the experimental results.

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CLAYS d-SPACINGS EFFECT ON THE FIRE RETARDANCE OF POLYMER NANOCOMPOSITES WITH AN INTUMESCENT FORMULATION

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The development of polymeric materials with flame retardant properties is becoming more important with time.[1] Organohalogenated compounds are gradually being replaced by other additives due to their high toxicity and environmental aggressiveness. Intumescent formulations and nanocomposites polymer-clays can be excellent alternatives for the development of polymeric flame retardants. However, it has been found that the exclusive addition of clays in a polymeric matrix, in spite of a polymer thermal stability increase and heat release rate decrease that is obtained, this practice does not avoid the complete degradation of the polymer. Therefore, the concomitant use of other fire retardant additives is important, especially if these additives play roles in a synergic way.

Our group has observed that both sodic and organophilic clays are able to play the role of a synergy agent in a matrix of poly[ethylene(30%)–butylacrylate] copolymer containing an intumescent formulation with ammonium polyphosphate (APP) and the pentaerythritol (PER)[2,3]. Besides, it has been found that the d-spacings of the clays have an influence on the synergy effect as well, with LOI values and UL-94 classification improving when d-spacings decrease[4].

In this work it was used the same polymeric matrix and intumescent formulation with APP and the PER. Nanocomposites containing clays and the intumescent formulation with fire retarding properties were studied and the results showed that sodium clays and organoclays with d-spacing of up to 24Å act as synergistic agents. In these cases, there was a significant improvement in the LOI, UL-94 and cone calorimetry results. However, the synergy obtained for systems with organoclays with d-spacings exceeding 30Å dropped dramatically. To elucidate this phenomenon the intumescent layer formed was studied through SEM and FTIR analysis of the burnt residues. Also, polymer-clay nanocomposites without the intumescent formulation were evaluated through the same techniques and the results revealed that an increase in the d-spacings of the clays did lead to an increase in the fire resistance of these materials. The SEM analysis results showed that the addition of clays with basal spacings larger than 30 Å led to the formation of an intumescent layer with morphology very similar to the one shown by the sample containing only the intumescent formulation, without synergistic agents. In this case, the formed char was less homogeneous and less structured than those from the materials containing clays with d-spacings of 13 and 22 Å. The FTIR analysis of the burnt residues indicated a late formation of phosphocarbonaceous species when the clays with higher basal spacing were added. These findings can justify the loss of the synergy effect and the morphology of the char formed for these materials.

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BLOWING-OUT EFFECT OF EPOXY COMPOSITES FLAME-RETARDED BY DOPO-POSS AND ITS CORRELATION WITH AMIDE CURING AGENTS

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An interesting phenomenon, called the “blowing-out effect”, has been observed in flame retarded epoxy resins loaded with a novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS). Model of the blowing-out effect is shown in Fig. 1 [1,2]. In order to further understand the reasons behind and the factors that influence the blowing-out effect, we have investigated the epoxy resins (diglycidyl ether of biphenol A: DEGBA) cured by both oligomeric polyamide 650 (PA650) and 4,4′-diaminodiphenylsulphone (DDS), respectively, with DOPO-POSS as a flame retardant. The epoxy composites with DOPO-POSS showed different flame retardant properties depending on the amides used. The results of UL-94 tests show that the DEGBA/DDS with DOPO-POSS exhibits a blowing-out effect through vigorous emission of pyrolytic gases, but the DEGBA/PA650 does not (Fig. 2). Moreover, only 2.5 wt. % DOPO-POSS imparts to the epoxy resin DEGBA/DDS a LOI value of 27.1 % and UL-94 V-1 rating. In contrast, 10 wt. % DOPO-POSS in the DEGBA/PA650 results in a LOI value of 25.9 % and a UL-94 V-1 rating. The details of fire behavior, such as the values of TTI, HRR, p-HRR, COPR, and CO_2PR have been tested using a cone calorimeter. DOPO-POSS in the DEGBA/DDS causes a lower value of p-HRR and longer TTI than in the DEGBA/PA650. The DEGBA/DDS with even as little as 2.5 wt. % DOPO-POSS easily forms a compact char. However, the DEGBA/PA650 with DOPO-POSS does not char until 10 wt. % DOPO-POSS. The thermal stability and pyrolytic gases of the two kinds of epoxy resins were detected by TGA-FTIR under a nitrogen atmosphere. DOPO-POSS performs better in accelerating charring in the DDS curing system compared with the PA650 curing system. It is postulated that for the

DEGBA/DDS/DOPO-POSS, fast and dense charring and accumulating of pyrolytic gases in the char contribute to the blowing-out effect. By contrast, the aliphatic chains of the PA650 are easy to break down and produce combustible gases, so are uneasy to form a crosslinking structure in the condensed phase until enough DOPO-POSS is added. These results may be very helpful for investigation of the conditions under which the blowing-out effect in epoxy resins can be caused by synergy of phosphorous (DOPO) and silicon (POSS).

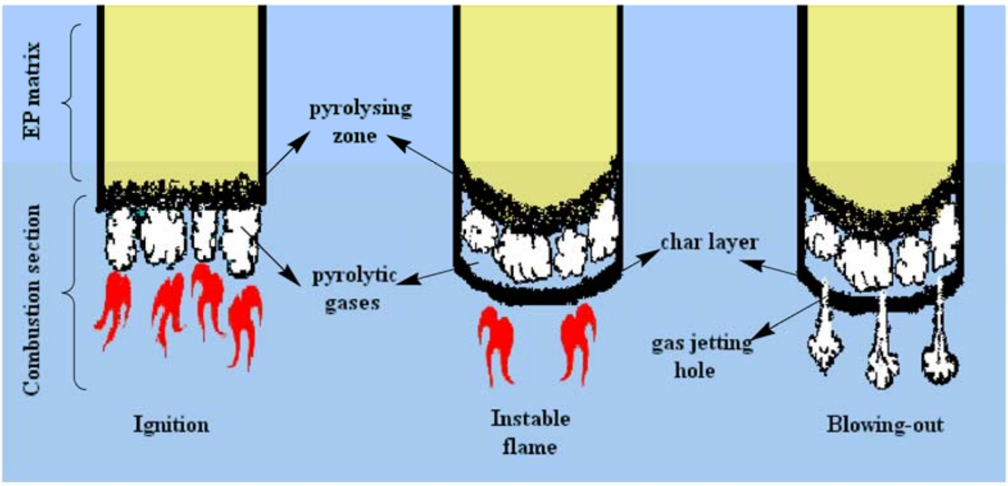

Fig. 1. The model of the blowing-out effect.

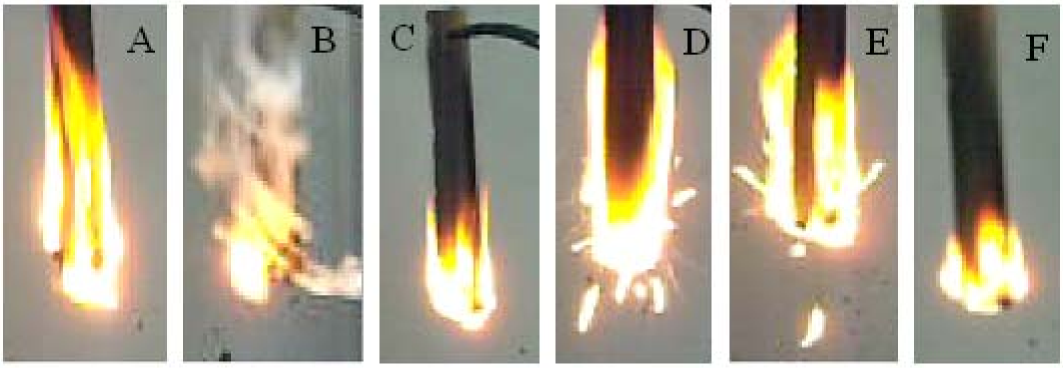

Fig. 2. (A) DGEBA/DDS, (B) DGEBA/DDS/2.5 wt. % DOPO-POSS, (C) DGEBA/DDS/10 wt. % DOPO-POSS, (D) DGEBA/PA650, (E) DGEBA/PA650/2.5 wt. % DOPO-POSS, and (F) DGEBA/PA650/10 wt. % DOPO-POSS.

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INFLUENCE OF ZINC BORATE ON FIRE PROTECTION AND THERMAL DEGRADATION OF INTUMESCENT COATING CONTAINING A NOVEL CAGED BICYCLIC PHOSPHATE

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Keywords: Intumescent; Zinc borate; Fire protection; Coating.

Fire protection and thermal degradation of intumescent epoxy coatings with a novel caged bicyclic phosphate (Trimer) [1], APP and zinc borate (ZB) were investigated. The experimental results as follows: compared to the coatings with ZB, No.1 coating shown the best initial fire protection property up to 300s due to the earliest expansion (Fig 1, Fig 2 and Table 1), however, at a longer time a plateau was achieved for No.2 and No.3 coatings and their final fire protection time was increased about 100% respectively when compared with that of No.1 coating. Compared to calculated TGA curve of No.3 coating in N_2, the experimental one changed slightly (Fig 3 (a) and Table 1), the experimental residue at 700℃ was increased by 1.5% on the base of calculated one. Moreover, the difference was obviously enlarged in air (Fig 3 (b) and Table 1), particular at temperature higher than 550℃, significant improvement was observed in thermo-oxidative stability of coating with the addition of 5%ZB. The final residue of No.3 coating was 38.2% at 700℃ compared to 27.0% for No.1 coating and the beneficial effect of ZB was clearly demonstrated as well. It is of interest to notice that the degradation curve of Trimer/APP abviously changed from 480℃ by incorporating ZB and the final residue increased from 14.6% to 47.8% (Fig 4). The ^{31}P solid-state NMR spectrum (Fig 4) shown a high peak at -30ppm, which is attributed to B-O-P bonds [2]. This result further confirmed that the interaction taken place between Trimer/APP and ZB which lead to the formation of borophosphate. Above mentioned results clearly indicated that an appropriate ZB may yield synergistic effect on improving the thermal stability of coating with Trimer/APP at high temperature, which could contribute to enhance the fire protection property of coating.

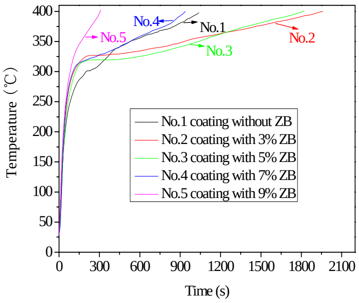


Fig 1. Fire protection curves of coatings.

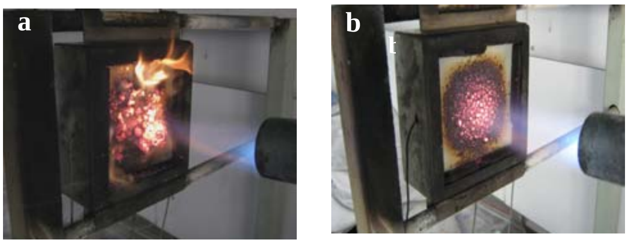


Fig 2. Image of (a) No.1 and (b) No.3 coatings at 30s in the fire protection test.

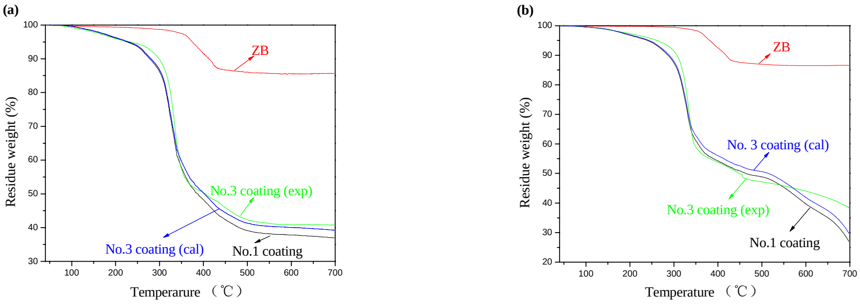
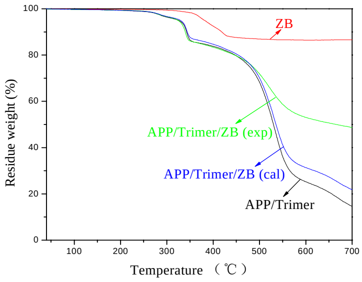


Fig 3. TGA curves of No.1 and No.3 coatings in (a) N_2 and (b) air.



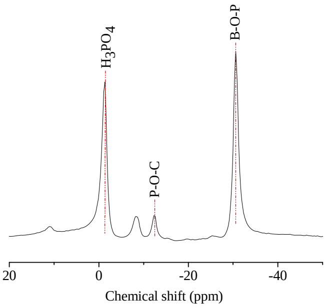


Fig 4. TGA curves of Trimer/APP, ZB and Trimer/APP/ZB in air.

Fig 5. ^{31}P solid-state NMR of Trimer/APP/ZB treated at 600℃ in air

Table 1. Fire protection and TGA data of coatings

Samples	Fire protection time (s)				N_2, 10℃/min		Air, 10℃/min	
	250℃	300℃	350℃	400℃	$T_{5\%}$/℃	CR/% (700℃)	$T_{5\%}$/℃	CR/% (700℃)
No.1	80	200	530	1040	223	37.0	240	27.0
No.3	70	121	1030	1800	224	40.8	260	38.3

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THERMAL DECOMPOSITION STUDY OF SOME POLYMERIC MULTICOMPONENT SYSTEMS BASED ON AROMATIC POLYURETHANE AND EPOXY RESIN NETWORK

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The aim of this study is to follow the thermal stability of some semi-interpenetrating polymer networks (SIPNs) obtained from an aromatic polyurethane (PU) with linear structure and a crosslinked epoxy network (ERN) based on bisphenol A. Studies of thermal stability were carried out by coupled techniques thermogravimetry-Fourier transform infrared spectroscopy and thermogravimetry-mass spectroscopy. Samples were heated in inert atmosphere, at temperatures between 40^{o}C and 600^{o}C in dinamic heating conditions. Four different heating rates (5, 10, 15 and 20 K min^{-1}) have been applied in the study. The volatile products evolved during thermal degradation have been identified. The kinetic parameters for thermal decomposition reaction were established using the isoconversional methods. Figure 1 shows a SIPN structure which was obtained by inclusion of linear polyurethane in the cross-linked epoxy resin.

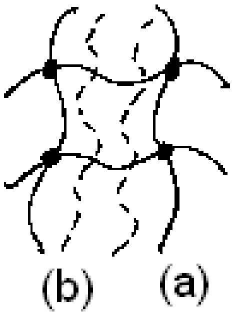

Figure 1. SIPN structure which was obtained by inclusion of linear polyurethane in the cross-linked epoxy resin: (a) polyurethane; (b) epoxy resin based on bisphenol A

The composition of the SIPNs synthesized from polyurethane and epoxy resin is: 5%, 10%, 15%, 20% and 40% ERN.

The thermal stability of the polymeric systems is very important because it determines the upper service temperature and the environmental conditions under which they can be employed. Therefore, a systematic thermal degradation study of the SIPN systems was conducted by thermogravimetric analysis at different heating rates in N_2. Since the thermal stability is related to both the initial degradation temperature and by the degradation rate of polymers, the determination of kinetic parameters associated with the degradation process is a very interesting topic in these polymeric systems. The results obtained provide useful information in defining of suitable processing conditions for applications and draw a correlation between thermal stability and structure of SIPNs.

The thermograms exhibit lower thermal stability compared to the crude components. The thermal stability of the samples decreases with ERN content increase. This behavior is generally specific for alloys or blends of polymers. Thermograms displacement to higher temperatures was observed with increasing of heating rates from 5K min^{-1} to 20K min^{-1} for SIPN samples. The PU sample exhibits a melting peak around 200°C. Other three endothermic processes can be observed at the peak values of 222°C, 352°C and 415°C attributed to thermal degradation. No significant differences are observed between the melting peak intensities of SIPNs with low epoxy resin content (5%, 10%). An important decrease in the intensity of the melting peaks is presented by the other samples with higher epoxy resin content (15%, 20%). The melting process DSC signals completely disappear at samples with epoxy resin content higher than 20%. This general behavior of the melting pattern can be explained by the increase of the crosslinking density of high content epoxy resin in SIPN samples. This aspect is further confirmed by the decreasing in melting heat values from 3.63 J g^{-1} in the PU sample up to 0.52 J g^{-1} in SIPN-5.

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USE OF PCFC TO PREDICT THE FLAMMABILITY PARAMETERS OF POLYMERS FROM THEIR CHEMICAL STRUCTURE

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Predicting the flammability parameters of a polymer from its chemical composition would open up many opportunities like the selection of the best structure without using an expensive trial and error approach. In a recent study Lyon *et al.* have proposed to calculate the main flammability parameters of polymers using a Van Krevelen approach [1]. Such approach allows predicting roughly the heat release capacity (HRC) and the total heat release (THR) as measured in microscale combustion calorimeter (PCFC) [2]. A first empirical database was proposed with the contributions to HRC and THR for almost 40 chemical groups. Figure 1 shows the good agreement between measured and calculated HRC for various EVA or EMA copolymers.

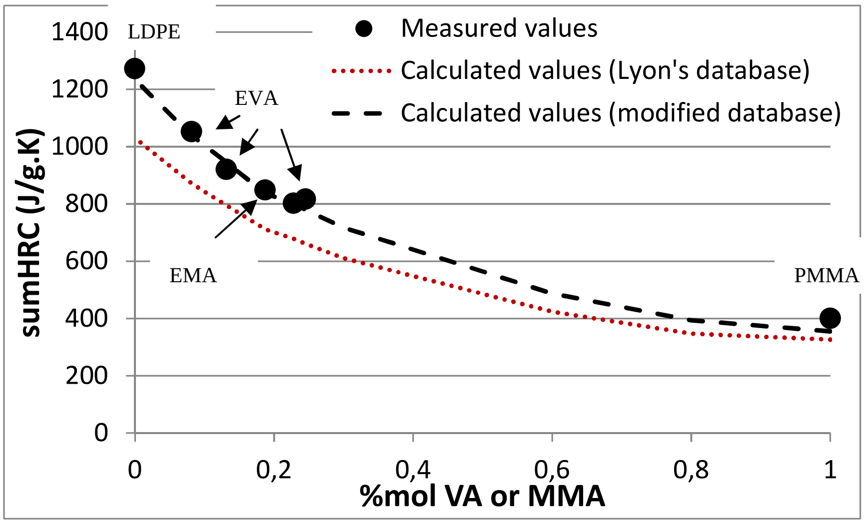

Figure 1 – Measured HRC and calculated HRC using Van Krevelen's approach for various EVA and EMA copolymers

The limits of this method are the interactions that may occur between chemical groups of a same structure during thermal decomposition. We have attempted to calculate the contributions of new chemical groups (not proposed in the Lyon's database) [3]. Figure 2 plots the calculated and experimental sumHRC of various molecules containing dioxaphosphorinane (series A) or phosphonate (series B) groups. A good agreement is observed when the contributions to sumHRC are fixed at 400 and 500 J/g.K (respectively for dioxaphosphorinane and phosphonate groups. Nevertheless the calculations fail to fit properly to the measured points for series C. This series gather molecules containing phosphonate and ester groups and possible interactions between these groups are believed to explain this absence of agreement.

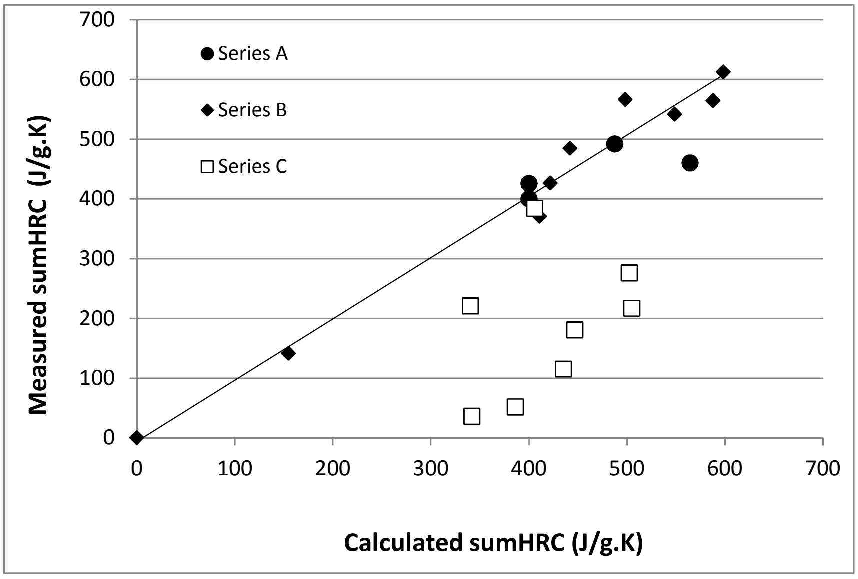

Figure 2 – Measured and calculated sumHRC for various phosphorus containing molecules [3]

Nevertheless in absence of agreement this method can be used as a tool to estimate interactions that occur during the thermal degradation [3]. The influence of fine details of the chemical structure on the flammability of a polymer can be evaluated by this method.

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NANOCOMPOSITES OF POLYPROPYLENE/POLYAMIDE BLENDS BASED ON THREE DIFFERENT NANOCLAYS: THERMAL STABILITY AND FIRE RETARDANCY

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The influence of various layered silicates: sepiolite (needle-like structure), halloysite (nanotube structure) or organomodified montmorillonite (lamellar structure) in combination with a phosphorous flame retardant (diethylphosphinate) on the properties and morphologies of compatibilized PP/PA-6 blends has been investigated. The blends were prepared using a twin screw extruder and different strategies were applied to achieve nanoparticles dispersion. The thermal degradation and fire retardancy of these blends were explored using TGA, cone calorimeter, LOI, microcalorimeter of combustion (PCFC) tests regarding their morphologies. The coupled TGA/FT-IR, Py-GC/MS and EDX analysis were used to evaluate the flame retardant mechanism of phosphinate in condensed and vapor phase.

Flame retardancy in polyethylene/CNT and polyethylene/silica nanocomposites

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Introduction. The properties of a composite material depend not only upon the properties of the individual component phases (matrix, filler, interface), but also upon their interaction. An improvement in flammability properties of polymers using the unique interface that can be developed with layered silicates, has been demonstrated for clay nanocomposites [1,2]. Nanoscale silica particles also can have a large interfacial area as long as the diameter of the particles is in the range of nanometers and they are well dispersed in the polymer. Although they do not have the structure of a layered clay, the improvement in physical properties and also some improvement in thermal stability by the addition of nanoscale silica particles to polymers were reported [3]. Carbon nanotubes provide another candidate as a flame retardant additive because of their highly elongated shape. Recent papers demonstrates the flame retardant effectiveness of nanocomposites made with several polymer resins [4,5]. These papers demonstrate that flame retardant effectiveness of those fillers is in someway similar to that verified for clay nanocomposites. The objective of this paper is to understand the flame retardant mechanism of polyethylene/carbon nanotubes or fumed silica nanocomposites by measuring certain thermal characteristics.

Experimental. High density polyethylene, PE, Eraclene® ML-70 produced by Polimeri Europa, was used as matrix for this work. The nanoscopic silica used was Fumed Silica (FS), Sigma-Aldrich, pyrogenic colloidal SiO2 with an average primary particles size of 7 nm. Multi-walled carbon nanotubes were provided by NanoCarbon Technologies Co. (αCNT).

Composite of PE filled with different wt% of αCNT and FS were prepared by melt compounding at 160°C using a Brabender internal mixer AEV330 with a screw speed of 50 rpm for 10 min. The composites were then pressed at 180±5°C and 100 bar, for 5 min, to obtain disk-shaped plates (75 mm diameter and 4 mm thickness). Sample of PE was prepared in the same conditions to be used as references.

The distribution of αCNT and FS in composites was studied recording images with respectively a ZEISS SUPRA™ 40 FESEM on cryo-fractured and chemically etched surfaces of samples and a Philips CM-12 TEM on thin sections cut from epoxy resin embedded samples. Dynamic rheological experiments were performed with a Rheometric Solid Analyzer ARES G2, TA Inc., samples 12.5x16x0.5 mm at 150°C to measure the storage and loss moduli as function of frequency (0.1 to 100 rad/s) at a constant strain of 0.5% in nitrogen flux. Flame retardancy of nanocomposite samples where measured by a radiant gasification apparatus designed and constructed at NIST to study the gasification processes of samples by measuring mass loss rate and temperatures of a sample exposed to a fire-like heat flux in a nitrogen atmosphere (no burning). All experiments were conducted at 50 kW/m2. Thermal degradation and thermo-oxidation were measured on approx. 10 mg sample in a TGA Q 500 balance, TA Inc., with alumina pan in a 70 cm3/min nitrogen or air flow and with a 10°C/min heating ramp from room temperature up to 800°C.

Results & discussion. TEM and FESEM (fig.1) images showed that fillers are well dispersed in polymer matrix. In silica nanocomposites aggregates are visible as black spots and their dimensions are of about 300 nm (figure 1A). MWCNT can be clearly identified through polymer matrix lamella as white filaments. In figure 1B CNT are uniformly dispersed as single nanotubes.

TGA curves (fig.2A) of nanocomposites containing CNT and FS, at all weight percentages, show a slightly stabilization as compared to pure polymer. In oxidant atmosphere (TGA curves not reported), a stronger effect is displayed. The stabilization is achieved due to the formation of a physical barrier of stacked filler nanoparticles. The behavior registered in nitrogen could indicate a weak effect of flame retardancy during combustion. However in literature [6] are reported data of nanocomposites which do not show stabilization in nitrogen but at the same time display flame retardancy in cone calorimeter test in a good correlation with the stabilization reached in air TGA. Another way, similar to cone calorimeter test, to study the combustion of polymeric materials is the gasification tests where the results are based only on the condensed phase. In the gasification tests (fig.2B) good performance in flame retardancy has been achieved for CNT samples where the mass loss rate is strongly decreased by the formation of a protective network layer covering the entire surface without any cracks or openings. This layer is observed in PE CNT samples also at lower concentrations but not for PE FS samples which show after the measure a gasification residue with many cracks. FS is someway less effective than CNT despite the viscoelastic characteristics of nanocomposites (fig.2C) indicate the formation of a network structure for both the samples containing FS and CNT at a loading of 4 wt% Thus, while viscoelastic characterization of polymer nanocomposites can be used as a screening method for seeking the formation of a network structure, to achieve effectively flame retarded nanocomposites also the stability of the network structure is required. Evidently, having a gel network is not enough to universally impart flammability reduction, the network must be stable under burning conditions. The tubes with their large aspect ratio, dense entanglement network and strong bridging interaction form physically stronger network compared to the less entangled silica nanoparticles.

Conclusions. In this work different kinds of nanocomposites were prepared with the same method that resulted effective to achieve good filler dispersion. Fillers with different morphologies slightly improve thermal stability and strongly decrease thermoxidation. This effect of stabilization depends on the formation of a physical barrier which is responsible also of the retardancy mechanism against degradation during gasification test.

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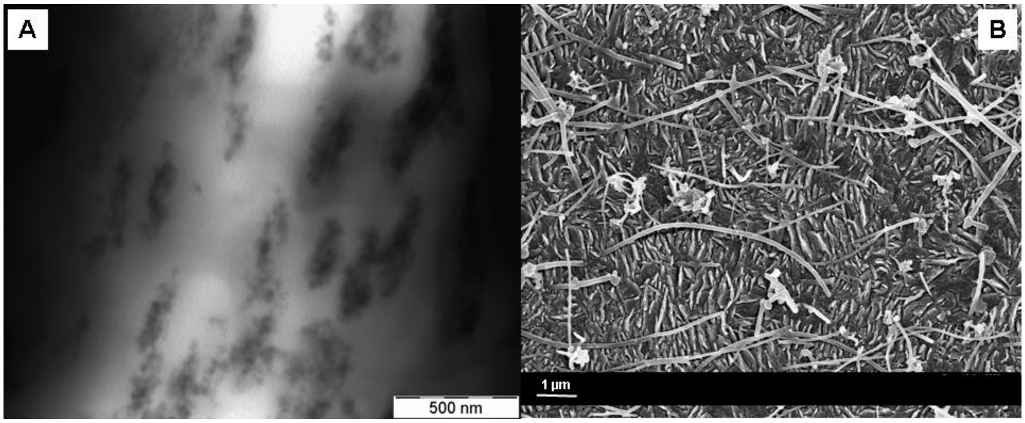

Fig. 1 TEM (A) and FESEM (B) images of PE nanocomposites filled with FS and CNT at about 4 wt%.

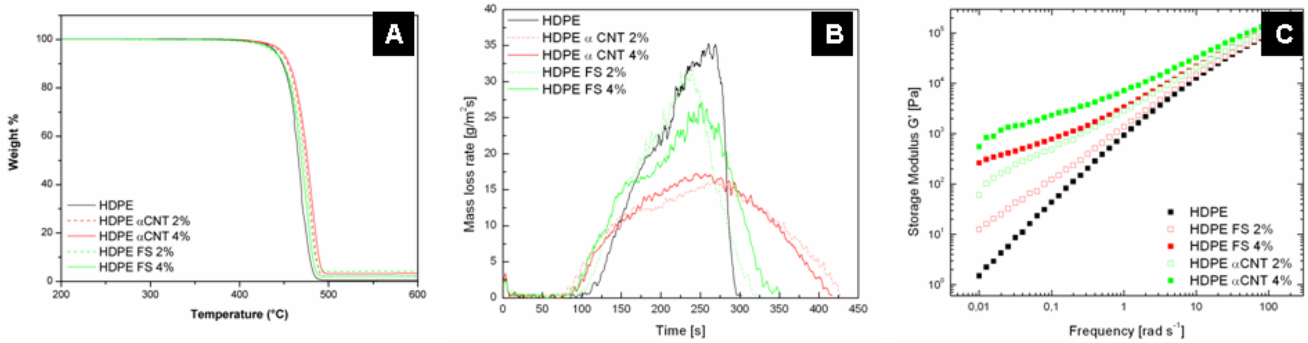

Fig. 2 Nitrogen TGA (A), gasificator (B) and viscoelastic (C) data for CNT and FS nanocomposites

INFLUENCE OF MICRO MAGNESIUM DIHYDROXIDE ON THERMAL DEGRADATION AND FIRE BEHAVIOR OF POLYESTERS

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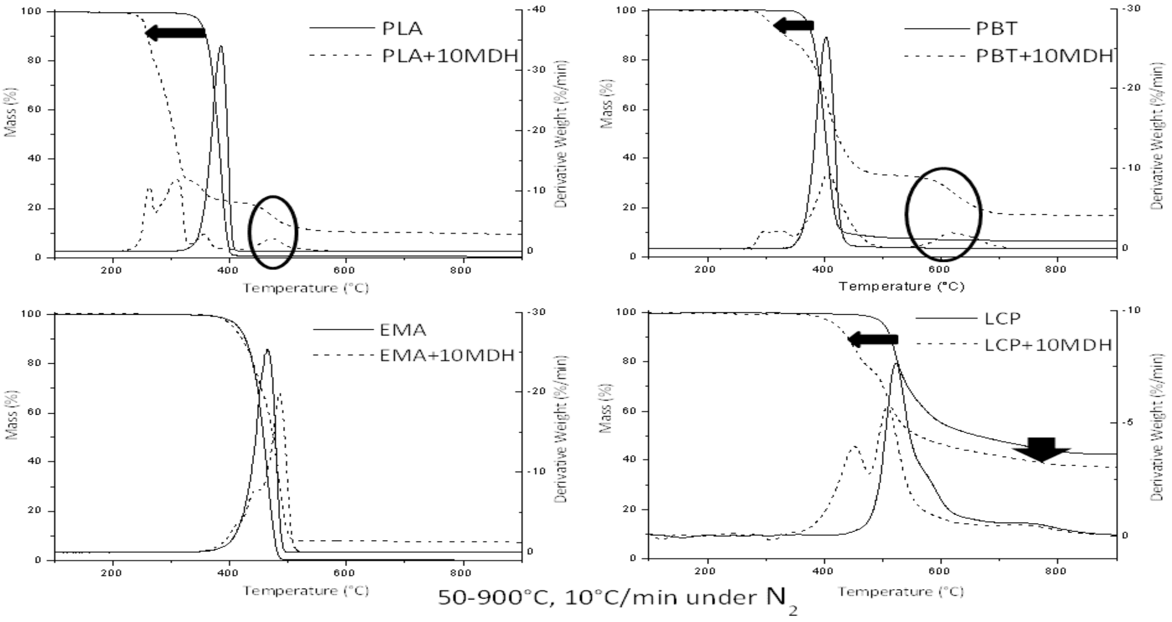
Magnesium dihydroxide (MDH) is a well-known flame retardant, particularly for polyolefins[1–3] and polyamides[4,5]. MDH decomposes through an endothermic reaction to give off water[6]. Many polymers are sensitive to the hydrolysis, such as polyamides and polyesters[7,8] which leads to an earlier thermal degradation. The phenomenon of hydrolysis could be promoted by the water release of metal hydroxides, charring can be observed that could promote flame retardancy in polyester-MDH formulations. This study was carried out to determine the influence of the chemical structure of various thermoplastic polyesters filled with MDH on thermal degradation and flammability of MDH-filled polyesters.

Various thermoplastic polymers with different chemical structures (aromatic, aliphatic and pendant ester groups) were filled with 10wt% MDH. These formulations were studied by TGA, PCFC and Pyrolysis-GC/MS to scrutinize the role of MDH on the degradation mechanisms of polyesters.

The studied polymers were divided into four series (A, B, C and D) according to their chemical structure. Series A gathers thermoplastic aliphatic polyesters (PLA, PCL, PBS, PHB and PHBV) while series B corresponds to thermoplastic aromatic polyesters (PET and PBT). Series C includes thermoplastic polymers or copolymers with pendant ester groups (EVA, EMA and PMMA). While the pure polymers from series A, B and C hardly form char during pyrolysis, Series D gathers char-forming polymers which present an ester group such as liquid crystal polyester (LCP) or a carbonate group such as polycarbonate (PC).

TGA and PCFC show that the addition of MDH significantly changes the thermal stability of studied polymers. Figure 1 shows the thermogravimetric analysis of four examples (four blank polymers and their MDH-filled formulations). PLA, PBT, EMA and LCP are representative for the series A, B, C and D respectively.

Four behaviours in thermal stability were observed in function of the polyester chemical structure when they are filled with MDH. The polymers of the series A and B showed an earlier degradation but an interesting char is formed at high temperature (it is observed at higher temperature for series B). There is no modification in thermal stability for series C when these polymers are MDH-filled. In case of series D, MDH promoted an earlier degradation and lower char content.



50-900°C, 10°C/min under N_2

Figure 1: Mass (%) and Derivative mass (%/min) versus temperature

Hence, we could demonstrate a clear relationship between the polyester chemical structure and the thermal stability and flammability in presence of MDH. MDH seems to be particularly efficient as flame retardant in aromatic polyesters (PBT and PET).

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CONE CALORIMETER TESTS IN THE RESEARCH OF MECHANISM OF POLYMERS BURNING

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Oxygen consumption calorimetry as it is used in a cone calorimeter provides a set of useful data concerning the sample ignition, burning and extinction and the kinetics of the heat release rate, release of smoke, CO and CO_2, mass changes, etc. may well be assessed. Many publications appeared from the first pioneering papers and construction of the first instrument designed by V. Babrauskas. The flammable sample is put at the arm of balance where it is exposed to the cone heater at a certain cone radiancy and ignited by a spark, microburner or self-ignited. The main parameter determined – the heat release rate (HRR) – is measured from the decrease of oxygen concentration in the flow of air (24 l/s approximately) in calorimeter exhaust duct. From 50 thermally thin polymers (up to 2 mm thick) from the ResinKit (Woodstock) HRR for burning of polypropylene filled with different inorganic fillers (calcium carbonate, glass, baryum sulfate) conducted at the heat radiance 35 kW/m^2 are shown in the Fig. 1. The time to ignition, smoke release, the average cone calorimeter combustion heats and the mass loss were compared and discussed from the viewpoint of the polymer degradation route and its composition. Nonisothermal thermogravimetry runs in nitrogen were related to the peak heat release rates in cone calorimeter experiments (Fig. 2) and to the total amount of volatiles being formed during polypropylene degradation. The significance of single parameters determined from cone calorimeter tests such as MARHE (maximum rate of average heat emission) has been outlined.

Acknowledgements

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THERMAL DEGRADATION MECHANISMS OF NUCLEAR EPOXY COATINGS

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The thermal and radio exposure of industrial epoxy coatings, used with amine hardener, have been the subject of many researches in order to study their degradation mechanisms and to predict lifetime of coatings. However, networks can be hard to study and to characterize. In this paper we propose a simple model system to study the chemical environment of crosslinking nods found in epoxy-amine networks. It can be synthesized by mixing monoepoxy monomer and aliphatic diamine. After reaction, the system is soluble in organic solvents, which give us more access to characterization methods, as GPC, than the ones used with epoxy network.

This model system (A), described in figure 1, is based on the reaction of phenyl glycidyl ether (PGE; 150g/mol; ether group present) with aliphatic diamine hardener (dodecance diamine; 200 g/mol). After reaction of this stoichiometric ratio (R (Amine/Epoxy) = 1), (A) system is a clear solution with high viscosity. Exposed at 110°C in air until 2000 hours, (A) system is characterized using several analytical methods such as FTIR in transmission mode, Gel Permeation chromatography (GPC) and High Resolution Mass spectroscopy (HRMS).

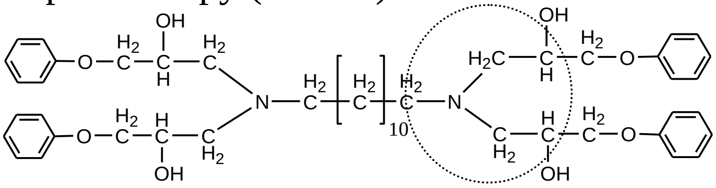

Figure 1. Chemical structure of model system (A) (800 g/mol), showing in the circle same chemical environment of crosslinking nods existing in the industrial coatings (epoxy/amine).

After performing GPC measurements, one can evaluate $[A]_R$, the concentration of (A) system Remaining (fig.2.(a) right axis), using GPC's values of refraction index. These latter are related to the concentration of correspondent product. The kinetics showed that the consumption of main product is very close to a 1st order reaction with kinetic rate of k ≈ 2.5 x10^{-3} h^{-1} at 110°C. In addition to that, GPC measurements has put in evidence the presence of lower molecular weight products formed after chain scission, caused by oxidation.

FTIR spectras, between 1800 and 1600 cm^{-1}, showed the increase of three main pics at 1660 cm^{-1}, 1705 cm^{-1} and 1735 cm^{-1}, attributed to amides and carbonyles (acids, and ketones) respectivley (1-2). Using Lambert-Beer law, one can study the increase of carbonyl concentration during aging (fig.2.(a) left axis). Combining GPC data and carbonyl formation, we can plot the chain scission number (S) ((S) = $[A]_0$ – $[A]_R$) as function as carbonyl concentration (Where $[A]_0$ is the initial concentration of (A)).

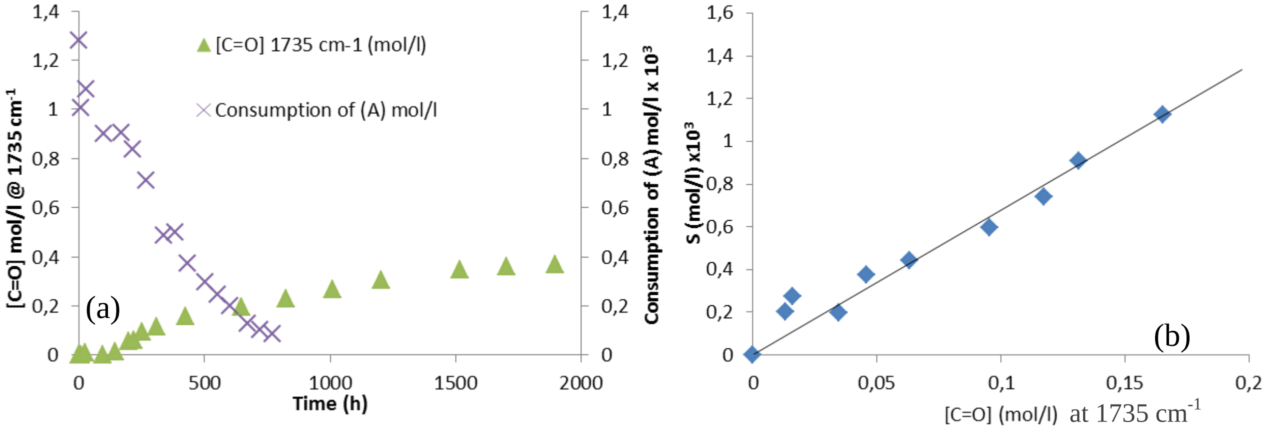

Figure 2. (a) On the left axis: Carbonyl increase during aging; on the right axis: Consumption of (A) system. (b) Chain scission number (S) as function as Carbonyl concentration at 1735 cm^{-1}.

According to these results, carbonyls are responsible of chain scission and probably resulting from α attack of methylene group adjacent to ether group. One of oxidation products have been identified as phenol obtained after β scission from secondary alcohol group in PGE part. (A) system provided better ideas about the oxidation mechanisms formed during aging in industrial epoxy coating used with amine hardener.

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LEVERAGING ISOTOPIC LABELS TO ELUCIDATE THE THERMAL-OXIDATIVE DEGRADATION MECHANISMS OF NYLON 6.6

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By leveraging isotopic labels in conjunction with cryo-GC/MS analysis, we have identified several key thermal-oxidative degradation species of nylon 6.6, including CO_2, NH_3, water, cyclopentanone, and pyridine.[1] Identification of these products (labeled and unlabeled) was pertinent in elucidating the origins and underlying degradation pathways that lead to their formation. To our knowledge, this work is the first account that quantitatively distinguishes oxygen containing degradation species originating from the polymer backbone and oxygen species coming from the ambient air during the oxidation process.[2] The methodologies employed here may be extended to other polymers and likely leveraged towards future sensor development to provide condition monitoring of aging materials.

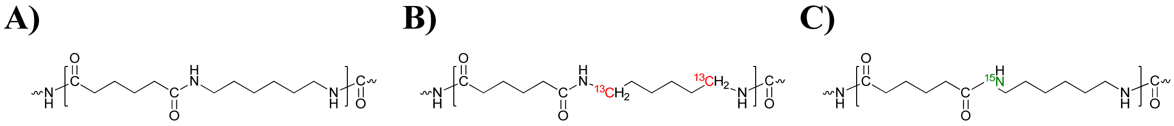

Figure 1. Schematic of Nylon 6.6 (A) unlabeled and (B) enriched with 13C or (C) 15N isotopic labels positioned in the 1,6-hexanediamine fragment employed in our aging studies.

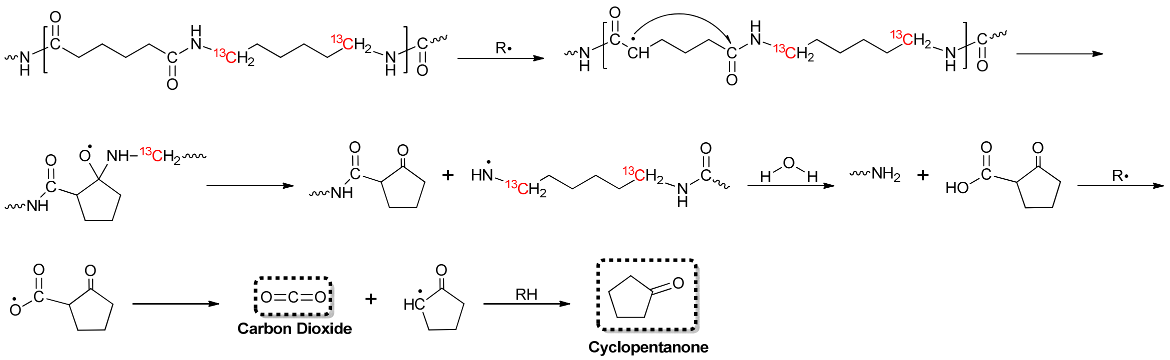

Figure 2. One possible thermal-oxidative degradation mechanism of nylon 6.6 within the nylon backbone that leads to the formation of cyclopentanone; alternatives may exist, e.g. the removal of the carboxylic group through a non-radical reaction.

Acknowledgement

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THE INFLUENCE OF PRELIMINARY PREPARATION OF RAW MATERIAL ON YIELD OF THE LARGE LABORATORY AND INDUSTRY INSTALLATIONS OF POLYOLEFIN WASTE THERMODESTRUCTION

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INTRODUCTION

After the Second World War an intensive increase in the polymer production and usable products received from them has been observed. Currently polyethylene is the most used polymer material (about 39 weight %: HDPE ~ 17 %; LDPE and LLDPE ~ 11 %), while the other polymers: PP ~ 23 %, PVC ~ 18 %, PS and PET ~ 7 %, ABS ~ 4 % and PC 2 %. Most of the products made of these polymers has a short lifetime as a useful product. It is known that the used polyolefin products have a high calorific value (about 40 MJ/kg). They can constitute perfect energy materials. It was important to find a safe way of their management with the recovery of their chemical energy. Because of a strong social opposition against the direct combustion of used polymer plastic materials, receiving a mixture of hydrocarbons as a result of polyolefins thermo-destruction seems to be reasonable, public acceptable way of their management. The obtained hydrocarbons, due to their properties, are more widely used as fuel for directly combustion in suitable burners, for generator, as a raw material for processing into gasoline or as a raw material for the preparation of paraffin.

EXPERIMENTAL

The heretofore studies conducted on the experimental line at the Department of Environment Chemistry and Technology, Institute of Chemistry, University of Silesia, and installations for polyolefins thermo-destruction working on an industrial scale indicate that the course of thermo-destruction process and its yield depends on the way of preliminary preparation of plastics for thermo-destruction process. It was decided to verify the results of research in this field conducted in the large laboratory scale in industrial installations. Wet and dry waste PE foil is used as a raw material for the large laboratory installation.

In one of the industrial installation in Poland the studies of course of the thermodestruction process of polyolefin waste were conducted with different content of damp and dirty and clean film in plastic input. For studies of the thermodestruction process in the other installation in Poland material from the same source (dirty and very moist), pre-prepared and without preparation was used.

RESULTS AND DISCUSSION

In the large laboratory installation the influence of the presence of water on the course of thermodestruction process was observed. The change of material moisture caused a slight increase in the efficiency from 78.9 % for the wet waste to 82.1 % for a dry waste and a significant decrease in the solid residue content after the thermodestruction process. Process was also much faster (by about 25 %) without the temperature jumps observed for the wet foil. Studying the thermodestruction process on four modules of the vertical installation the highest yield (73.6 %) subjecting the thermodestruction of plastic input containing the highest content of pure waste (40 %) was obtained. The lowest yield (52.8 %) was obtained for input with almost 80 % of dirty, damp waste. It was stated that the introduction of preliminary preparation of material for themodestruction process allowed to improve the efficiency from 60 % (using material without preliminary preparation) to about 85 % for pre-prepared material.

CONCLUSION

The research of polyolefins termodestruction conducted on laboratory and industrial installations show a high correlation between the quality of raw material and the course and efficiency of the thermodestruction process.

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THERMAL DECOMPOSITION OF IRRADIATED POLY (VINYL CHLORIDE)

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Introduction: Poly (vinyl chloride) is widely used in nuclear industry (plastic bags, filter…) making it one of the main constituent of nuclear waste packages. Radiolysis of PVC and its behavior in nuclear waste package has been widely studied at room temperature [1]. However, the temperature of waste materials contained in transportation packages is often higher than room temperature and can reach up to 150°C in accident conditions (i.e. in case of fire of the transportation casks). Few studies have investigated the behavior of irradiated PVC at high temperature. The objective of this study is to determine the impact of the dose on the thermal decomposition of PVC. Industrial PVC was first irradiated in air at high doses (2, 4, 6 and 10 MGy) with a γ cobalt source at room temperature. Then, TGA/MS/FTIR analysis and FTIR analysis of the PVC polymer are used to characterize the thermal degradation.

Results and discussion: In non-irradiated industrial PVC, the thermal decomposition is initiated by dehydrochlorination at 250°C [2]. In irradiated industrial PVC, from 2 MGy up to 10 MGy, the thermal degradation is accelerated and occurs at lower temperature (100°C) as shown in Figure 1a. The analysis by mass spectrometry and gas FTIR reveals the formation of water, hydrogen chloride, CO_2 and small amount of benzene (Figure 1b). Moreover, FTIR of the PVC material reveals the decomposition of oxidation products, mainly hydroperoxides. Figure 2a and 2b illustrate the evolution of bands characteristic of hydroxyl groups ($\bar{\upsilon}_{O\text{-}H}$) and of chlorine ($\bar{\upsilon}_{C\text{-}Cl}$) when PVC is heated at 120°C, after irradiation at room temperature under oxidative conditions.

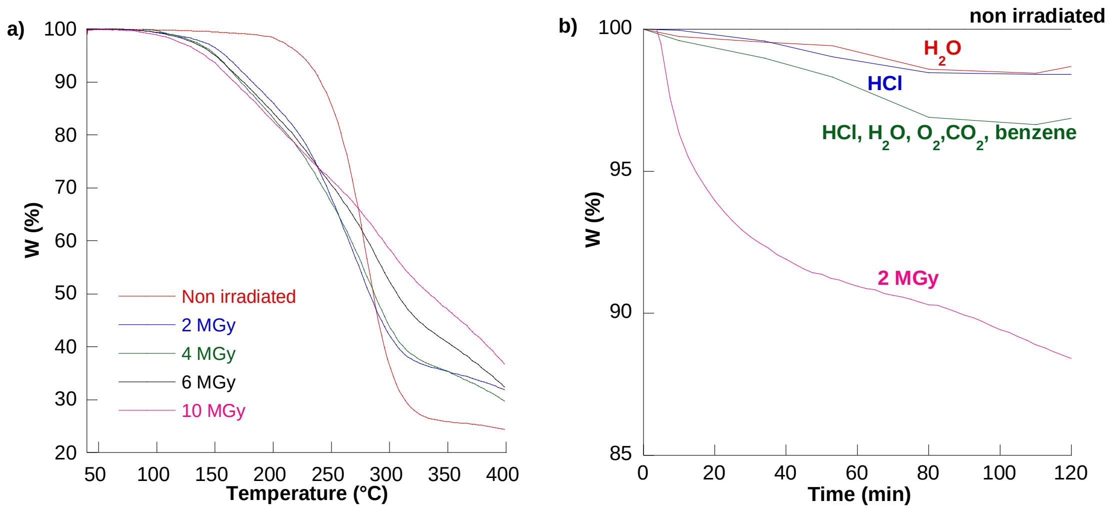

Figure 1: Thermal decomposition of PVC: a) Dose effect, b) Isothermal weight loss and HCl and water formation at 120°C.

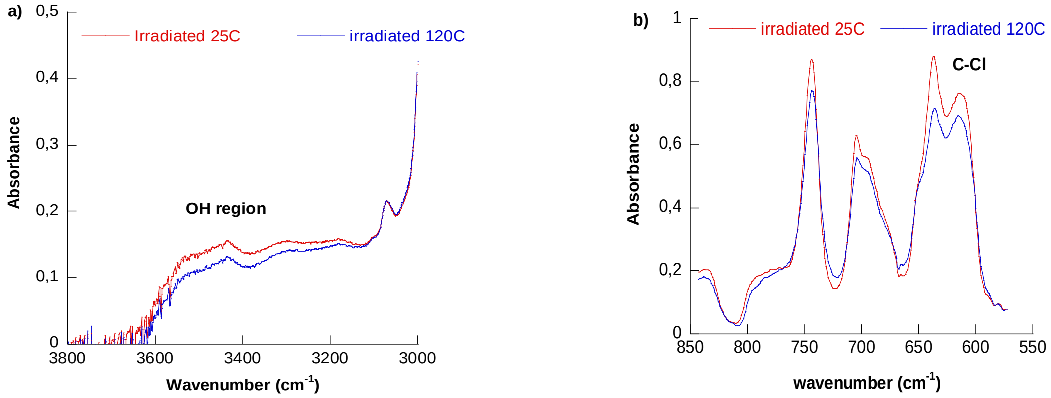

Figure 2: FTIR spectra of industrial PVC film irradiated at room temperature under air and followed at room temperature (in red) and at 120°C (in blue) under inert atmosphere: a) OH region b) C-Cl region.

Key words: PVC, radiolysis, thermolysis, thermogravimetry analysis

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PHOTOOXIDATION OF POLYMER SYSTEMS UNDER STRESS. A NEW APPARATUS.

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The photo-oxidation of polymers is usually investigated by measuring the changes of some properties (mechanical, structural, morphological) as a function of the irradiation time. Moreover, in the apparatuses for accelerated ageing the samples are stress free, so they do not give any indications about the effect of the applied stress on the photo-oxidation kinetics.

The new apparatus[1] here presented overcomes these two shortcomings, indeed, the samples are irradiated under stress and the record of a mechanical property – the creep behavior – is monitored during the irradiation. In this way the change of the property can be seen during the irradiation itself and not after the irradiation and the real behavior of the polymer during the use is investigated. Of course, the change of the creep curve must be compared with the creep curve of the non irradiated sample.

The creep curve is the deformation undergone by a polymer sample subjected to a given stress. This is an important mechanical characteristic of the polymeric materials which, as it is well known, undergo a continuous deformation with time when a stress is applied on. The measurements can be made as a function of the irradiation time, of the applied stress and of temperature and humidity.

In the following, two examples are reported concerning the effect of humidity and stress on the creep behavior during UV irradiation of a polyamide 6 sample.

In Fig.1 the creep curves of the 95°C, 15% RH samples measured in the presence or not of UV irradiation are reported.

The UV irradiation increases the creep rate and intensity. The irradiated sample presents a maximum in the creep curve, but earlier respect to the non irradiated sample. After the maximum, instead of having a plateau-like zone like in the irradiated sample, the strain increases until the end of the test. This behavior can be explained considering that UV provokes an increase of the degradation rate in the polyamide as confirmed by the intrinsic viscosity which, for this sample, is the lowest one among all the measured values. The decreasing of the molecular weight, that in the non-irradiated sample is only caused by the high temperature, in the irradiated sample is exalted by the photo-degradation. This earlier and more intense decrease of the molecular weight provokes and earlier maximum in the creep curve, but also an earlier yielding, thus explaining the increase of the creep in the last part of the test.

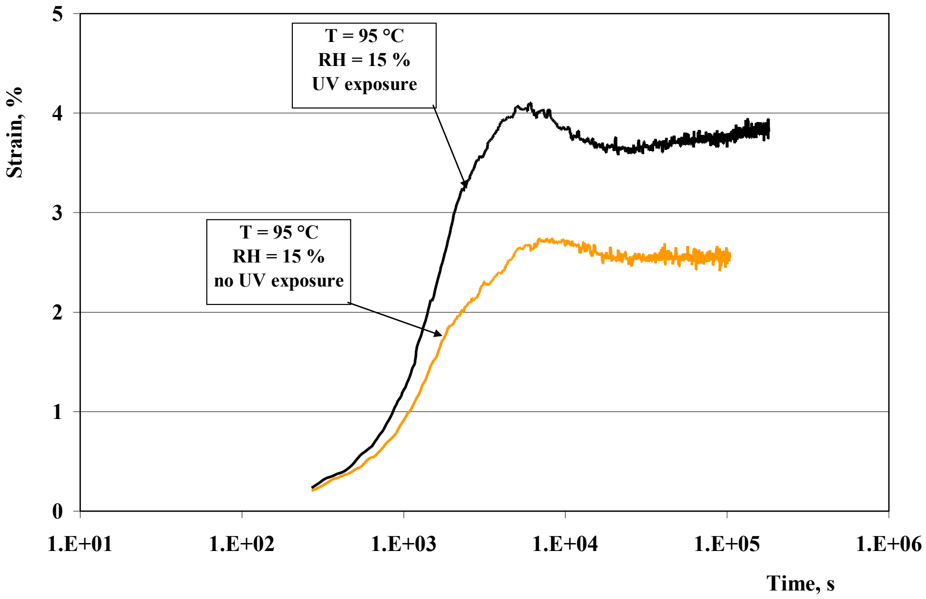

Figure 1 Creep curves of the 95°C, 15% RH samples measured in the presence or not of UV irradiation

The new apparatus allows to monitor the contemporary effects of the applied stress and of the photo-oxidation on the mechanical (viscoelastic) properties during the test itself and at the same time allows to have a sample for further characterization.

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SYSTEM FOR DETERMINISTIC ACCELERATION OF LABORATORY WEATHERING

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A realization of deterministic acceleration of laboratory weathering under controlled conditions is an essential requirement for delivering reliable and fast prediction of material durability in comparison to real use aging behavior. We present a laboratory weathering system capable of predicting the aging rate of material specimens, e.g. coatings, under interest independent on the aging mechanisms as a function of radiant exposure. The irradiance and the spectral power distribution will be extended above the normal level on earth surface while keeping all relevant temperature parameters fixed. These tests are performed in compliance with the essential international standards. As an example, we demonstrate the aging acceleration rate of different materials for the irradiance level of up to 2.5 suns (140 W/m² in the total UV range).

However, the applicability of an increased irradiance for deterministic acceleration of weathering without a specific knowledge of material properties requires that the degradation of material should be dependent on the applied radiant exposure only, irrespective of the irradiance level and resulting exposure duration used during the test. For some materials fulfilling this criterion, the acceleration of weathering has been demonstrated successfully.[1,2,3,4]

It is of essential importance to validate an appropriate test procedure under controlled conditions in laboratory with an artificial light source which can provide high irradiances above the natural level with the spectral power distribution closely mimicking the natural solar radiation. Simultaneously, the temperature of the sample specimen surface and of the ambient air must be kept constant in a wide range of irradiance level. In addition the usual wetting and rain option should be available.

The test procedure is validated with well known standard reference materials.[7,8,9]

Table 1: Summary of the test results where no water spray was applied. Exposure in accordance with ISO 4892-2[5,6] with different irradiance levels (55W/m² to 140W/m² (wavelength range 300nm-400nm)) without application of water spray cycle. SRM- standard reference material, A- axis intercept, M-slope in Δ E* /(MJ/m^2) for ORWET ORANGE and Blue Wool Type 6 (Δ b* /(MJ/m^2) for PS chip), R²-Pearson correlation coefficient.

SRM	ORWET Orange		PS Chip		Blue Wool Type6	
Zero point	included	excluded	included	excluded	included	excluded
A	0	-1.23	0	0.49	0	0.98
M	0.23	0.25	0.07	0.06	0.16	0.14
R²	0.98	0.99	0.89	0.92	0.91	0.93

In Table 2 the results of the test where no water spray was used is summarized. The effect and a correct application of the rain phase needs further careful investigation.

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OXIDATIVE DEGRADATION PRODUCTS ANALYSIS BY PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROSCOPY[*]

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Pyrolysis gas chromatography-mass spectroscopy (PGC-MS) is proved to be a powerful method to analyze the small degradation fragments and the changes in macromolecular backbone during photo-oxidative degradation of polymers. 1) Different small molecules were found for different polymers. For example, n-alkanes with carbon number from 14 to 29 were detected in aged polyethylene (PE), while no oxidative product was found (shown in Fig.1) [1]. In contrast, various oxidative products could be found in aged polypropylene (PP) [2]. 2) The effects of inorganic fillers and chemical agents can be evaluated. For example, in nano-SiO_2 and nano-$CaCO_3$ filled PP, nanoparticles were demonstrated to accelerate the chain scission of PP, with more degradation fragments such as ketones, alcohols, esters and unsaturated species formed (shown in Fig.2). However, they did not change the photo-oxidation mechanism. In addition, the surface treatment of particles can also be characterized by PGC-MS. 3) Migration of additives in polymer can be detected. For example, migration of additives such as paraffins and antioxidants in Nitrile rubber (NBR) during aging can be monitored. And the crosslinking of the backbone can also be characterized by comparing the programs before and after aging. Therefore, PGC-MS can supply abundant information of photo-oxidation products and helpful for mechanism research.

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[*] Project 21144003 supported by NSFC of China

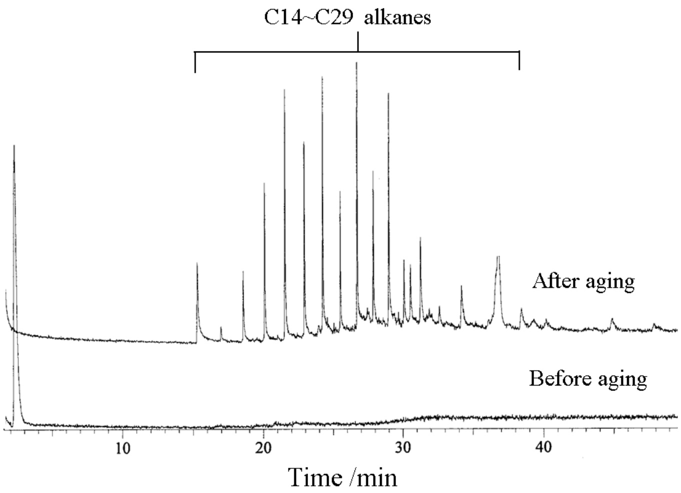

Figure 1 Volatile degradation products in polyethylene before and after aging.

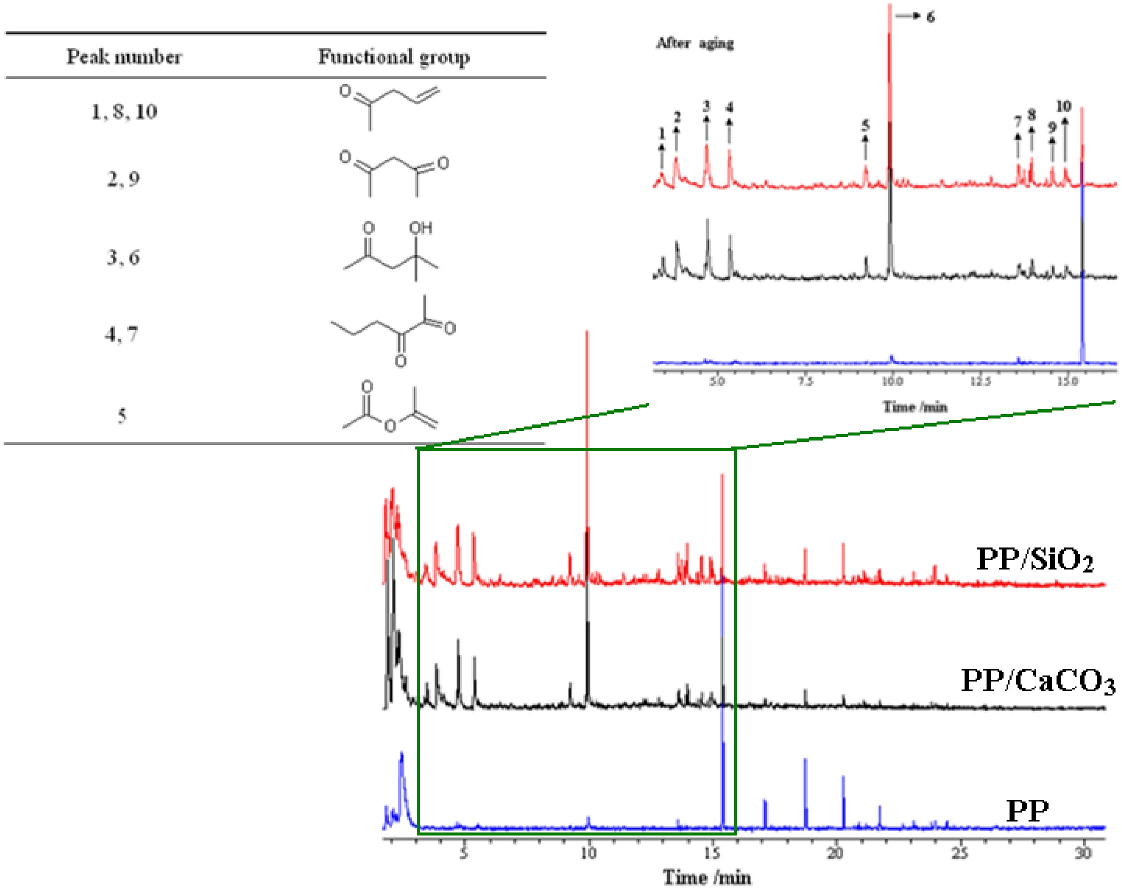

Figure 2 Oxidative degradation products in PP nanocomposites.

SEC/DAD AND ^{1}H NMR STUDY OF MOLECULAR WEIGHT AND CONFIGURATIONAL STABILITY OF HIGH-CIS POLY(PHENYLACETYLENE) AND POLY[(2,4-DIFLUOROPHENYL)ACETYLENE]

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High-cis poly[(2,4-difluorophenyl)acetylene] (PdFPhA) and poly(phenylacetylene) (PPhA) were prepared by polymerization of respective monomers with [Rh(diene)acac] catalysts and the molecular-weight (MW) and configurational stability of these polymers were studied by SEC/DAD and ^{1}H NMR techniques. Polymers dissolved in THF-d_8 and exposed to the atmosphere and daylight at room temperature were found to undergo simultaneously proceeding cis-to-trans isomerization and oxidative degradation. The rate of these procesess was considerably lower for PdFPhA compared to PPhA. Partly aged PPhA and PdFPhA were revealed to contain two microstructurally differing fractions: deeply isomerized macromolecules (lower-MW fraction) and microstructurally unperturbed high-cis macromolecules (higher-MW fraction). The SEC/DAD technique provided a high chromatographic separation and spectral distinction of these fractions in the case of partly aged PdFPhA and SEC/DAD was demonstrated as a very powerfull tool for the characterization of polydisperse conjugated polymers. The hypothesis was postulated explaining the non-uniform distribution of high-cis and isomerized trans-rich macromolecules along the MW distribution of partly aged PPhA and PdFPhA. The hypothesis particularly assumed the acceleration of degradation of polymer chains by simultaneously proceeding cis-to-trans isomerization due to which the unpaired electron content was enhanced on the isomerized chains.

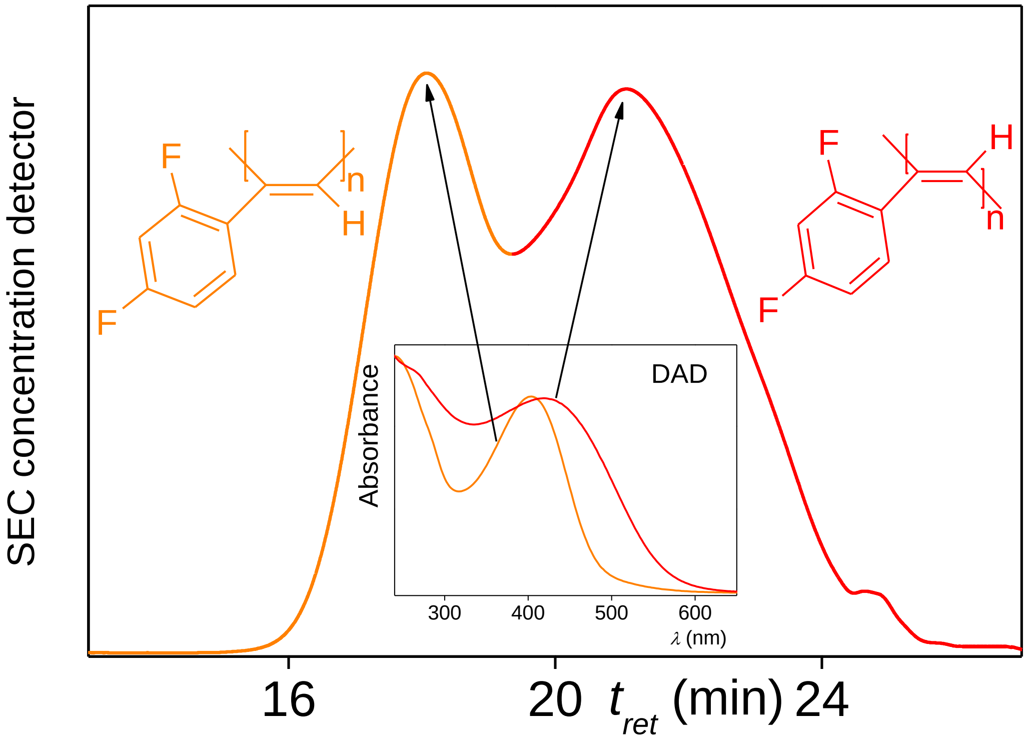

Figure: SEC/DAD chromatogram of PdFPhA aged in THF-d_8 for 337 hours. The solution was kept in contact with the atmosphere and diffuse daylight at room temperature. Corresponding UV vis spectrum is shown for each maximum of SEC/DAD chromatogram.

NOVEL ORGANIC SOLVENT-FREE PURIFICATION OF POLY (PROPYLENE CARBONATE): TAILORING THE COMPOSITION AND THERMAL PROPERTIES

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The report is based on our recent work[1] and departs from the societal aspect of utilization of carbon dioxide as environmentally-benign feedstock to synthesize polymers. Herein, the main focus is on the study of the purification and stabilization of poly (propylene carbonate) synthesized from the reaction of carbon dioxide and propylene oxide using a zinc glutarate catalyst. The raw polymer comprises primarily, in addition to the polyalkylene carbonate, cyclic propylene carbonate (CPC) which acts as plasticizer and catalyst residues which are detrimental for the thermal stability. Inherently PPC has a low decomposition temperature which is a limitation for its processing and application. It is therefore necessary, as a post reactor step, to tailor the amounts of CPC, catalyst residues and improve the thermal stability, all of this in order to facilitate its processing and achieve a suitable mechanical performance from the material.

The effect on the thermal stability and mechanical performance of an aqueous solid-liquid treatment, free of organic solvents, and in the presence of maleic acid is studied on raw PPC using FTIR, ^{1}H-NMR, AAS, DMTA and TGA characterizations. From FTIR it is found that the content of CPC decreases. This is reflected in the increase of T_g and of stiffness as

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[1] Carlos Barreto, Eddy Hansen, Siw Fredriksen, Novel solventless purification of poly (propylene carbonate): Tailoring the composition and thermal properties of PPC, Polymer Degradation and Stability, Volume 97, Issue 6, June 2012, Pages 893-90410.1016/j.polymdegradstab.2012.03.033.

measured from the DMTA. A significant amount of zinc residues is found after the treatment and quantified using AAS and an outstanding improvement in the thermal stability is found in the TGA characterizations (Fig. 1).

The unexpectedly high increase in the thermal stability of the PPC materials after the treatment may be explained by considering the effects of residues of zinc and maleate species on the PPC material. Based on ^{1}H-NMR and AAS investigations, it is hypothesized that the resulting zinc species and the carbonyl groups in the polymer enable metal-ion coordination and, consequently, a stabilization that explains the unexpectedly high thermal stability of the PPC material.

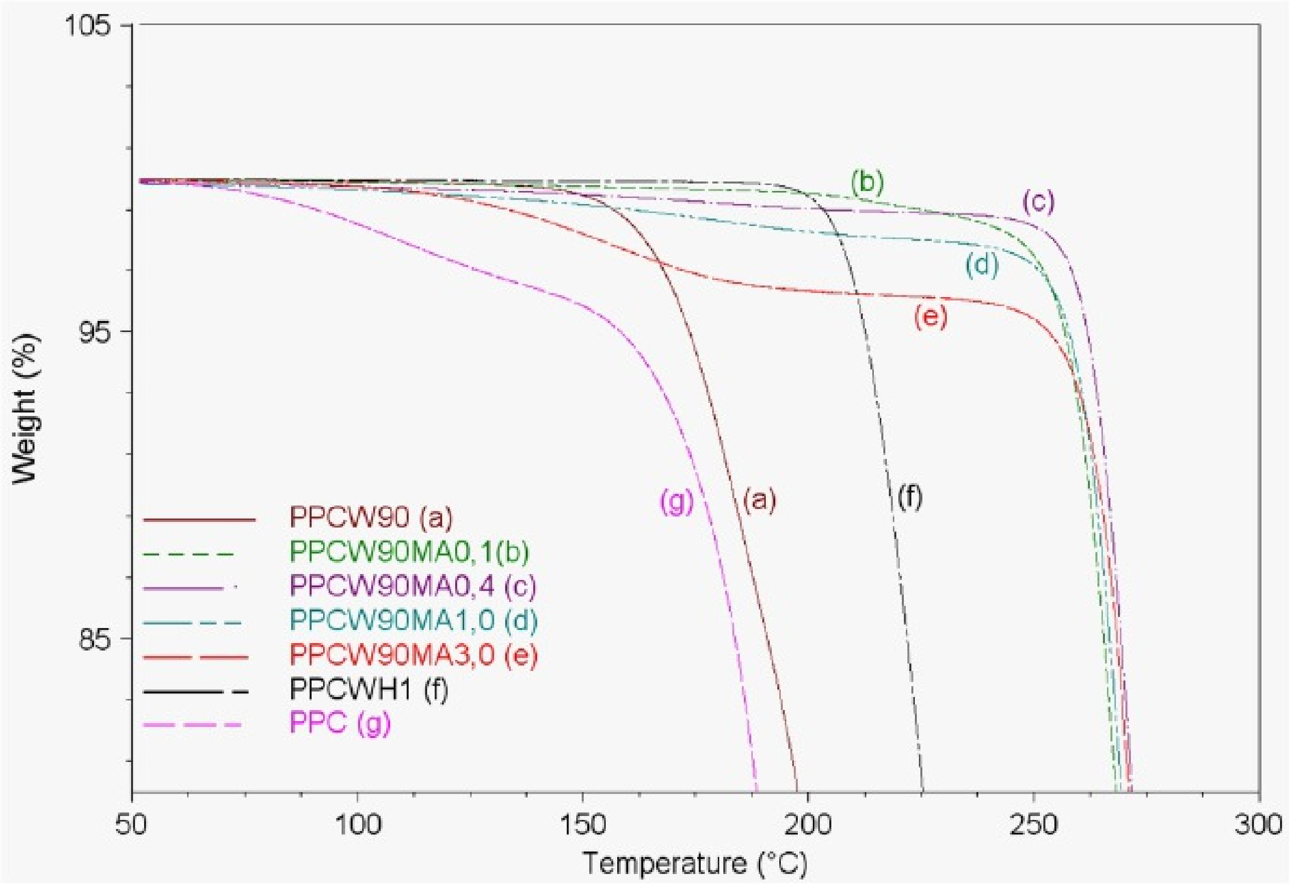

Fig. 1 TGA characterizations (N_2-5°C/min) of raw PPC (g), PPC "free" of metal residues (f) purified using a regular solvent / $HCl_{(aq)}$ based purification, PPC samples purified using the treatment in aqueous maleic acid (MA) treatment at various MA concentrations (a-e)

EFFECT OF EXTERNAL MECHANICAL STRESSES ON THE HYGROTHERMAL AGEING OF DGEBA/TETA EPOXY RESIN

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Organic coatings have been abundantly used to prevent metals from corrosion. Among them, epoxy-based paints are often industrially chosen, due to their low cost and their efficiency in corrosive medium like seawater. The degradation of these coatings is usually due to the action of environmental factors such as water, UV, temperature and external mechanical stress. The objective of this study is to highlight synergies existing between different ageing factors (temperature, mechanical stress, water) for polymer coating degradation. In order to avoid the influence of pigments, adjuvants and other fillers, a model epoxy system DGEBA/TETA was chosen to obtain the response of the sole polymer.

Firstly, dry DGEBA/TETA free films were mechanically studied using Dynamic Mechanical Thermal Analyzer. Visco-elasto plastic behavior of the DGEBA/TETA networks was characterized using a loading–unloading recovery test [1-2]. By varying the stress – strain state in these loading–unloading recovery tests, the limits between the mechanical domains (EL/VE and VE/VP) can be estimated as $\sigma_{EL/VE}$ = 6 MPa and $\sigma_{VE/VP}$ = 12 MPa.

Secondly, the water absorption of free films was studied. The totally cured DGEBA/TETA specimens were immersed in a NaCl 3wt% aqueous solution at 30, 40, 50 and 60°C, respectively. The water uptake and diffusion coefficients were determined by gravimetry for non-bent free films. It was found that the water uptake and the diffusion coefficient are thermally dependent.

Finally, in order to study the effect of an external visco-elastic stress onto the water absorption process, the DGEBA/TETA system was applied onto plane steel sheets. These coated panels were bent so as to maintain the coatings under a visco-elastic strain between 6 and 12 MPa. Stressed coated panels (compressed and stretched sides) have been immersed in NaCl 3wt% solution at different temperatures and followed Electrochemical Impedance Spectroscopy (EIS) to determine the volumic water content and the diffusion coefficients under different stress and temperature values.

Gravimetric and electrochemical results were compared in order to identify synergies between the different ageing factors and the following points have been observed:

- the diffusion coefficients of water determined by gravimetry (free films) and by EIS (non-bent coatings) are similar;
- for all kinds of DGEBA/TETA films (free or deposed onto steel panel) and regardless the studied methods (gravimetry or EIS), the diffusion coefficients increase with the increase of temperature.
- the visco-elastic stresses applied on the coated panels (both compressed and stretched sides) lead to the decrease of diffusion coefficients in comparison with the non-bent systems.

A thermodynamic approach [3] was used to propose the explanations of these results.

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NATURAL ANTIOXIDANTS – STUDY OF THE PROCESSING STABILIZING EFFICIENCY AND MECHANISM OF CURCUMIN IN POLYETHYLENE

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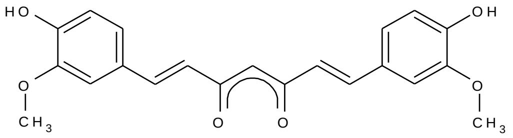
Lately our interest turned towards natural antioxidants because of some health issues related to the reaction products of commercial phenolic stabilisers used in polyolefins. Curcumin is obtained from curcuma longa rhizomes. The powdered root is used as a spice, food colorant, and food perservative[1]. The medical activity of curcumin has been known since ancient times. It is an efficient free radical scavenger and inhibits lipid peroxidation[2]. The question is how it behaves under the conditions of polyethylene processing and whether it can protect the polymer from degradation.



Stabilization experiments were run with the Phillips type ethylene-1-hexene copolymer, Tipelin FS 471 (*TVK*). The polymer was stabilized with curcumin (*Sigma-Aldrich*) in concentrations changing between 0 and 1000 ppm. Stabilization efficiency was determined with and without Sandostab PEPQ phosphonite secondary antioxidant (PEPQ, 1000 and 2000 ppm; *Clariant*). Irganox 1010 (I1010; *BASF Switzerland*) was used as a reference phenolic antioxidant. The polymer was homogenized with the additives then extruded six times consecutively at 260 °C. FT-IR spectroscopy, optical microscopy rheology (MFI), residual thermo-oxidative stability (OIT), and color were used for the characterization of the samples after each extrusion step.

The results reveal that curcumin protects polyethylene from thermal- and thermo-oxidative degradation during processing more efficiently than the same amount of I1010. Its efficiency is increased by the addition of the phosphonite secondary antioxidant. Although the processing stability of PE is controlled by the phosphorous compound[3], curcumin enhances its efficiency already in a very small concentration, at 5 ppm. The decrease in MFI and the consumption of the phosphorous stabilizer are reduced in the multiple extrusion process compared to the effect of the phosphonite alone. Contrary to the behaviour of polyethylene processed with I1010 or its combination with PEPQ, melt flow index increases and yellowness index decreases with increasing number of extrusions when 1000 ppm curcumin or its mixture with PEPQ are used for stabilization. It is remarkable that the decrease in the concentration of vinyl groups with increasing number of extrusions is influenced more by the amount of the phosphonite than by the type of the phenolic antioxidant.

The analysis of polymer characteristics supported by model reactions of curcumin indicate that the stabilizing efficiency of this natural antioxidant is influenced by several factors at high temperatures, by its reactions with hydroperoxides, alkyl, hydroperoxy and oxy radicals, as well as by its self association and specific interaction with the phosphonite secondary stabilizer. The reaction mechanism is controlled by the ability of the phenolic group to donate hydrogen, but the heptadienone linkage between the two methoxyphenol rings also participates in the stabilization of PE.

Although curcumin discolours the polymer, its medical activity and food preservative properties can be especially advantageous in food packaging films and bottles.

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Acknowledgement: The National Research Fund of Hungary (OTKA K 77860 and K 101124) is greatly acknowledged for the financial support of the research.

IDENTIFICATION OF LOW-MOLECULAR WEIGHT VOLATIVE THERMAL-OXIDATIVE NYLON 6.6 DEGRADATION PRODUCTS USING SELECTIVE ISOTOPIC LABELING AND CRYO-GC/MS

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INTRODUCTION Polyamides, in particular nylons, are commercially and widely used in automotive parts, carpets, ropes, food packaging, barrier materials, and clothing. Certain high-reliability applications require that nylon fibers are either stored or used for times up to several decades. It is therefore critical to enhance the current knowledgebase of nylon aging, in particular nylon aged under thermal-oxidative conditions as a means to correlate degradation product formation to physical properties. Identification and characterization of degradation species that outgas during nylon aging at specific times can be used as a foundation to create detailed decomposition mechanisms and to develop chemical sensors tailored to monitor specific volatile compounds that can provide early warning of potential changes in the mechanical properties of materials.

METHODS Nylon 6.6 monomers and polymers used in these experiments were: unlabeled adipic acid and 1,6-hexandiamine; C-13 adipic acid; unlabeled nylon; and C-13 and N-15 nylon. Duplicates of all samples were placed in sealed SS vessels (5 cc) and placed within a circulating oven for up to 243 days at 138 ºC. Compounds were aged under either ambient conditions or an enriched oxygenated environment (O-18, 99%). Headspace gas was preconcentrated, separated, and detected using cryofocusing gas chromatography mass spectrometry (cryo-GC/MS; Jeol GCMateII). GC chromatograms and mass spectra for all volatile degradation species were compared and used to determine the exact location for isotopically labeled atoms, where applicable.

RESULTS Selective isotopic labeling of monomers, polymers, and aging environments combined with cryo-GC/MS enabled the identification of eighteen volatile low-molecular weight thermal oxidative degradation products of nylon 6.6: butene, butane, carbon dioxide, ammonia, 1-pentene, acetone, methyl acetate, cyclopentene, 2-butanone, tetrahydrofuran, benzene, 2-pentanone, tetrahydropyran, pyridine, toluene, 2-hexanone, cyclopentanone, and water. Highly reproducible gas chromatograms and mass spectra were produced for all unlabeled and isotopically labeled samples. Unlabeled and isotopically labeled (C-13 and N-15) nylon 6.6 monomers and polymer were used to verify the identity of and aid in the understanding of the origin of each degradation product. Nylon 6.6 was also aged under an O-18 enriched environment to better understand the origin of oxygen in degradation products containing one or two oxygen atoms (i.e., an intermolecular oxygen source, an intramolecular oxygen source, or both). The presence of isotopically labeled oxygen atoms was also used to verify the applicable compounds formed *via* thermal-oxidation of nylon 6.6. Relative ratios for unlabeled to isotopically labeled degradation products were used to make general observations regarding compound formation. The exact location of the isotopically labeled ion was determined with absolute certainty for all but three compounds by comparing the mass spectra for the NIST library match, unlabeled nylon, and isotopically labeled species. Knowing the location for isotopically labeled atoms in nylon 6.6 thermal-oxidative degradation products will enable us to map individual compounds onto the nylon 6.6 structure and determine the mechanisms used to form each specific compound. An understanding of the complex degradation mechanisms of nylon 6.6 can be used to develop chemical sensors that detect and monitor for specific molecules that outgas as the polymer ages and thus serve as an indicator for changes in physical properties (ex., a loss in tensile strength or material integrity).

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PHOSPHITES IN PROCESS STABILIZATION OF PVC AND POLYOLEFINS

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Phosphites are used in processing PVC and Polyolefins to give good initial colour. The mechanism of phosphite process stabilization of polymers is discussed and the effects of ligands are discussed. The choice of phosphites in PVC and Polyolefins are discussed.

POLYMER DEGRADATION AND STABILIZATION

Full Abstracts of Poster Presentations

MECHANISM OF SURFACE DISCOLORATION OF POLYMER IN CONTACT WITH WATER

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Introduction. White-colored inner surface of a polymer material in contact with water discolored and turned yellow selectively at the air-polymer-water interface. The purpose of this study is to conduct an in-depth analysis of the discoloration mechanism of the polymer surface. .

Methods. A variety of technical approaches, including microscopic analysis (using a scanning electron microscope (SEM)), spectroscopic analysis (using attenuated total reflection Fourier transform (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS)), and chromatographic analysis (using gas chromatography-mass spectrometry (GC-MS)) techniques, were employed to investigate the nature of discoloration and the root cause.

Results and Discussion. The discoloration occurred selectively on the surface where the contact line with water formed. No sign of deterioration or degradation of the polymer at the discolored surface was not confirmed. From the observations and experimental results, the discoloration was ascribed principally to a phenol transformation compound having the structure of a quinone methide as shown in Figure 1.[1-2] It is expected that one of the additives, a primary antioxidant, was released into water and hydrolyzed into the phenol transformation compound.[3] As the additive leaches into the water, the degradation compound constantly would continuously was formed and accumulated on the polymer surface where the contact line with water formed as shown in Figure 2.

Conclusions. Based on the observations and experimental results, a plausible discoloration mechanism was proposed. Based on the observations and experimental results, a plausible discoloration mechanism was proposed.

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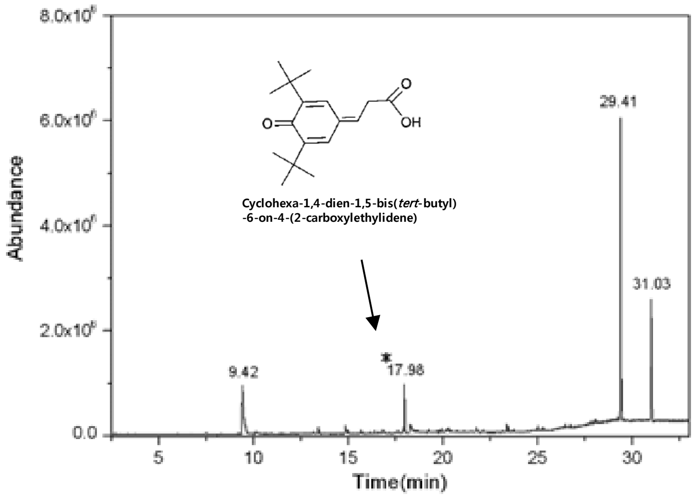

Figure 1. GC Chromatogram of discolored polymer samples.

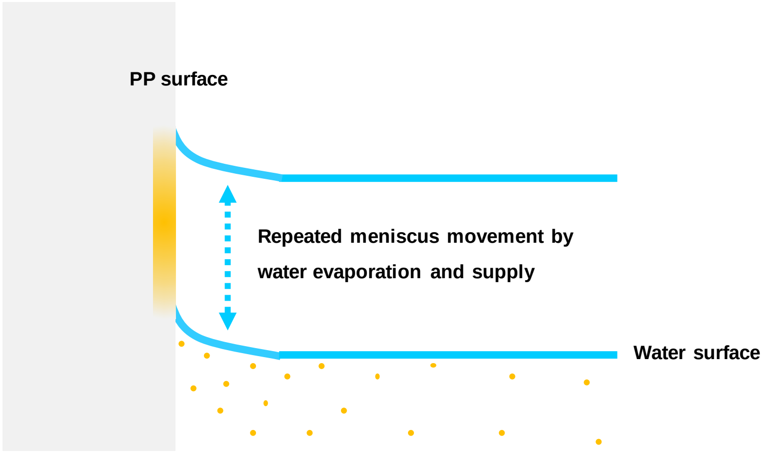

Figure 2. A schematic illustration of compound accumulation on the polymer surface where the contact line with water forms.

COMPOSITIONAL AND FAILURE ANALYSIS OF DISCOLORED UV-CURABLE POLYMER/METAL HYBRID COATING

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Inctoduction. Discoloration of white or light-colored polymer materials has long been a serious commercial problem affecting commercial polymers in the polyolefin industry.[1] Herein, an in-depth analysis on discoloration mechanism of UV-curable polymer/metal hybrid coating was conducted.

Methods. FT-IR analytical characterization was performed for polymer identification. The surface compositions of the hybird coating were investigated using a SEM/EDS and XPS. Thickness and crystalline state of metal layer in the hybrid coating was observed using TEM. An Agilent GC-MS system was used to separate and obtain the mass spectra of the additives of the UV-curable polymer film sample.

Results and Discussion. The hybrid coating has a multilayered structure consisting of base coat, vacuum deposited metal layer, and top coat. The base and top coats were same material based on UV-curable acrylic polymer and the main component of metal layer was tin. The results obtained by microscopic and spectroscopic analysis demonstrated that the discoloration of hybrid coating stemmed from yellowing of the top coat as shown in Figure 1. The deterioration or degradation of metal component in the vacuum deposited metal layer was not confirmed. Analysis of additives of the discolored top coat showed that there is a small quantity of unreacted photoinitiators left in the UV-cured coat. From the results of solvent extraction (Figure 2) and gel content measurement, it is expected that an excessive amount of photoinitiators was used in the resin of top coat and one of residual unreacted photoinitiators caused the yellowing of the top coat.[2]

Conclusion. Based on the experimental results, a plausible discoloration mechanism was proposed. We believe that the analysis methods and results can find important technological applications ranging from industrial trouble shooting to product design specification.

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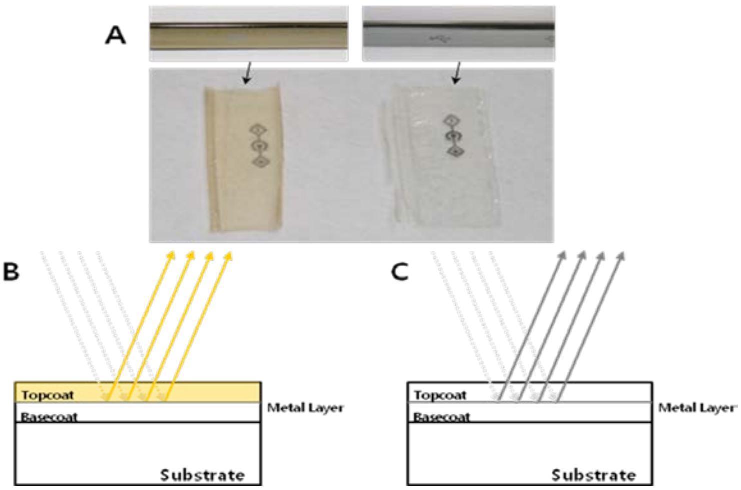

Figure 1. (A). Images of UV-curable top coat film taken from discolored and normal samples, and schematic illustration of light rays propagating through the hybrid coating. (B) Normal sample and (C) discolored sample.

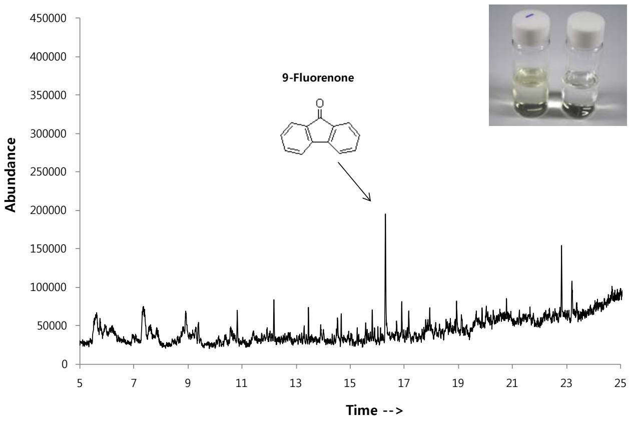

Figure 2. Chromatogram of the ethanol extract of the discolored UV-curable top coat film.

NOVEL FLAME RETARDED BIO-BASED POLYURETHANE FOAMS

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Introduction Novel polyurethane foams have been obtained with a complete substitution of the polyol components with renewable polyols. Beside well known soy-based polyols[1], new polyols have been used[2]. Such polyols have been obtained by modification of cardanol, a renewable resource and a waste of the cashew industry. The physical-mechanical properties as well as the thermal stability of such foams have been fully characterized. To improve fire behavior, also several bio-based polyurethane foams filled with environmental friendly flame retardants have been studied.

Methods Polyurethane foams were prepared by hand mixing technique, that is the isocyanate was added to the formulated polyol (i.e. the mixture of polyols, catalysts, surfactant, filler, blowing agent); then the mixture mixed for 15 seconds and poured into an open mould for free rise polymerization. During the expansion several kinetic parameters (cream time, gel time and tack free time) were recorded.

Characterization The physical and mechanical properties were measured using standard test methods. In particular, the apparent density was measured according to ASTM D1622-08, the compression strength according to ASTM D1621-10 and the thermal conductivity according to ASTM C518-10. The thermal stability was studied by thermogravimetric analyzer in inert (nitrogen) and oxidizing (air) atmosphere. The fire behaviour has been investigated by means of oxygen index (LOI) tests, according to ISO 4589.

Conclusions It is observed that the halogen-free retardants provide similar performance as the corresponding chlorine-based products: therefore, in order to develop a product more sustainable, as well as for the toxicity of the gases released by the halogenated compounds, further studies on retardants containing chlorine have not been conducted. The optimization has been carried out on phosphorus-based and inorganic magnesium and aluminum oxides retardants. Inorganic phosphinate (IPA) showed good performance of thermal stability and fire behavior without compromising the mechanical properties and thermal insulation capability. TGA curves, studied by thermogravimetric analyzer with heating rate of 20°C min-1 from 25 to 800°C, indicate the increase of the thermal stability in samples containing IPA.

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Table 1 LOI and physical-mechanical properties for unfilled (REF) and filled PU foams.

	REF	IPA	TEP	DMPP	IPA+TEP	IPA+DMPP
LOI (%)	20.5	23.7	24.5	25	24.8	24.9
Thermal conductivity (mW/mK)	24.3	23.7	25.6	24.8	23.4	23.6
Parallel comp. strength (kPa)	264	191	164	181	227	205
Perpend. comp. strength (kPa)	104	48	39	46	73	80

EFFECTS OF BLENDING POLYAMIDE, POLYPROPYLENE OR POLYOLEFIN PLASTOMER WITH POLYOXYMETHYLENE HOMOPOLYMER ON THERMAL DEGRADATION PROPERTIES

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The reason for blending different polymers e.g. by melt mixing via an extruder is primarily to obtain a blend that shows enhanced properties like increased strength or toughness, or decreased moisture sensitivity or shrinkage and warpage, etc. Polyoxymethylene (POM) is an engineering thermoplastic derived from formaldehyde and known for its good mechanical properties and dimensional stability. However, the drawback with POM homopolymer is the poor thermal stability. To date there are several possibilities to increase the thermal stability e.g. by acetylation of the thermal instable –OH endgroups or by copolymerisation with low amounts of a cyclic ether[1]. Further, all commercial products contain thermal and oxidative stabilisers. These stabilisers cover antioxidants and compounds being able to inhibit degradation by secondary thermo-oxidation products like urea and polyamide[1,2]. The aim of this study was to determine the effects of adding semi-crystalline polymers with a melting temperature in the range or lower than that of POM (table 1) on the thermal degradation behaviour of the blends. A melting temperature close to that of POM (or lower) means that the typical processing temperature range has not to be extended to higher temperatures as this may negatively affect the degradation resistance of POM on the long run.

POM Homopolymer (Delrin® 1700 P, DuPont) was blended with 10 m.-% of PA 12 (Rilsan® AESN O 14 TL, Arkema), PP (HD 120MO, Borealis) and polyolefin plastomer (POP) (Affinity® PL 1881 G, Dow) respectively. For that purpose the pellets were melt mixed in a twin-screw extruder (MiniLab2, Haake) at 30 min^{-1} for 5 min. The mixing temperature was 200 °C and 220 °C. All samples including the neat polymers were extruded once. The thermal stability was determined by thermogravimetric analysis (TG). The TG was performed in air (purge gas flow 100 ml/min) by means of a TGA 2050 (TA Instruments) using a sample mass of 20 mg in an alumina pan and a heating rate of 10 K.min^{-1}. The onset temperature was defined as the temperature at which a mass loss of 3 % of the initial sample mass was reached (doted line in figure 1).

Table 1 Melting temperature peak in °C determined by DSC at 10 K.min^{-1} (2nd run).

POM	*PA 12*	*PP*	*POP*
176	178	158	97

The TG results showed that blends processed at higher temperature had a reduced thermo-oxidative stability in comparison to those prepared at lower temperature. Further, the onset temperature of the blends was not improved with respect to unmodified and unprocessed POM pellets (figure 1). However, the rate of the decomposition reaction was clearly slowed down. Regrettably, the initial expectation to increase the thermal stability of POM by the blending procedure was not met by any of the added semi-crystalline polymers.

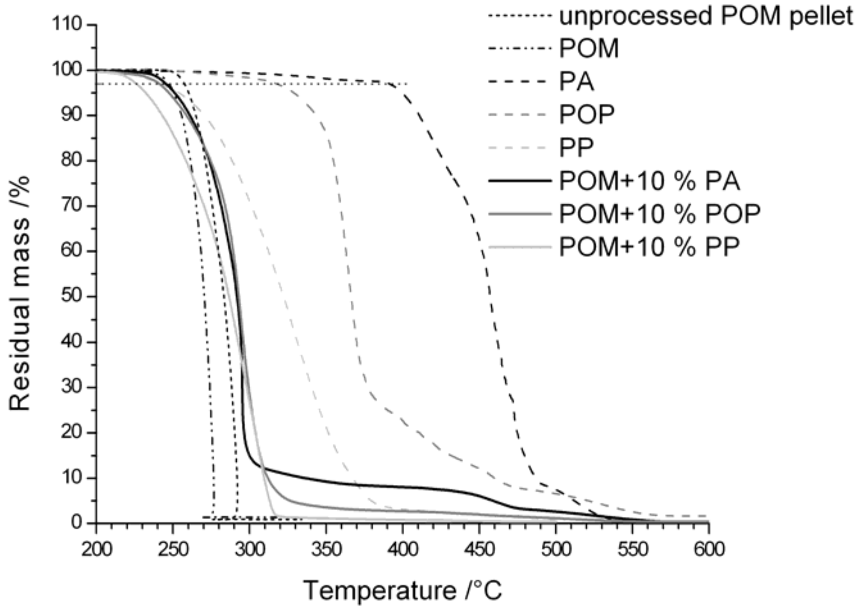

Figure 1 TG in air of the different samples mixed during 5 min at 220 °C in the extruder.

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HOW THE POSS MOLECULES IMPROVE THE UV STABILITY OF POLYSTYRENE BASED NANOCOMPOSITES?

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The preparation of polyolefin-based nanocomposites has attracted in recent years the interest of both academia and industry but the expectations of a successful improvement of the physical and mechanical performance of the polymer at very low nanofiller contents have not fully materialised. From an applicative point of view, especially for some outdoor applications, the photo-stability of polyolefin-based nanocomposites is a very important asset.

Incorporation of Polyhedral oligomeric silsesquioxanes (POSS) into organic polymers results into a better thermo-resistance of the polymers, reduction of the flammability of the polyolefin matrices and an increase of the temperature at which starts, and this makes these molecules excellent candidates as flammability and thermo-oxidative retardants[1].

Howewer, it has been reported in the recent literature that, by using POSS in polymer-based nanocomposites, it is possible to design high-performance materials finding several interesting applications, while photo-oxidation behaviour of POSS filled nanocomposites was poorly investigated[2].

POSS having different inorganic framework and pendent organic groups have been used in PS based nanocomposite preparation and the formulated films were subjected to accelerated weathering. The photo-ageing behavior was monitored by FT-IR spectroscopy[3]. The results show that, compared to pristine PS, the POSS-containing PS developed a lower level of carbonyl and hydroxyl groups as a function of the exposure time (Fig.1), indicating improved resistance of the nanocomposites to photo-degradation.

POSS molecules play a protective role acting, most likely, as UV filters and may extend the in-use lifetime of the polymeric matrix. The protection efficiency depends on the type of the inorganic framework and the pendent organic groups. In particular, the protection efficacy against photo-oxidation, i.e. the ability on energy dissipation is correlated with the mobility of the vertex groups.

All open-cage POSS systems exert a more pronounced protective role then the close-cage POSS systems against photo-oxidation. The enhanced PS stability due to the open-cage POSS loadings could be attributed to one or more of the following mechanisms:

- non-radical heterolytic decomposition of PS hydropeoxides, promoted by the acid OH groups of POSS-triol
- H-atom donation by POSS-triol to the PS chain-propating peroxy radical
- distancing the macromolecules, according POSS plasticizing action, and so slowing down the peroxide polystyrene radicals propagation.
- co-ordination and sequestering deleterious metal ions by POSS-triols.

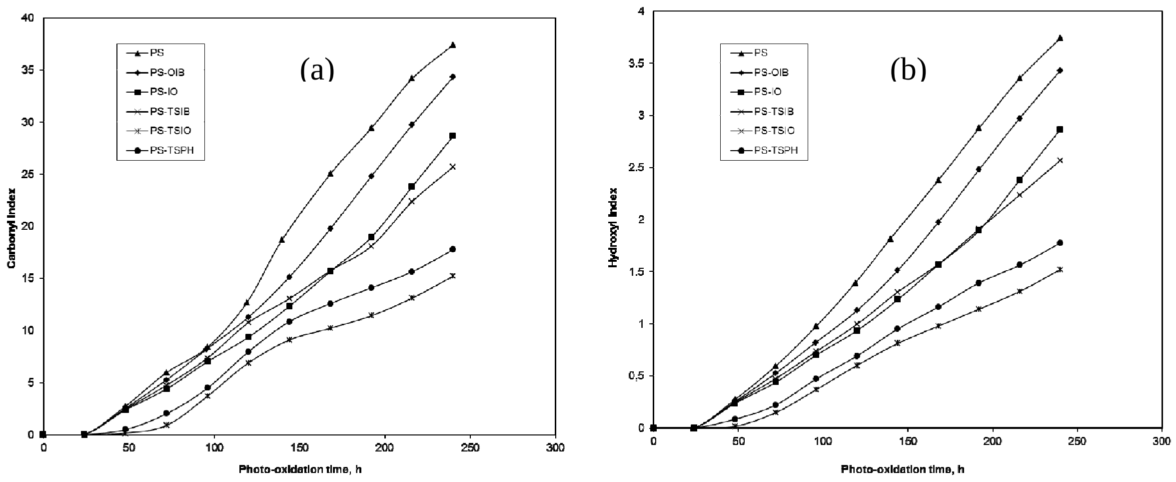

Figure 1: Variation of carbonyl (a) and hydroxyl (b) band area of PS and POSS-PS samples as a function of the exposure time.

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ASSESSMENT OF OXIDATION PROCESSES IN PARCHMENT USING CHEMILUMINOMETRY

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Introduction

Degradation of parchment, a natural collagen-based material, is of high importance to heritage institutions, yet it is still poorly understood. Chemiluminometry seems to be an appropriate method for the study of parchment degradation[1,2], however, it has not yet been used to its full potential.

A systematic study has been performed to investigate chemiluminescence (CL) phenomena, related not only to oxidation processes, but also to degradation in an inert atmosphere.

Results

A number of different types of experimental approaches have been used: static, dynamic and perturbation experiments. The one in Figure 1 presents CL intensity during a perturbation experiment, where the atmosphere is rapidly and cyclically changed from oxidative to inert to explore CL as a consequence of the presence or absence of oxygen. A new goat parchment sample from 2005 (Talas, New York) was used.

The intensity of the CL signal is higher in oxygen atmosphere due to decomposition of oxidation products, e.g. peroxides[1]. The rapid increase of the CL signal (Figure 1) each time nitrogen is replaced with oxygen ($N_2 \rightarrow O_2$) indicates that during degradation in an inert atmosphere (thermolysis), radicals are formed that are long-lived enough to react rapidly once oxygen is reintroduced. This probably leads to the formation of peroxides, increasing the CL intensity, which was confirmed by an additional experiment, where the sample was exposed to nitrogen atmosphere (3 L h^{-1}) at 180 °C for different periods of time (1, 3, 5, or 7 h).

After the atmosphere was changed to oxygen (still at 180 °C), the peak area was shown to corresponds with the duration of heating in the inert atmosphere.

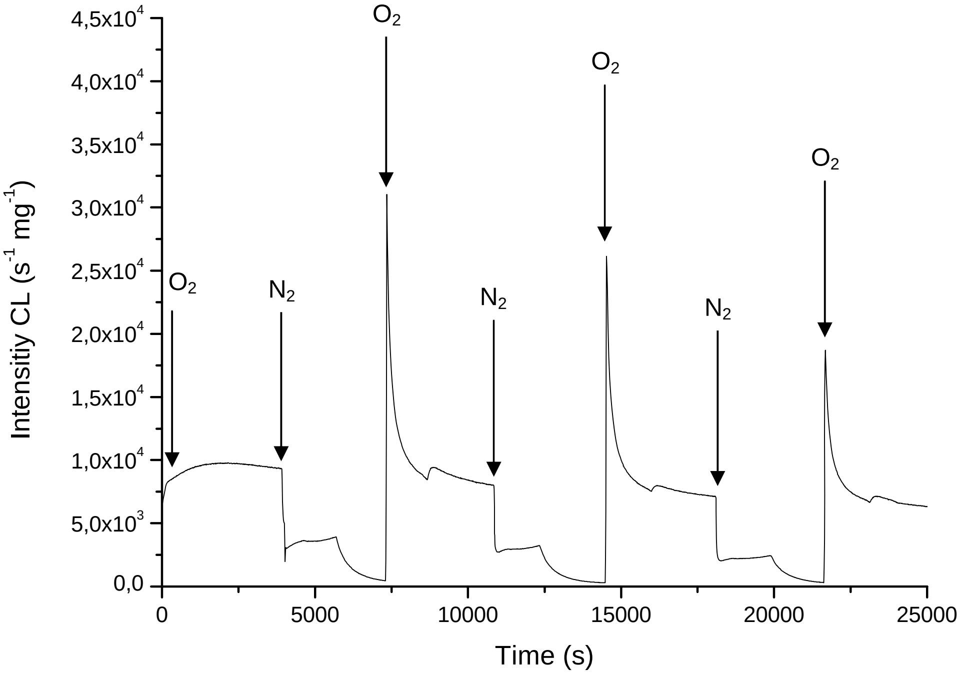

Figure 1: Intensity of chemiluminescence for a new goat parchment.

Other experiments have been performed to explore the dynamics of the processes in both inert and oxidative atmospheres, using a larger set of well-defined materials.

Conclusion

The research demonstrates the potential of chemiluminometry to increase our understanding of thermolysis and thermooxidative degradation of parchment.

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SOLID STATE POLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE): THE PROCESS EFFECT ON POLYMER CRYSTAL MORPHOLOGY

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INTRODUCTION

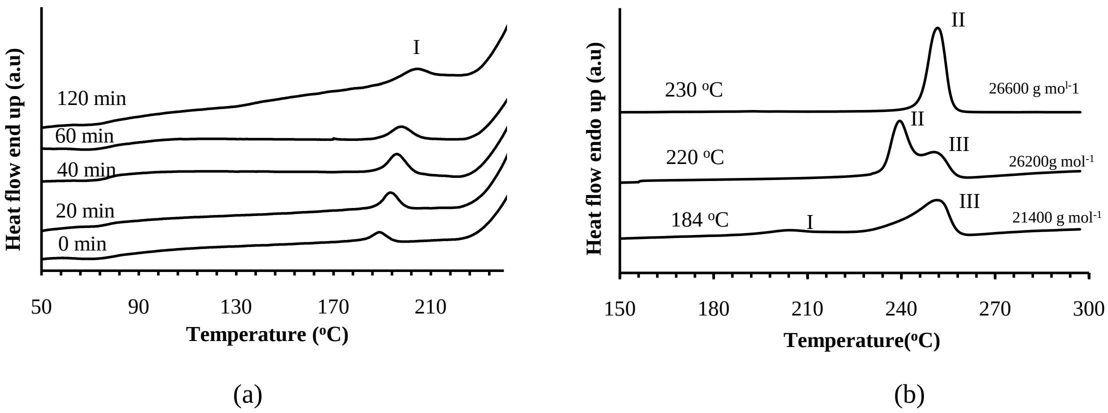
Poly(ethylene terephthalate) (PET) resins of high intrinsic viscosity ($[\eta]>0.7$ dl g^{-1}) are produced through solid state polymerization (SSP). SSP involves the heating of polymer particles to 200–240°C for 10–30 h under inert gas flow or vacuum[1-3], while crystallization may also take place risking to yield SSP products of considerable high melting points. The latter is undesirable because it may lead to processability difficulties and to increased acetaldehyde levels in the preforms[4]. Therefore, in the current work, PET crystallization during SSP was studied systematically and correlated to reaction temperature, time and molecular weight build-up[5].

EXPERIMENTAL

Amorphous PET was used as starting material. The SSP runs were carried out at 184, 220 and 230 ^{o}C (0–120 min) in a cylindrical stainless steel reactor, which was equipped with a gas inlet line to allow feed of dry nitrogen[5].

RESULTS AND DISCUSSION

SSP temperature emerged as a critical parameter for PET melting behavior: running SSP at 184 ^{o}C, a weak melting peak (I) appeared varying between 189.0–203.4 ^{o}C and increasing with SSP time (Fig. 1a). When running SSP for longer time (120 min) (Fig. 1b), the behavior was the following: at 184 ^{o}C a prominent broad endotherm (III) was found at 251.7–253.7 ^{o}C along with peak I.



(a) (b)

Fig. 1. DSC scans of PET SSP grades during isothermal reaction a) at 184 ^{o}C, b) after 120 min at the three SSP temperatures.

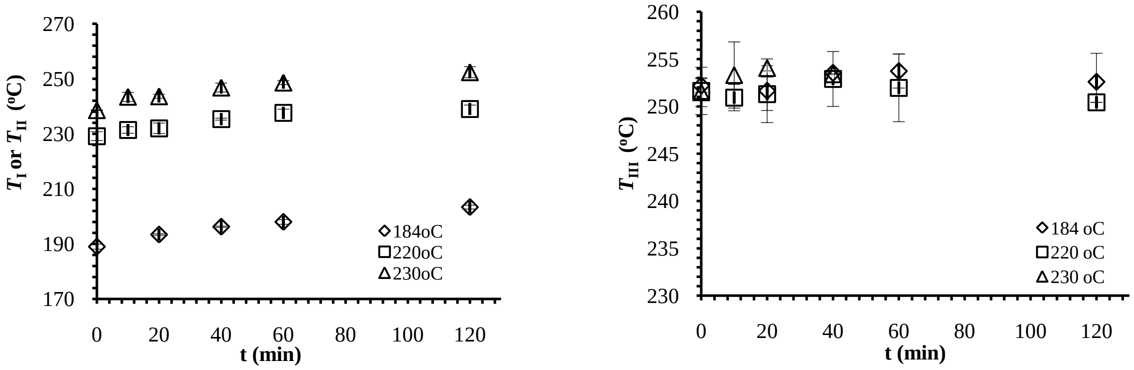
At 220 ^{o}C, peak I weakened significantly and disappeared, meanwhile binodial peaks (II and III) were observed in the range of 229.1–254.1 ^{o}C. At 230 ^{o}C, peak III almost disappeared and peak II dominated.

Considering that peaks I and II are attributed to secondary crystallization (SC)$^{6-7}$, the higher the SSP temperature, the faster the SC due to enhanced segmental mobility, leading to thickening and larger amounts of pertinent crystals and changing the behavior from two or three to one melting endotherm.

Peaks I or II (T_{I} or T_{II}) were found to increase linearly with the reaction time (Fig.2a), while the melting points III (T_{III}) of the primary-parent crystals were constant (Fig.2b). An empirical equation was built expressing T_m as a function of SSP temperature and time and time:

$$\mathrm{T_m} = 0.10 \times \mathrm{t} + 2544.27 \times \exp\left(\frac{-9845.44}{\mathrm{RT}}\right)$$

where, T_m is the melting point due to SC (^{o}C), T the SSP temperature (K), t the SSP time (min) and R the gas universal constant (J mol^{-1} K^{-1}).



(a) (b)

Fig. 2. Change of melting peaks as a function of SSP reaction time a) I and II endotherms (T_{I} or T_{II}) and b) III endotherm (T_{III}).

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HETEROGENEITY OF PHOTOOXIDATION PROCESSES IN BULK COMMODITY POLYMERS STUDIED BY ESRI OF NITROXIDES GENERATED IN THE COURSE OF HAS PROTECTION MECHANISM

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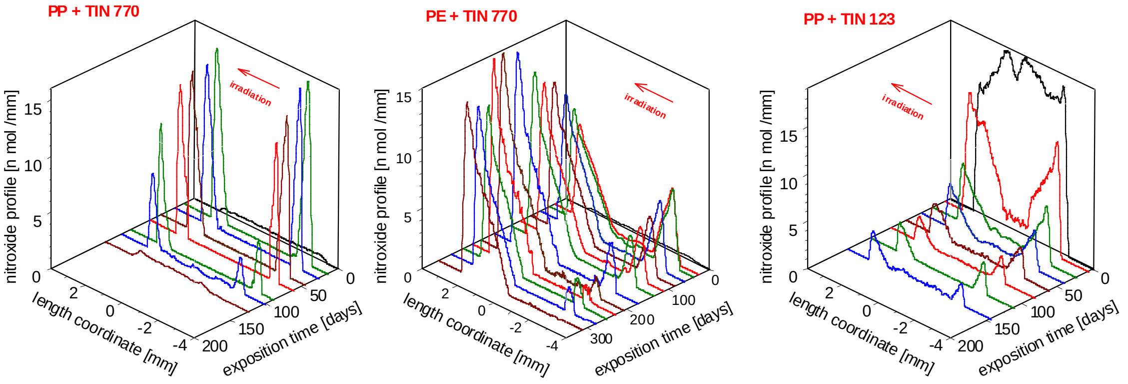
Polymers are protected during outdoor exposure by hindered amine stabilizers (HAS) against loose of their material properties due to the solar radiation-triggered photooxidation. Photooxidation of bulk polymers comprises a large number of chemical and physical processes which affect distinct regions in the material in various time scales and with different intensity. Nitroxides are the key intermediates in the mechanism of polymer protection by secondary HAS and can be used as markers localizing spatial occurrence of the oxidation process [1,2].

Plaques 6 mm thick made of polypropylene (PP), polyethylene (PE), polystyrene (PS) and poly(ethylene-*co*-norbornene) copolymer (Topas®, TP), stabilized with secondary HAS or *O*-alkylhydroxylamine (>NOR) HAS were subjected to accelerated photooxidation. Concentration profiles of nitroxides inside the plaques along the direction of incident irradiation (perpendicular to their irradiated surface) were determined by electron spin resonance imaging (ESRI) in dependence on the net exposition time. In the same dependence changes in polymer transparency and changes in concentrations of oxidation products (carbonyl and hydroxy groups) on the surface and inside the samples were studied by optical spectroscopy and IR, respectively.

Symmetric U-shape concentration profiles of nitroxides were found in the plaques made of PP and TP polymers stabilized with secondary HAS (e.g Tinuvin 770®) after photooxidation. These observations indicate that in these polymers characterized by high transmittance of terrestrial range of solar UV radiation incident light at sufficient intensity can penetrate through the plaques, reach their back surface, and along its way equally activate chromophores and initiators which start the degradation process by creation polymer alkyl radicals P$^•$. Their oxidation in the oxygen rich surface layers of the plaques is accompanied by stabilization activity of the HAS added and results in generation of approximately same concentrations of nitroxides in both surface layers of the plaques. Negligible concentration of nitroxides detected in inner layers of the plaque indicates that due to slow diffusion of oxygen no propagation of oxidation processes is active inside. The nitroxides may be quenched by polymer alkyl radicals P$^•$ and transformed to polymer-borne species >NOP, no longer detectable by ESR, or they may be transformed into inactive products. In the case of plaques made of polymers characterized by limited optical transmission (PE, PS) the concentration of polymer alkyl radicals created inside the plaque decreases with the distance from the front (irradiated) surface layer. Resulting asymmetry of the nitroxide profiles and time development of the overall nitroxide concentration in the plaques depend on the reactivity ratio of polymer radicals P$^•$ in oxidation and recombination reactions.



High concentration of homogeneously distributed nitroxides was observed in the fresh plaques stabilized with NOR HAS stabilizers (e.g Tinuvin 123$^®$) before photooxidation due to thermal decomposition of NOR HAS into nitroxides at plaque processing temperature (up to 200 °C). It follows that stabilization cycle of NOR HAS is shorter than that of the secondary HAS because of the creation of active nitroxides is before polymer hydroperoxide POOH is formed and because of occurrence of direct reaction of >NOR with POO$^•$.

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INFLUENCE OF NANOCLAYS ON THE FIRE BEHAVIOUR OF A FURAN RESIN

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Introduction

The high flammability and release toxic gases have become a critical limitation for the increasing usage of polymers. Nowadays, the security requirements are more rigorous and the utilization of flame retardants is required for inhibiting the polymer combustion process. Polymer nanocomposites are a promising alternative to traditional retardant formulations, as low loads are enough to achieve significant improvements in the properties. In particular, nanoclays are the most used because of its wide availability, low cost and null toxicity. They can migrate to the surface to act as a barrier to mass and heat. In combination, thermosetting matrices, like phenolics, have good chemical resistance and thermal stability because of the formation of a carbonaceous residue or “char” during their thermal degradation. In this work, a less environmental impact furan resin and three types of nanocomposites were evaluated and compared with traditional phenolic resins.

Methods

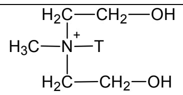
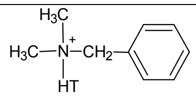
The cone calorimeter is the most used instrument to assess the material properties against fire, because it records many parameters such as the time of ignition, heat release rate, effective combustion heat, etc.

Its measurement principle relates the oxygen consumption with the heat release rate through an empirical assumption. Plates of 10x10x0,5 cm of four different furan materials (Table 1) were tested in a cone calorimeter Fire Testing Technology with heat flux of 50 kW/m^2 according to ASTM 1354. An horizontal configuration was used and the samples were placed 25 cm apart from the radiating source. Besides, the smoke production and optical density was measured in a Smoke Density Chamber, as it is an essential factor to allow the escape in case of fire.

Results

The ′fire risk′ shown in Figure 1 is a global value that bundles different parameters to compare the material fire behavior in a global way. Similarly, the opacity index in Table 1 shows an integral performance regarding the smoke production, quantity and optical density.

Table 1. **Furan resin and nanocomposites**

Material	*Clay (2%)*	*Organic modifier*	*Clays spatial distribution*	*Opacity index*
F	-	-	-	22,56
FNa	Cloisite® Na^+ (CNa)	-	Zones of large agglomerations	17,54
F30B	Cloisite®30B (C30B)	 $H_3C-\overset{+}{N}(CH_2CH_2OH)_2-T$	Intercalated	16,53
F10A	Cloisite®10A (C10A)		Intercalated	20,61

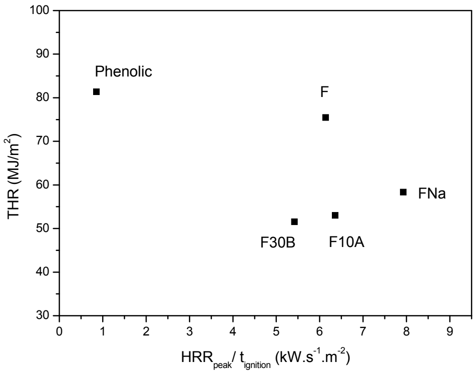


Figure 1. Fire risk of all materials. The x-axis measures the tendency to develop fast growing fire, while the y-axis compares the tendency to develop long duration fires.

The clay dispersion in the materials was previously evaluated. While the final clay interlayer distance measured by XRay Difraction (XRD) was similar in all composites, the TEM images showed differences in the spatial distribution of the fillers.

Conclusions

Furan resins fires grow faster than phenolics' ones, but the addition of clays shortens the flame duration. F30B showed the best performance against fire and smokes.

SEMI-INTERPENETRATING POLYMER NETWORKS POLYURETHANE-EPOXY RESIN. STUDY OF PHOTOCHEMICAL STABILITY

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Photochemical stability investigation of some semi-interpenetrating polymer networks derived from an aromatic polyurethane (PU) and an epoxy resin (ER) based on bisphenol A cured with ethylene diamine under the action of UV radiation with $\lambda > 300$ nm is the aim of this paper. Irradiation was conducted with a mercury lamp of 100W, with filtered light. Irradiation time varied between 0 and 200 hours. The samples were analysed at intervals of 25 hours. The crosslinked epoxy resin content in the semi-interpenetrated polimer networks (SIPN) varied between 5 and 40%. It was found that some surface properties variations such is color, gloss, and contact angle are lower in SIPN structures than in the polyurethane. The structural changes during irradiation were monitored by FTIR spectroscopy.

The SIPN samples were irradiated in air, in an accelerated weathering rotative device equipped with a middle pressure mercury lamp HQE-40 type, having a polychrome emission spectrum in the field of 240–570 nm, with a 30 mW/cm^2 light intensity. During the accelerated weathering, the surface colour difference of the test samples was measured in order to record the photochemical degradation. The surface colour difference (ΔE^*) was measured using a Pocket Spec Colour (USA) colour comparison spectro-photometer. The FT-IR spectra were recorded with a Bruker Vertex 70 Spectrophotometer. The peak surface was used to evaluate the FT-IR intensity, which is expressed in absorbance. The gloss variation on the surfaces of the samples was determined at 60^o with Horiba IG-320 Gloss-Checker apparatus. The gloss values were measured by comparing the intensity of luminous reflection on the sample surface with the value obtained for the standard (polished black glass). The most significant increase of ΔE was observed in the first 25 h irradiation time for polyurethane. The ΔE value for polyurethane after 200 h irradiation was 31.1, which means there were important differences between the colour of irradiated samples and the colour of non-irradiated samples. The ΔE values of SIPNs after 200 h exposure time were lower than the colour differences which characterize the polyurethane sample.

The decrease of G_f on SIPNs surface during irradiation can be explained by changing their roughness because there is a direct relationship between gloss and roughness. It is well known that the rough surfaces are less glossy. An explanation of the higher decrease of gloss of the polyurethane sample compared with SIPN samples is the high transparency of the polyurethane film. Therefore, the UV light penetrates deeper the PU, generating an advanced deterioration of the film.

Presence of primary amine groups and of the oxidation products in irradiated samples structure increases the water retention in SIPNs. Increasing the concentration of epoxy network enhances the OH group number in SIPN structure which is able to interact with water molecules. A higher number of OH groups means more retained water. Formation of chemical structures with high polarity as a result of photo-chemical and photo-oxidation processes further increases the amount of retained water. The UV radiations are partially absorbed by the epoxy network or are hindered to penetrate in depth of the film sample having the effect of urethane polymer protection.

Formation of some oxidation products and ortho-amino ester structures as a result of photo-Fries rearrangement in urethane bond could increase the affinity of water for the SIPNs irradiated surface. The decrease of surfaces polarity due to the accumulation of some saturated and unsaturated hydrocarbon structures resulted from the photo-decomposition of aliphatic ester in PU by Norrish type reactions may explain the increase of the contact angle above the initial values after 200 h of irradiation.

The decrease of PU lightness factor is higher than the decrease of SIPN lightness factor, calculated at the same irradiation level. In conclusion, the polyurethane sample is more affected by UV light than the SIPNs.

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DETERMINATION OF PRIMARY OXIDATION PRODUCTS IN HYDROCARBON POLYMERS

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The knowledge of products, mainly the primary ones, which are formed during chain oxidation of polymers is useful not only for describing kinetics and mechanism of oxidation process itself but also for lifetime prediction of any polymer under consideration.

This poster presents our first results of primary oxidation products analysis in hydrocarbon polymers that tend to improve their quantification for better understanding oxidation phenomena.

PE and PP films with thickness between 50-80 μm were produced using a film blowing machine. Thermo-oxidation of prepared samples was performed in an air-draft oven.

Special adaptors designed for both oven oxidation and monitoring FTIR spectra enabled us to fix five separated thin films into adaptor. Advantage of such an arrangement is seen in acceleration of oxidation due to a better access of oxygen into polymer through ten surfaces, and also more precise and reproducible FTIR spectra determination on fixed sample area measured.

Determination of hydroperoxides representing the very primary oxidation products indeed was performed by the thiocyanate method[1]. Thiocyanate method is able to determine the sum of all hydroperoxides including peracids. As our attention is very focused to peracides, we modified our standard thiocyanate method by the addition of diphenyl sulphide which decomposes all peracids quantitatively before hydroperoxides determination. The difference got equals to the peracids content.

The samples were oxidized at 120°C and analyses were focused on determination of carbonyls and hydroperoxides. During the first part of oxidation the concentration of hydroperoxides was slowly increasing, but carbonyls were not detected in infrared spectrum. When first carbonyls were detected, their concentration rapidly increased more times than concentration of hydroperoxides.

The peracids determination by modified thiocyanate method was tested on PP containing theoretically 50% of primary C-H bonds where peracids formation is to be expected.
Our goal is to study kinetics and mechanisms of primary oxidation products accumulation in hydrocarbon polymers differing in their structure and perform correlation with theoretical models.

Acknowledgement is given to IGA VUT project FCH-S-12-5 for financial support and Polymer Institute Brno for device support.

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STUDY OF THE EFFECT OF QUERCETIN ON THE MELT STABILITY OF POLYETHYLENE

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In the last decade some questions arose about the possible effect of the reaction products of phenolic antioxidants on human health[1]. Therefore our interest is turned towards the study of the potential use of natural antioxidants in polyolefins. In the present work quercetin was studied alone and in combination with a phosphorous secondary antioxidant in polyethylene processed by multiple extrusions. Quercetin (Fig. 1), a flavonol, is a plant-derived flavonoid found in fruits, vegetables, leaves and grains. It has antioxidant, antiviral, and anti-inflammatory effect in the human body. It is a question how it behaves in an apolar polymer at high temperatures.

The experiments were carried out with the Phillips type ethylene-1-hexene copolymer, Tipelin FS 471 (*TVK*). 1000 ppm quercetin, 2000 ppm Sandostab P-EPQ (*Clariant*), and combinations of 2000 ppm P-EPQ with different amounts (5-1000 ppm) of quercetin were homogenized with the nascent polymer powder then processed by six consecutive extrusions at 260 °C. FT-IR spectroscopy, optical microscopy rheology (MFI), residual thermo-oxidative stability (OIT), and color were used for the characterization of the samples after each extrusion step.

The thermal degradation of a Phillips type polyethylene results in an increase of its molecular mass and in the formation of long chain branches due to the high concentration of vinyl groups. Quercetin itself increases the processing stability of the polymer but the effect of the phosphonite secondary antioxidant is more significant in the first extrusion step. However, the phosphorous antioxidant is consumed fast during multiple extrusions when used alone. The addition of quercetin to the phosphonite –

even at a concentration of 5 ppm – enhances the stability of the polymer. Below 200 ppm the effect of quercetin depends both on its concentration and on the processing history of the polymer (Fig. 1). With decreasing amounts of quercetin, MFI increases after the first extrusion, but this effect is gradually lost in subsequent extrusions. Above 200 ppm quercetin, MFI is independent of the concentration of the phenol and the processing history of the polymer. This effect can be explained by the association of the phenolic OH groups proved by microscopy. At 1000 ppm quercetin concentration crystalline needles are dispersed in the polymer matrix.

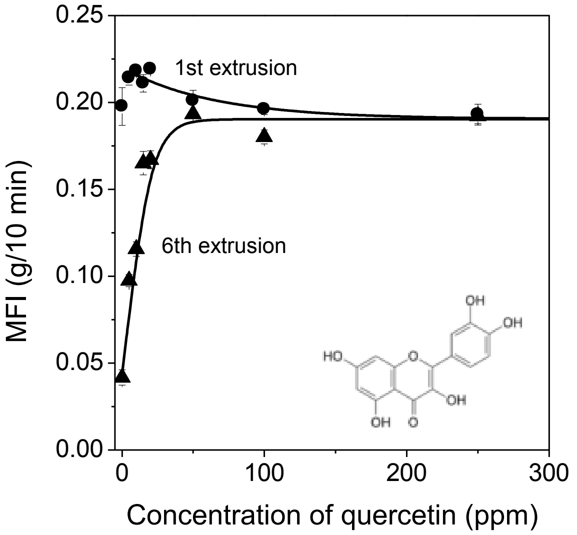

Figure 1 Effect of the amount of quercetin and processing history on the melt flow index of polyethylene at 2000 ppm phosphonite secondary antioxidant content.

Quercetin itself and even more its combinations with a phosphonite enhance also the thermo-oxidative stability of polyethylene. OIT increases with increasing concentration of quercetin and with the number of extrusions. This phenol discolours the polymer strongly, but yellowness index decreases with its decreasing concentration, and below 1000 ppm also with the number of extrusions.

The increase in OIT and the decrease of YI with increasing number of extrusions can be attributed to the gradually improving dispersion of the phenol in the polymer. We may conclude that quercetin is an efficient melt stabilizer in polyethylene with some special characteristics.

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Acknowledgement: The National Research Fund of Hungary (OTKA K 77860 and K 101124) is greatly acknowledged for the financial support of the research.

EXAMINING THE THERMAL STABILITY AND DEGRADATION MECHANISMS OF POLYBENZOXAZINES

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Introduction: Polybenzoxazines (PBzs) are attracting great technological interest in many applications (*e.g.* aerospace[1], microelectronics[2], membranes[3] and fuel cells[4]) as they offer potential advantages over existing phenolic resins, including heat resistance, good electrical properties and flame retardance. Additionally, they confer other attractive characteristics: near zero volumetric change upon curing, low water absorption, and high char yield[5]. These predominantly aromatic, addition-cured polymers degrade thermally *via* a 3-stage process[6]. The present work focuses on the influence of monomer structure and cure schedule on the development of different thermoset networks for which different thermal stability is observed.

Experimental: All monomers (Fig. 1) were supplied by Huntsman Advanced Materials (Basel). The designations refer to the cured PBzs. TGA (RT-800°C, N_2, 10 K/min) was carried out on cured, ground resins.

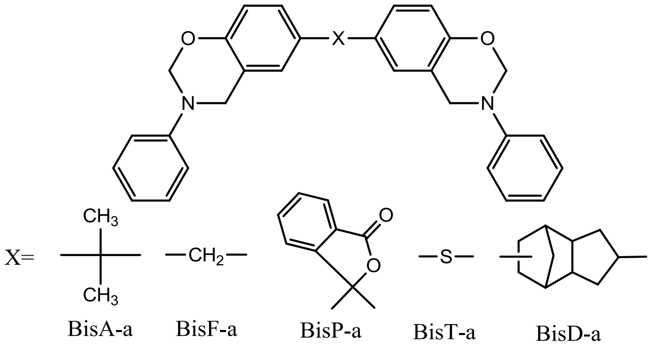

Figure 1 *bis*-benzoxazine monomers

Results and Discussion: The PBz backbone has a dramatic effect on thermal stability and char yield (Fig. 2). At 800 °C (N_2) BisA-a and BisD-a have char yields < 30 %, *cf* BisT-a and BisP-a (*ca.* 54 %), suggesting that the phenolphthalein and sulfur linkages are much stronger than their counterparts. From the derivative weight loss data for BisF-a (Fig. 3,) three discrete decomposition steps are apparent. The bridging groups influence the complexity of the degradation pathways.

The same data also demonstrates the effect of particle size: at any temperature the char yield is proportionate to particle size for all the polybenzoxazines studied. CT-Scanning shows the internal structure of the char (Fig. 4): BisF-a develops a porous structure when heated to 400 °C in an air circulating furnace.

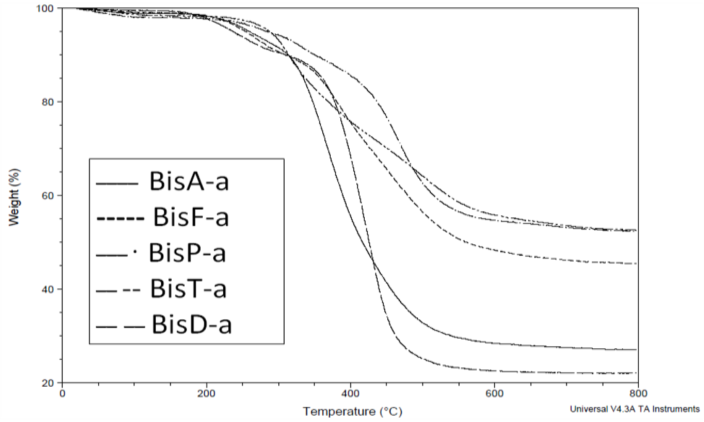

Figure 2 TGA Plot of PBz Samples taken from RT to 800 °C at 10 K/min

Conclusion: The PBz backbone and particle size have a significant effect on thermal degradation. TGA has proven to be a useful method to monitor thermal degradation processes and CT-Scanning provides a good method for imaging the porous network formed upon exposure to heat.

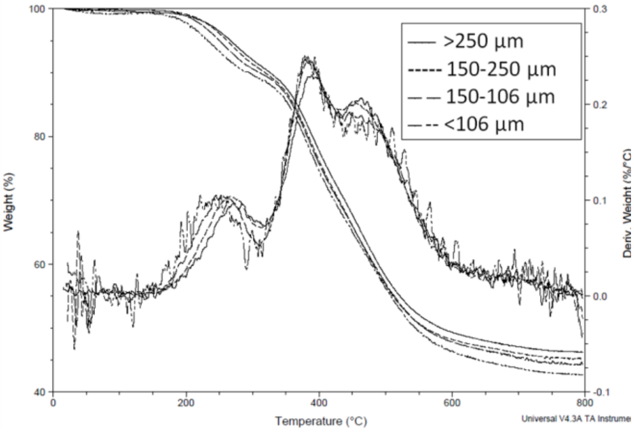

Figure 3 TGA Plot of BisF-a Samples taken from RT to 800 °C at 10 K/min.

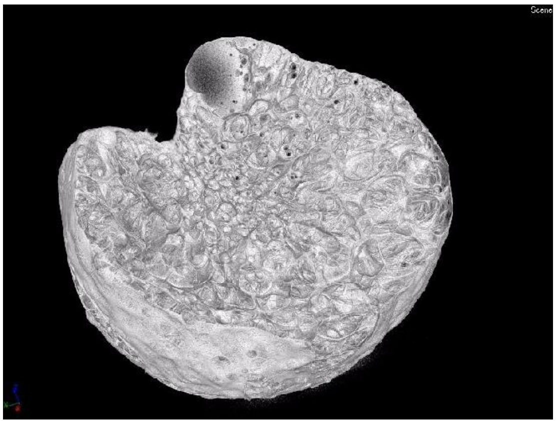

Figure 4 CT-Scan of BisF-a heated to 400 °C.

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Some aspects of correlation of UV accelerated ageing vs. outdoor exposure

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Keywords: UV, accelerated ageing, degradation, carbonyl index, polypropylene, temperature, copolymer, outdoor exposure

Abstract

The presented results hereby deal with the effect of temperature on the rate and efficiency of UV accelerated ageing carried out under the conditions of xenon light source exposure. Correlation of accelerated ageing data with outdoor exposure was carried using the non-UV-stabilized polypropylene (PP) compression moulded films – homopolymer, random copolymer (C2 = 3.5 wt.%) and impact copolymer (TOT C2 =6.4 wt.%). Accelerated ageing was realized in Q-Sun Xe-1 exposure chamber using a filtered Xe-light source (irradiation 0.47 W/m^2@340nm) and a dry cycle; outdoor exposure was carried out in Brno, Czech Republic, representing the typical mid-European climate.

The extent of changes due to photo-oxidative degradation was quantified using a carbonyl index (CI), defined upon FITR absorption within 1705-1720 cm^{-1} wavenumber band and a reference band at 1892 cm^{-1}, CI = $A_{C=O}/A_{ref}$. Accelerated ageing for all the materials investigated was carried out at black panel temperatures 40, 50, 60 and 70°C. Time to degradation (= induction period IP) was defined as an exposure time up to the onset of

intensive increase in carbonyl absorption. Different times to degradation attained for individual polymers and temperatures were correlated with the weathering data after 6 months of outdoor exposure.

The comparison of results attained during the experiment was carried out in three principle ways. Prediction of service life-time period for an average outdoor temperature was carried out: 1) Using an extrapolation of ln IP vs. 1/T plot, 2) Using the calculation of radiant energy in the critical TUVR 300-400 nm wavelength interval up to the onset of carbonyls absorption increase and 3) using a direct comparison of relative increase in carbonyl index value.

The data from accelerated ageing and outdoor exposure were, thus, compared and critically considered.

CAVITATION EROSION DAMAGE OF VARIOUS POLYMERIC MATERIALS AND THE METHOD FOR LOWERING THEIR EROSION RATE

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In fluid systems, when the velocity and/or pressure change abruptly the cavitation erosion is caused frequently. On the other hand, use of polymeric materials in these environments has been increasing especially to decrease the corrosion damage of metal as structural material. In this study, the cavitation erosion performances of various polymeric materials have been investigated, and the method for lowering their erosion rates has investigated experimentally.

Experimental method↨ Magnetostrictive vibratory system was used as experimental apparatus. The materials used were shown in Table1. To evaluate the effect of amount of dissolved gas and pressure on erosion damage, the specimen was covered by enclosed vessel. Experiments were carried out by using several gases (N_2, O_2, Ar, F12, F22, C_2H_4) with saturated dissolved conditions, and several amount of dissolved air and CO_2.

Table 1 Materials used

		Abbreviation	Crystallinity (%)
thermo-plastics	polystyrene	PS	≑
	styrene acrylonitrile	SAN	≑
	High inmpact polystyrene	HIPS	≑
	polumethylmethacrylate	PMMA	≑
	polyvinyl chloride	PVC	≑
	polycarbonate	PC	15.4
	polytetrafluoroethylene	PTFE	63.5
	polyethylene	PE	70.6
	polyoxymethylene	POM	80.5
thermosets & composites	epoxy resin	EP	≑
	polycarbonate(glass powder)	PC(glass)	≑
	FRP(Mat)	FRP(Mat)	≑
	FRP(Roving)	FRP(Roving)	≑
	phenolic resin(pulp)	PF_1	≑
	phenolic resin(wood powder)	PF_2	≑

Erosion performance of plastics↨ The change of volume loss with exposed time were shown in Fig.1. Brittle plastics such as PS, SAN, PMMA showed low resistance for erosion, on the other hand ductile thermoplastics such as PC, PTFE, PE, POM showed high resistance. Composites showed characteristic erosion behavior because of their unhomogeneous structure. In brittle plastics the discontinuous increase of volume loss is remarkable. In ductile plastics, the larger in crystallinity, the higher resistance were observed.

Method for lowering erosion damage ↨ The behavior of cavitation initiation is closely related with dissolved gas and vapor pressure. The effect of dissolved gas content, therefore, on cavitation damage has been investigated, and discussed the availability as method for lowering erosion damage.

The effect of the amount of dissolved gas on damage was shown in Fig.2. At the region in fewer dissolved gas content, the damage increased with increase of gas content, however the damage decrease with increase of gas content at higher gas content. These are due to increase in number of generated cavities with increase of gas content at lower gas content, and to the larger cushion effect by liberated gas at higher gas content.

The same tendency as behavior shown in Fig.2 has been observed in the effect of pressure on damage, the damage showed maximum values at intermediate region of pressure.

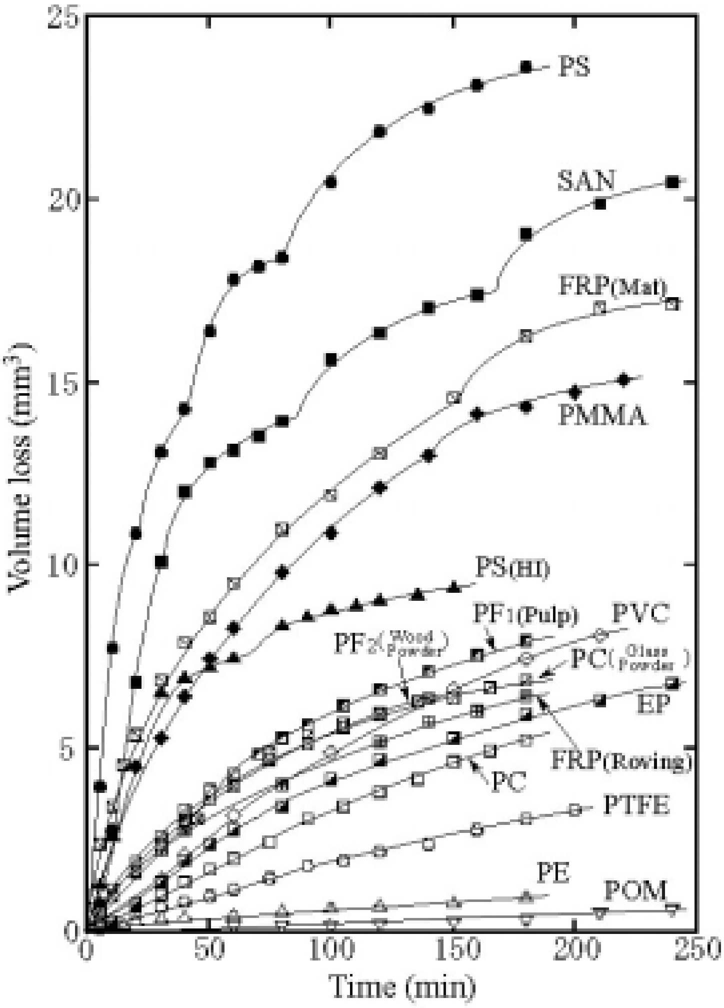

Fig.1 Change of volume loss. (6.5 kHz. 40μm)

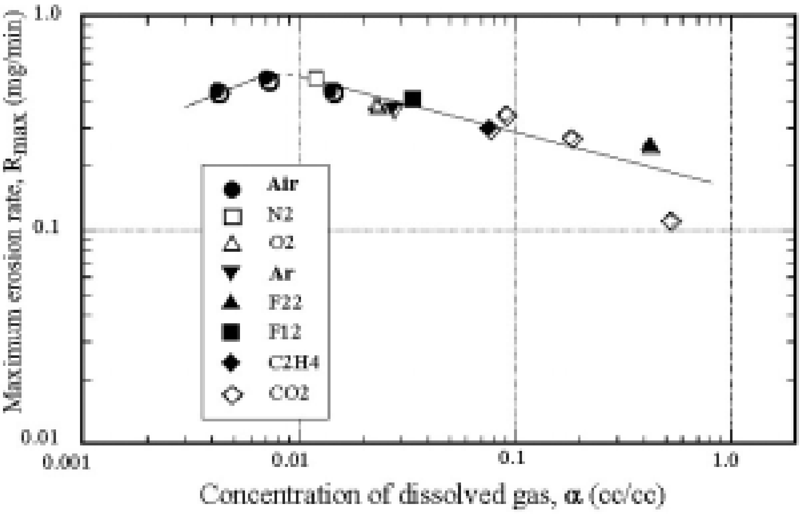

Fig.2 Change of maximum erosion rate with dissolved gas content. (6.5kHz, 55μm)

THERMAL STABILITY OF CORE-SHELL HYDROPHILIC NANOPARTICLES FOR BIOMEDICINE

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The aim of this study was the investigation of thermal degradation process at the interface of a core-shell type structure. Such hybrid compound was comprised of an inorganic core of magnetite nanoparticles and an organic shell consisting of 3-aminopropyltriethoxysilane. The thermal degradation has been studied by thermogravimetry in nitrogen atmosphere, up to 500^{o}C. The evolved gases analysis was performed using a coupling to a quadrupole mass spectrometer and a Fourier transform infrared spectrophotometer equipped with external modulus for gas analyses.

The non isothermal data extracted from the thermograms were processed with a specialized software for thermal degradation kinetic study. Isoconversional kinetic study[1-3] was conducted and a three stage thermal degradation mechanism was proposed and displayed in Figure 1.

Multivariate non-linear regression method was performed to determine reaction model for the three heating rates and to find the real form of the conversion function[4]. A model of thermal decomposition in three successive stages was proposed. A conversion function of n order was found to best fit the thermal degradation process. The software yielded a good correlation between experimental data and data calculated with the established kinetic model.

Thermal decomposition of the core-shell hydrophilic nanoparticles began with water and ammonia elimination throughout the whole degradation process, and the formation of C=C and C=O bonds. The second and third thermal decomposition stages presented losses of covalently bonded water, carbon dioxide and carbonyl and olefin products. Some of these products underwent [2+2] cycloadditions[5] with cyclobutanone formation in the third stage of thermal decomposition. Aziridine cycle was formed also in the third stage of thermal decomposition via cyclization reactions[6].

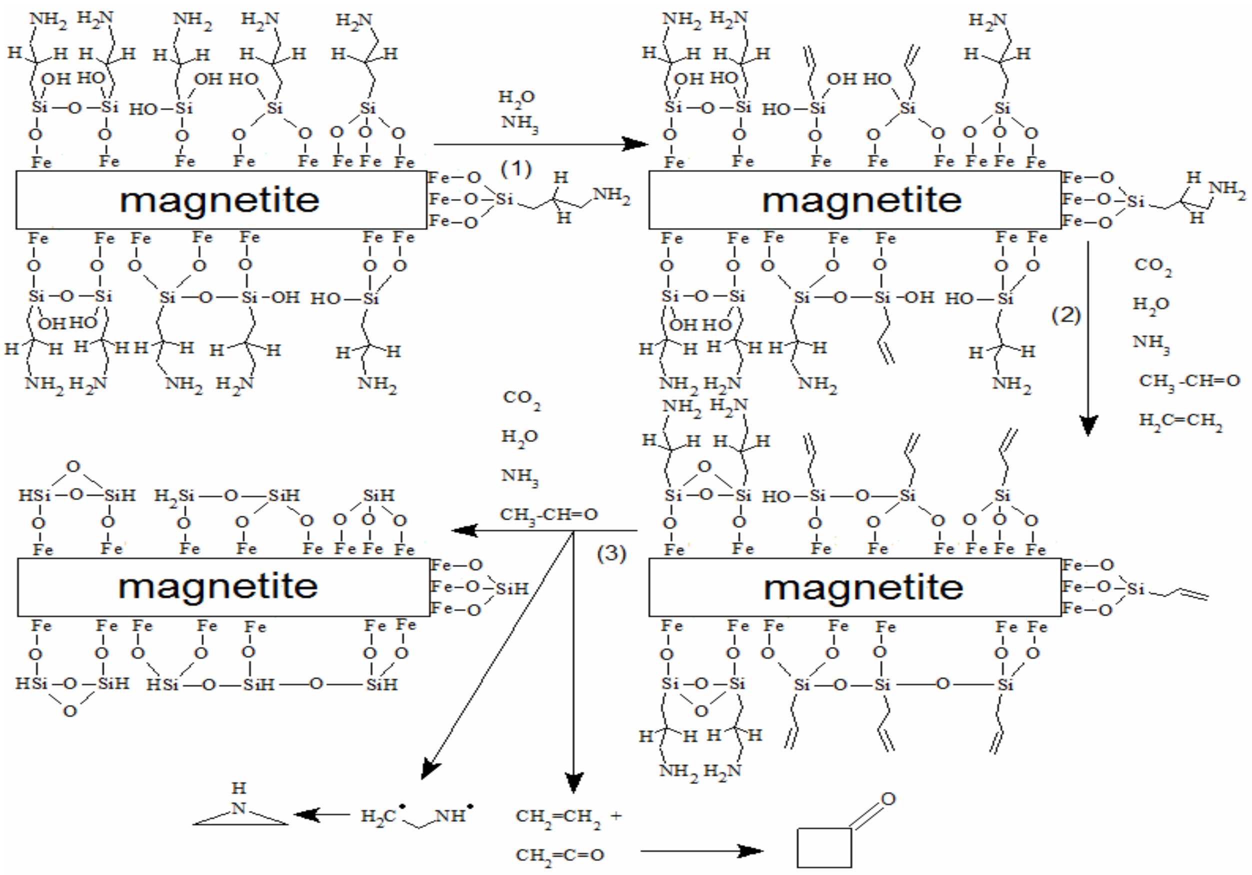

Figure 1. Schematic of the proposed thermal degradation mechanism of the core-shell structure

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THE INFLUENCE OF S-4-(BENZOYL)PHENYL THIOBENZOATE ON PHOTODEHYROCHLORINATION AND PHOTO-OXIDATIVE DEGRADATION OF POLY(VINYL CHLORIDE)

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Poly(vinyl chloride) (PVC) is widely used in industry and present almost everywhere. Commercial PVC (Anwil, Włocławek) ($\overline{M_w}$ =128 000) and purchased by Sigma-Aldrich ($\overline{M_w}$ =97 000) in the form of the films were studied with and without the presence of 1% of S-4-(benzoyl)phenyl thiobenzoate. S-4-(benzoyl)phenyl thiobenzoate is a photoinitiator of free radical polymerization of some monomers.

The PVC films were irradiated with high pressure mercury vapour lamp HPK 125 W, emitting radiation in the 248-578 nm range. UV-Vis spectra were collected on UV-1601 PC spectrometer (Shimadzu, Japan), infrared specra - on FTIR Genesis II spectrophotometer (Mattson, USA). GPC was applied to analyze the molecular weight distribution (Chromatograph - Viscotek, USA).

Gel permeation chromatography (GPC) results showed that degradation of PVC with the addition of the photoinitiator was hampered. After UV-irradiation a decrease in the number-average molecular weight ($\overline{M_n}$) and an increase in polydispersity was observed for pure PVC, which suggested that PVC underwent photodegradation. The subtle changes in $\overline{M_n}$ and polydispersity was noticed for samples with the additive. An increase in the weight-average molecular weight ($\overline{M_w}$) was observed for studied samples, which might be caused by cross-linking and branching reactions. Irregular changes in molecular weights ($\overline{M_n}$, $\overline{M_w}$) suggests that degradation competes with cross-linking reactions.

The effectiveness of the formation of polyene sequences, monitored by UV-Vis spectroscopy, was lower for PVC (Aldrich) with the photoinitiator than for PVC without additive, but in the case of commercial PVC there was no influence of the photoinitiator on this process.

Photo-oxidation of PVC was observed by FTIR in the range of carbonyl and hydroxyl groups vibrations. The rate and the efficiency of photo-oxidation of PVC with the addition of photoinitiator were higher then that for pure PVC. In the presence of photoinitiator free radicals from PVC undergo mostly oxidation, especially in the case of PVC (Aldrich) as for this polymer dehydrochlorination was hampered.

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CYCLODEXTRIN NANOSPONGES AND PHOSPHORUS COMPOUNDS AS NOVEL GREEN FLAME RETARDANTS

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Novel green flame retardant systems based on a complex of cyclodextrin nanosponges and phosphorus derivatives have been prepared by melt compounding with different polymer matrices (ethylene-vinyl acetate copolymer, polypropylene, linear low density polyethylene or polyamide 6), in order to improve the thermal stability of the different polymers in nitrogen and air and their flame retardancy (assessed by combustion and flammability tests). The role of cyclodextrin nanosponges both as a carbon source and a foaming agent in such intumescent formulations has been demonstrated: indeed, the phosphorus derivatives are embedded and protected by the nanosponge architectures and thus are able to generate phosphoric acid directly in situ at high temperatures. As a consequence, cyclodextrin nanosponges dehydrate in presence of this acid source, giving rise to water vapour, favouring char formation and thus significantly enhancing the polymer resistance toward combustion.

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PHOTO-OXIDATION RESISTANCE OF POLYETHYLENE/CARBON NANOTUBES COMPOSITES: ASPECT RATIO AND SURFACE FUNCTIONALIZATION EFFECT

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Carbon nanotubes (CNTs) can find wide application in nanotechnology, electronics, optics, special packaging and other fields of materials science, as they are endowed with high electrical and thermal conductivity. The final properties of CNTs based nanocomposite materials depend on the type of CNTs, i.e. single, double or multi walled CNTs, on the degree of CNTs dispersion within polymeric matrix, on the integrity of CNTs after the composite formulation and on the extent of chemical and/or physical interaction between the nanotubes and the matrix. In particular, nanocomposites with improved mechanical properties can be obtained when the CNTs can effectively be incorporated and randomly aligned into polymer. In order to improve their dispersion into the polymeric matrix various reactive groups are grafted onto the surface of carbon nanotubes. Thus far the photo-oxidation of polymer/CNTs nanocomposites has not received particular attention. Morlat-Therias et al.[1] have reported the influence on the photo-oxidation behavior of EVA/CNTs nanocomposites. They found that CNTs can play three roles, i.e. inner filter, antioxidant and pro-degradant; the global effect of CNTs depends on different factors, as concentration of the CNTs, their morphology and the functionalization of the CNTs surface. The effect of the CNTs concentration on the photo-oxidation behavior of polyethylene based nanocomposites films has been studied by our research group[2] and the results obtained suggest that at low CNTs concentration the pro-degradant effect is significantly pronounced while, at high concentration, the prevailing effect is an antioxidant action. Recently Shi et al.[3] studied the influence of wall number and surface functionalization on CNTs antioxidant behavior in polyethylene based nanocomposites. Their results show that the antioxidant effect of CNTs follows a free radical scavenging mechanism.

In this work the resistance to accelerated weathering of polyethylene/CNTs composite films was compared with that of neat polyethylene film. Multi-walled carbon nanotubes with different morphological regularity, hydroxylated and carboxylated multi-walled carbon nanotubes were involved to investigate the influence of lattice defect and surface functionalization on the photo-oxidative stability of polyethylene. The nanocomposite films were subjected to accelerated UV-B exposure, and the photo-oxidation of all samples was followed by FT-IR spectroscopy.

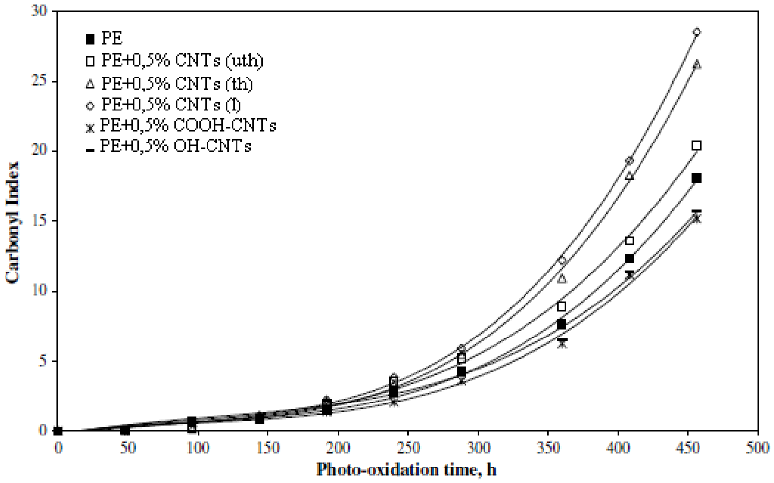

Figure 1: carbonyl index as a function of the exposure time of all investigated systems

In Figure 1 the carbonyl index as a function of the exposure time for all investigated sample is reported. The photo-degradation rate of nanocomposites containing functionalized CNTs is less pronounced than that observed for the pristine polyethylene. Then, the multi-walled carbon nanotubes with more structural defects are more able in the matrix protection against photo-oxidation.

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A STUDY OF VOLATILE ORGANIC COMPOUND (VOC) EMISSIONS DURING THE DEGRADATION OF EARLY 20TH CENTURY PLASTICS

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As part of the Heritage Smells project, a study of modern materials is ongoing in order to characterise the volatile organic compound (VOC) signatures (the “smell”) of historic plastic objects and to gain a deeper understanding of the relationships between these VOC signatures and the condition, stability or potential hazards of historical plastics. This work will enable practitioners to make well-informed decisions regarding the conservation and storage of heritage collections.

A method is being developed for the analysis of a series of historic plastic objects dating from 1910 onwards from the Historic Plastics Reference Collection at the Centre for Sustainable Heritage using solid-phase microextraction (SPME) gas chromatography/mass spectrometry (GC/MS). CAR/PDMS SPME fibres are being used. The objects collected are composed of a variety of materials, including cellulose acetate, cellulose nitrate, polyurethane and poly(vinyl chloride), the four plastic types known to deteriorate most rapidly in museum collections[1]. Some of the samples have been degraded at 80 °C and 65% relative humidity for 2, 4, 6, 8 or 10 weeks.

As part of method development, various sources of uncertainty have been studied, including plastic sampling, vial tightness, SPME sampling temperature and intra- and interday repeatability. The use of internal standards has also been explored. The developed method has been applied to study the VOC signatures of historic samples of various base compositions. The VOC emission profiles vary according to plastic formulation, degradation period, or even between samples taken from the same object. The current work explores whether these differences can be used to study the relationship between VOC signatures, polymer identity and different levels of degradation.

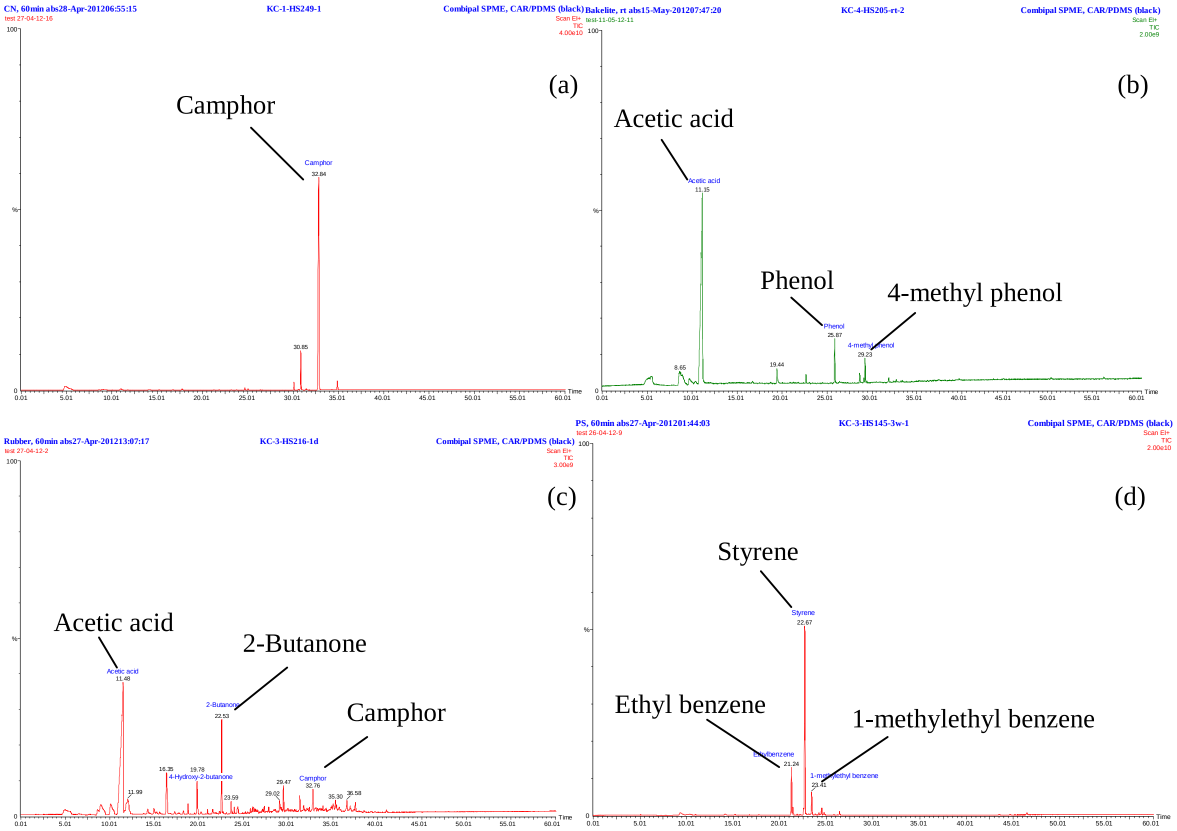

Figure 1. Chromatograms showing VOCs emitted from various plastic samples: (a) Cellulose nitrate, (b) Bakelite, (c) Rubber, (d) Polystyrene.

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The authors acknowledge the support of the AHRC/EPSRC Science and Heritage Programme.

MODELING OF BIO-DETERIORATION OF POLYETHYLENE USED IN TOTAL JOINT REPLACEMENTS

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The *in vivo* failure of implanted polymeric products justifiably receives a great deal of attention and diagnostic resources. Ultra-high molecular weight polyethylene (UHMWPE) has been used in orthopedics for total joint replacements. Consequently, UHMWPE components are bathed in body fluids containing potential free radical initiators, as well as molecular oxygen, superoxide and hydroxyl radicals as oxidizing agents for *in vivo* oxidation[1]. In spite of numbers of studies, the exact mechanism of *in vivo* oxidation of UHMWPE has not been described yet.

The model experiments of accelerated ageing simulating bio-deterioration of polyethylene were done on high density polyethylene (HDPE) samples in liquid medium containing salts of peroxyacids. Infrared (IR) spectra recorded on FTIR microscope with MCT detector were used for determination of oxidative degradation profile (oxidation and trans-vinylene index, crystallinity) from surface to depth of the samples. The obtained results were extrapolated to higher molecular weights and compared with the results done on UHMWPE samples. Finally, the degree of oxidative degradation of model materials after accelerated ageing tests were compared with really failed UHMWPE components of total joint replacements.

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Acknowledgement: financial support from Technology Agency of the Czech Republic (grant no. TA01011406) is greatly acknowledged.

Developing Profluorescent Nitroxide Additives as Probes for Polymer Degradation: The Use of a Liquid Model for Polyolefins

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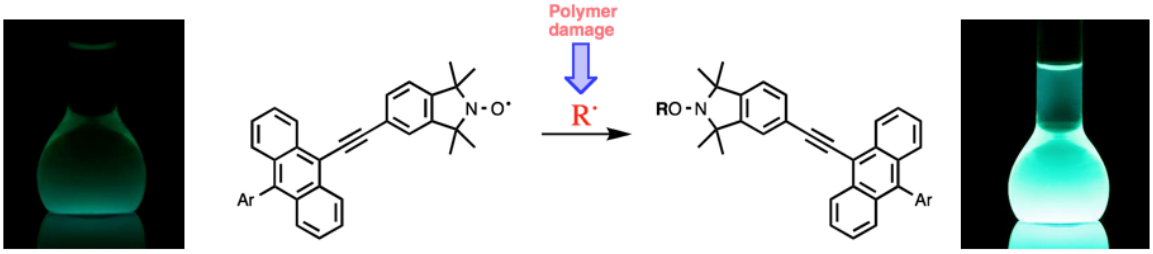
Nitroxides are powerful antioxidants and scavengers of free radicals. They have been widely used since the 70's as probes for reactive species and as stabilizers for polymers. We have more recently synthesized a range of novel fused aryl nitroxides that have found applications as fluorescent sensors for oxidative damage in materials[1] and for monitoring pollution from ultra-fine particles[2]. Our approach employs nitroxides that contain potent, yet masked, fluorophores. These probes allow the monitoring of radical reactions according to the fluorescence generated by the resultant diamagnetic scavenging products[3]. When the nitroxide captures a free radical to form the stable alkoxylamine, the natural fluorescent nature of these compounds is no longer suppressed and up to a 100-fold increase in fluorescence can be detected over the parent. We have described these nitroxide-fluorophore systems as *profluorescent* nitroxides (PFNs) and they represent a powerful new methodology for monitoring free radical reactions.

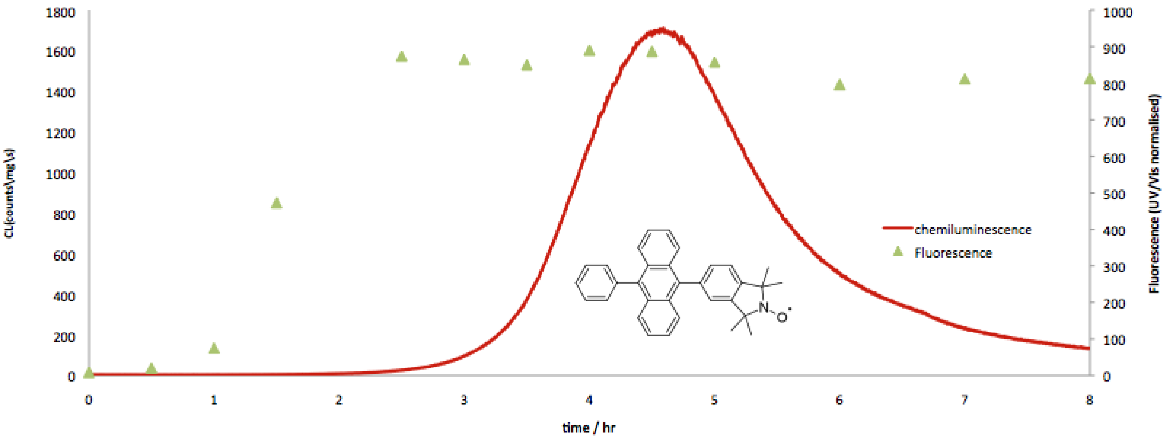


We have shown that PFNs are sensitive probes for the early detection of thermo-oxidative degradation in polyolefins.[4] Radical scavenging by the nitroxide moiety present in PFNs leads to the formation of highly fluorescent species that may be detected even at very low concentrations in the degrading polymer. Polypropylene was used in our initial polymer degradation studies, as it has a well-defined[5] thermo-oxidative degradation mechanism.

To be effective sensors for polymer degradation, PFN probes need to display an efficient nitroxide-dependent fluorescence switch-on and also high chemical stability within the degrading polymer matrix. Comparing the chemistry of

PFNs is crucial for determining those that will make effective polymer degradation probes. Such comparisons are complicated by challenges in determining probe concentrations within solid polymers as well as sample-to-sample variations in doping limits, polymer crystallinity and light scattering levels. Currently, semi-quantitative methods are employed to determine PFN concentrations, but total quantitation cannot easily be confirmed in the solid state without lengthy sample preparation.

A liquid model system circumvents many of the limitations of a solid polymer matrix. Using a polyolefin liquid that follows a similar degradation profile to polypropylene, allows PFN concentration to be accurately determined by spectroscopic techniques. Analysis of a liquid limits the challenges occurring during the later stages of solid polymer degradation (discolouration, cracking and crazing). Using a liquid model also simplifies sample preparation required by supporting analytical techniques[6] such as NMR, GPC, GC-MS and LC-MS.



Paraffin oil is a simple, saturated hydrocarbon liquid that is inexpensive and readily available. In the study described here, we used paraffin oil as a liquid model for polyolefins and investigated whether solutions containing PFNs show similar degradation sensing and stabilisation properties as are observed for polypropylene under the same oxidative degradation conditions. This study will present results from paraffin oil liquid model experiments that may be used to evaluate existing and novel PFNs under highly reproducible conditions.

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STUDY OF ACCELERATED BIODEGRADATION OF POLYPROPYLENE WITH ORGANIC ADDITIVE

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Introduction

Polymers due to their versatility became an essential material which provides better life quality, but these synthetic polymers have a short useful life, in most cases less than two years [1]. This consume of plastic had led, in recent years to a significant increase in the amount of plastic waste, and biodegradation of polymers is seen as one of the solutions for current plastic waste management, such as accumulation and expensive recycling [2]. The biodegradable polymers are those that are degraded into carbon dioxide, water and biomass as a result of the action of living organisms or enzymes [3]. The aim of this work is report the influence of the additive free of transition metal on the polypropylene (PP) degradation samples, after it being kept in an accelerated biodegradation test. The biodegradation was evaluated by evolution of CO_2 and weight loss.

Methodology

PP with melt flow index of 38g/10min supported by Braskem, and an organic pro-degradant, containing potassium salt and 1,2-oxo-hydroxy group free of transition metal. The samples were prepared using a screw simples extruder and then grounded with liquid nitrogen. The samples in plate forms were molded by thermal compression molding (TCM). Accelerated biodegradation tests were carried out in cylindrical glass vessels with soil, perlite, water and the samples, during 120 days. The biodegradation has been assessed with measurements of evaluated by evolution of CO_2 and weight loss.

Results and discussion

Fig. 1 shows the accumulative CO_2 emissions monitored during 120 days. The biodegradation test appeared to be satisfactory, because the high level of CO_2 production from the cellulosic samples (positive control). Within of the same time is observed a significant increase in the production of CO_2 in the case of PP modified when compared to neat PP. Table 1 show the weight loss total (100%) for the cellulosic samples, because it to be is a biodegradable material and the condition in the accelerated respirometric test was facilitated a complete degradation; and the weight loss of the PP modified was 10% and de neat PP only 0.08%. These results combined with the CO_2 production confirms that the organic additive influences in the biodegradation process of PP.

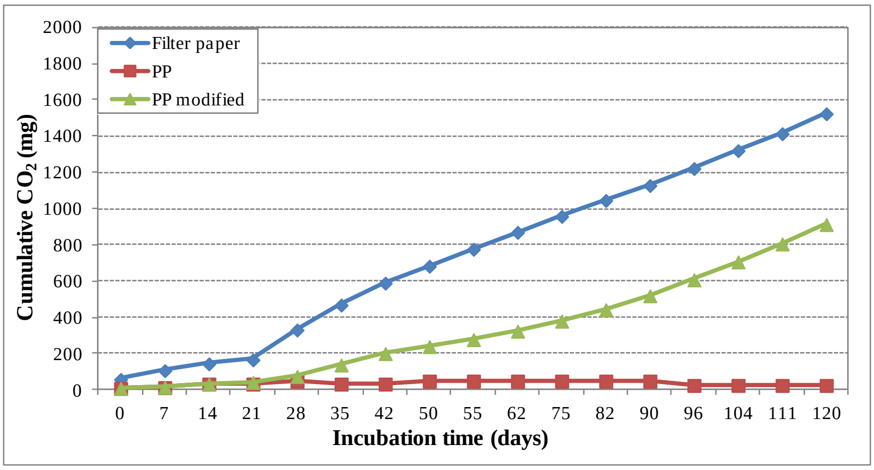

Figure 1 Cumulative CO_2 emissions of cellulosic samples, neat PP and PP modified during 120 days in the accelerated biodegradation test.

Table 1 Weight loss of the samples after accelereted biodegradation test.

Samples	Weight (g) before test (M_0)	Weight (g) after test (M_F)	Weight loss
Cellulosic	0.2026	0	-
Neat PP	0.4628	0.4624	0.08
PP modified	0.3296	0.2966	10.01

Conclusion

The PP modified in accelerated biodegradation test showed a high level in the production of CO_2 and the weight loss of the PP modified compared with the neat PP, confirm that the organic additive are efficient in biodegrading polypropylene.

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INFLUENCE OF INORGANIC FILLER IN NATURAL AGEING OF SAMPLES OF NATURAL RUBBER

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Decomposition time of the natural rubber (NR) products post-use is an important point to be considered, since this material has a long decomposition time. Some researches incorporated montmorilonitic nanoclays in their formulations of elastomers to increase its mechanical properties but it was also found an increasing of the material degradation with the course of time[1]. Other authors affirmed that these nanoclays retard the degradation due to the effect of the increasing the barrier properties of these materials[2]. Other studies have shown that the titanium dioxide (anatase phase) has photocatalytic activity and low toxicity[3]. Therefore, the aim of this work was to evaluate the effect of nanoclays (Cloisite Na+ and Cloisite 20A) and titanium dioxide in the degradation of vulcanized NR products before and after natural ageing in 30, 60 and 90 days. After exposure to weathering, visual characteristics of the samples have been modified, and it can be seen visually in Figure1-a. To quantify the degradation, colorimetric measurements were performed. Results of colorimetric analyzes (Figure 1-b) showed an increasing of the variation of the color, that was calculated by $\Delta E=[(L_n-L_0)^2+(a_n-a_0)^2+(b_n-b_0)^2]^{1/2}$, where "L" represents the luminosity and the "a" and "b" refer to the content of red and yellow, respectively. This increase of the ΔE is more evident in the filled samples, especially in NR Na+ and NR 20A samples in comparison with the sample of NR pure. Results of tensile tests (Figure 2) showed that there was a significant change in the mechanical properties of NR. The maximal rupture tension increased for samples NR Na + and NR 20A when compared with the NR pure in the initial time. However, it was observed a decreasing of rupture tensile of the samples with nanoclays when compared to the others after exposition at natural environment. These results indicated that the presence of nanoclays in NR have influence in accelerating the NR degradation.

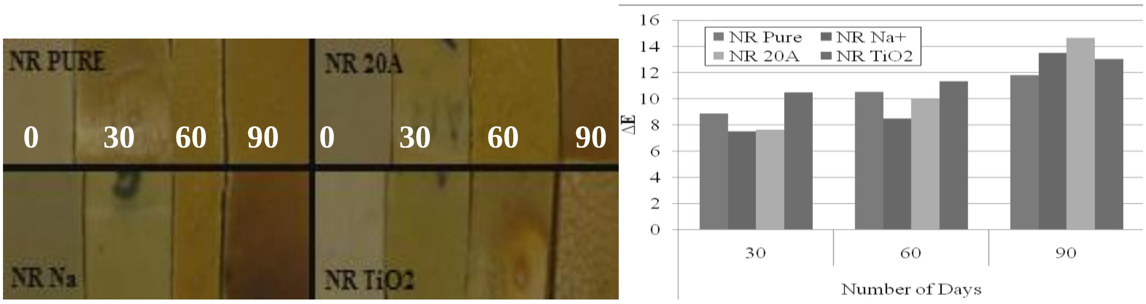

Figure 1 –Variation of the coloration of the samples with the time – left- (a) and (b) ΔE.

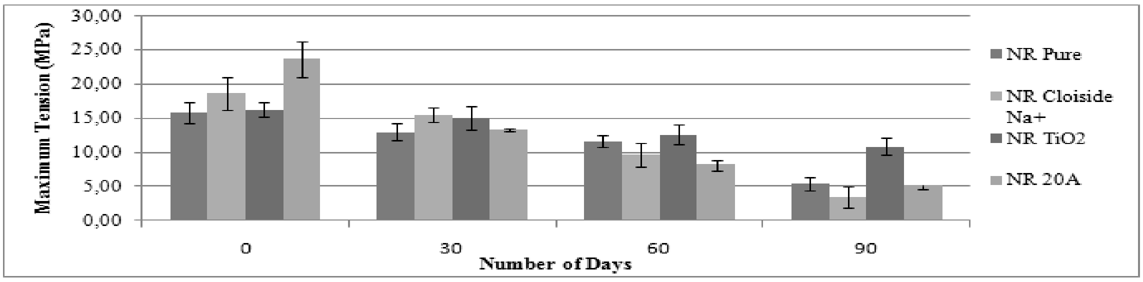

Figure 2 –Monitoring of the rupture tension of the samples in function of exposition time.

Analyses of the samples surface were performed with FTIR-ATR where the carbonyl index was calculated, considering the reference peak a 1450cm^{-1}. It was seen after 60 days that NR Na+ showed the higher carbonyl index, followed by NR TiO_2, NR Pure and NR 20A, as can be seen in Table 1.

Table 1 – Variation of Carbonyl Index (CI) of the samples with the exposition time.

Sample	CI_0	CI_{30}	CI_{60}
NR Pure	1,0860E-02	1,8555E-02	3,3584E-02
NR Na+	4,8074E-03	1,9056E-02	9,5194E-02
NR 20A	5,7141E-03	1,4602E-02	2,6690E-02
NR TiO_2	1,2248E-02	3,8094E-02	8,9975E-02

It was concluded that the addition of nanoclays increase initially the mechanical properties of the product but also act as a pro-degrading in natural environment, by accelerating aging, which was perceived by a decrease of mechanical properties, variation in color and carbonyl index compared with the NR pure in the period evaluated (90 days).

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THERMAL AND THERMO-OXIDATIVE DEGRADATION PATHWAYS IN BIODEGRADABLE POLY(BUTYLENE SUCCINATE)

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We have investigated the thermal and thermo-oxidative degradation processes occurring in synthetic and commercial poly(butylene succinate) (PBSu) samples[1]. Thermal-oxidation was performed in atmospheric air using extremely thin polymeric films at 170°C up to six hours. Degradation produces a sensible reduction of the molar mass of the polyesters (Fig. 1), promoting the formation of PBSu oligomers with different end groups. A considerable amount of structural information on the thermo-oxidation products of PBSu has been extracted from MALDI analysis. The complete identification of the structures and end groups attached to the oligomers produced is important, since the end groups reveal the particular mechanism that has been active in the degradation processes. Based on the structures of the mass ions identified, an α-H abstraction mechanism has been unambiguously ascertained to occur in PBSu and in Bionolle 1001. The initial step in this process consists of α hydrogen abstraction from the methylene group adjacent to the ester linkage, leading to the formation of a hydroperoxide intermediate. Remarkably, the hydroperoxide intermediate (I) decomposes by radical rearrangement reactions via the hydroxyl ester (III) (Scheme 1, route 1) or from the radical (II) which may follow two different pathways (Scheme 1, routes 2 and 3). The oxidized polymer chains originated from the decomposition mechanism summarized in scheme 1 had not been revealed before. Interesting, these three degradation pathways have been revealed to be time-resolved, showing a different induction period. In addition, thermal degradation experiments were also performed under nitrogen at 240-260°C. The new species identified in the MALDI spectra of both samples support a decomposition pathway taking place through a α-hydrogen transfer bond scission, followed by the production of succinic anhydride from succinic acid end molecules via a cyclisation decomposition mechanism.

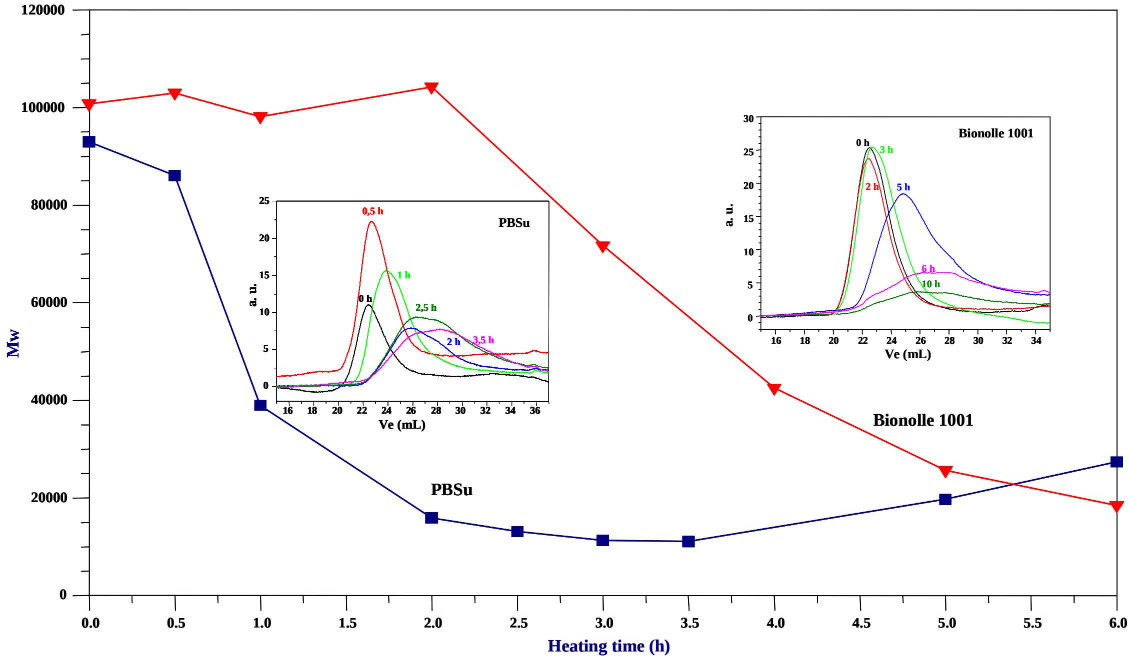
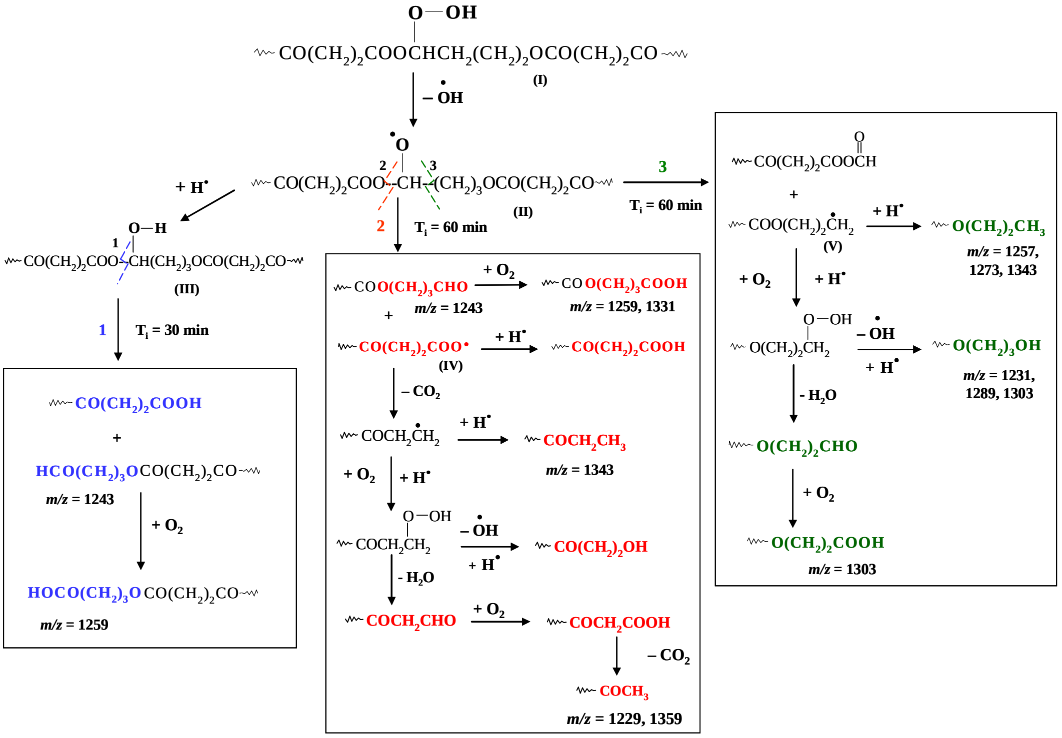


Figure 1. Molar mass values and SEC curve traces of (■) PBSu and (▼) Bionolle 1001 samples thermo-oxidized at 170 °C as a function of the heating time.



Scheme 1. Overall thermal-oxidation processes in PBSu (Ti = induction time).

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THERMO-OXIDATIVE DEGRADATION PRODUCTS IN POLY(BISPHENOL A CARBONATE) BY ESI AND MALDI MASS SPECTROMETRY

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The oxidative degradation of PC films having a thikness of 3-4 µm was carried out at 300 °C and the extracted products in methanol/acetonitrile (90:10,v/v) were analyzed for the first time by using direct Electrospray Mass Spectrometry. Matrix Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry (MALDI) analysis were also performed on soluble parts of PC samples. More than 50 compounds originated from PC oxidation at 300°C were detected. Together with the formation of BPA and its related oligomers, several new structures containing BPA and biphenyl units, phenols, acetophenones, alcohols, acids and xanthones molecules were identified. PC species detected allowed to get precisely information about the degradation mechanisms involved during thermo-oxidation of PC materials, revealing the concomitant contribution of diverse well known thermal and thermo-oxidative processes. In particular, the use of thin film instead of PC bulk allowed to establish a new order of priorities among the degradative reactions during thermo-oxidative processes. Hydrolysis of carbonate groups with the production of BPA is the predominant degradative reaction at 300°C, followed by thermal and thermal-oxidative reactions on the PC isopropenyl units. Remarkable, alcoholic intermediate oxidation species as well as benzoic and benzylic acids, due to oxidation of acetophenone and phenyl substitutes acetone, which had escaped previous studies[1,2], have been detected. When heating times increases, the oxidative coupling reactions leading to the formation of BPA oligomers characterized by biphenyl bridges become significant (Figure 1). Furthermore, structures having xanthone rings along the chains, due to pure thermal degradation mechanisms, are produced and revealed. Finally, the extraction of o-carboxyl p,p'-isopropyl bisphenol molecules (*m/z* 271.103) among the thermo-oxidized compounds strongly supports the isomerization of the carbonate groups with the consequent production of xanthones units (Figure 2).

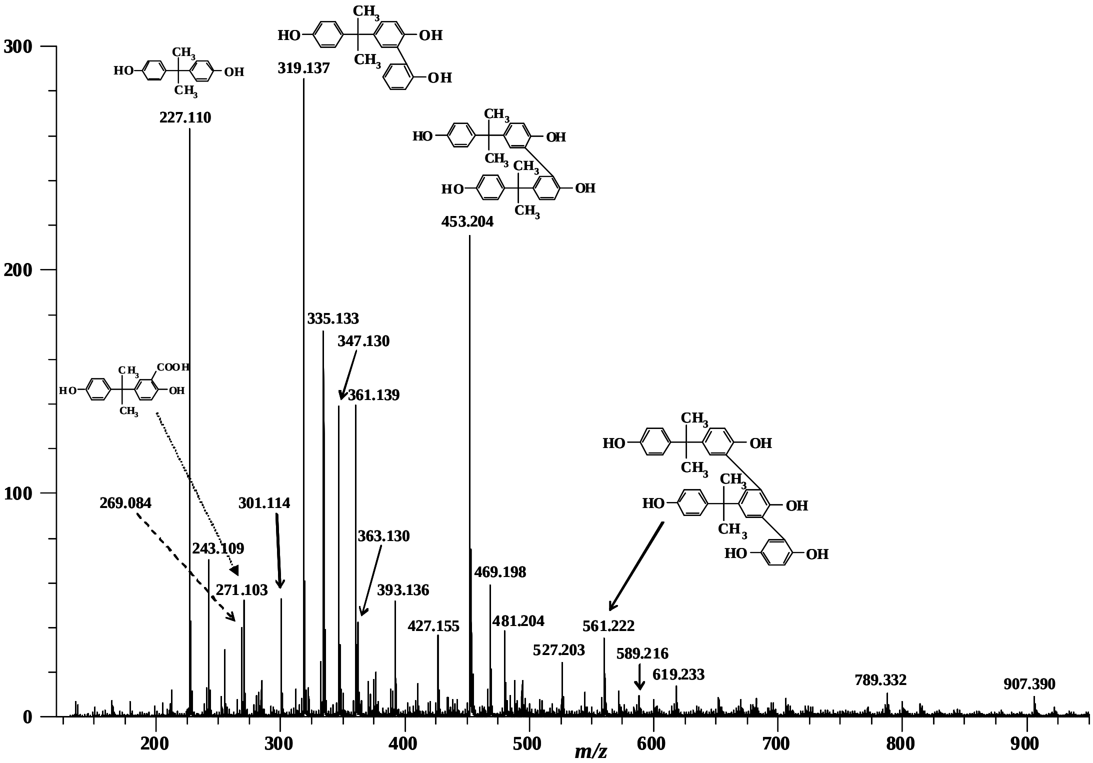

Figure 1. ESI mass spectra, in negative ion mode, of the degradation products extracted in CH_3OH/CH_3CN 90/10 at 300°C

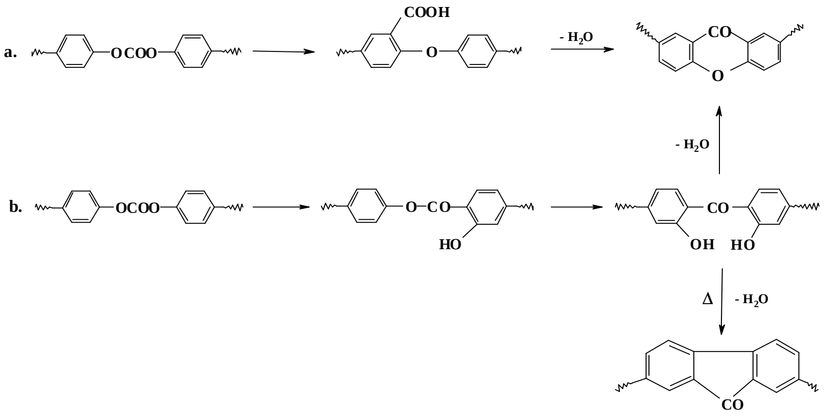

Figure 2. Alternative isomerization and degradation processes leading to xanthones.

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PHOTO AND THERMAL-OXIDATION PROCESSES IN POLY(BUTYLENE TEREPHTHALATE): A COMPARATIVE STUDY

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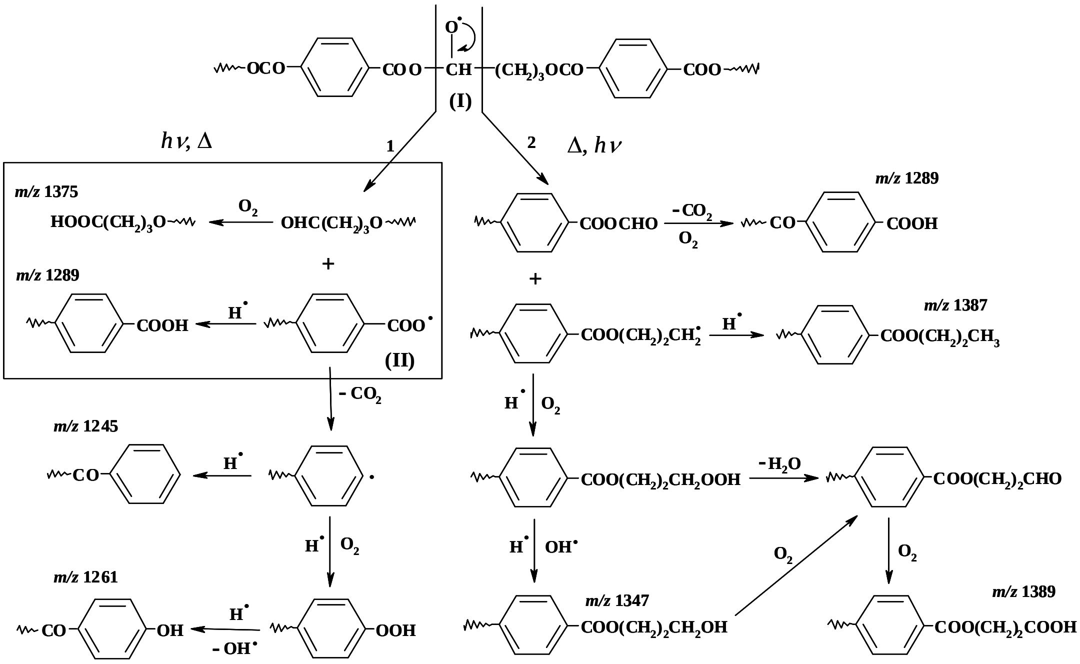
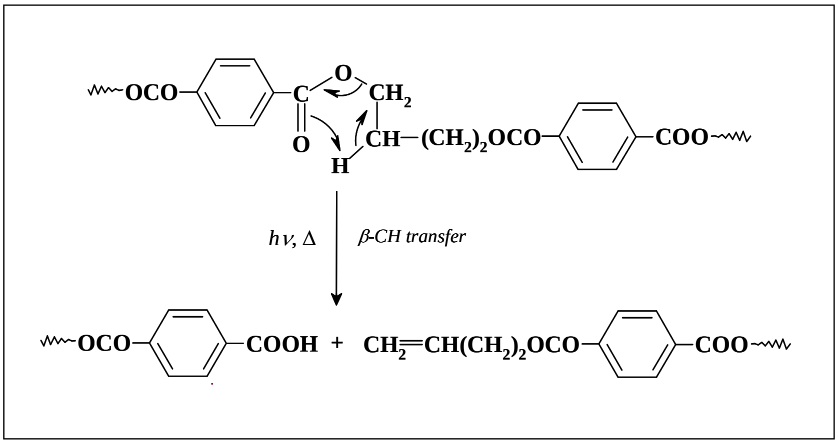
In this work we have reported the thermal and photo-oxidation studies of a PBT sample by using the highly sensitive MALDI-TOF MS instrument[1]. The structural analysis of the oxidation products provided by MALDI allowed construction of an exhaustive scheme of the thermal and photo-oxidation mechanisms of poly(1,4-butylene terephthalate). According to the structure of the major oxidation products detected by MALDI (Scheme 1), two thermo-oxidation processes and two photo-oxidation cleavages have been unambiguously ascertained to occur in PBT. A *α-H hydrogen abstraction* mechanism contributes to both the photo and thermal oxidation of PBT at 250 and 280°C, leading to the formation of similar series of oligomers discriminated by MALDI. In fact, the extraction of a methyl hydrogen, yielding a methylene radical which reacts with oxygen to form a hydroperoxide intermediate (Scheme 1) activates both the photo- and thermal processes. The decomposition of this hydroperoxide, when occurring thermally at 250 and 280°C, leads straightforwardly to all the end groups represented in Scheme 1 (route 1 and 2). On the other hand, the photo-oxidation, performed at 70°C, is more selective, and the oxidation products bearing phenyl and phenol end groups, deriving from loss of CO_2, are not observed (Scheme 2, route 1). Our results evidence that the *α-H hydrogen abstraction* plays an important role in the photo-oxidative degradation process and becomes the prominent mechanism at higher exposure times. Furthermore, MALDI mass spectra support a specific thermo-oxidative pathway: the oxidative coupling of phenyl rings that create byphenyl bridges between PBT chains. This reaction produces char-like structures that escaped in previous studies. Additionally, the inspection of the data acquired by MALDI allowed discriminating the degradation mechanisms entirely induced by light or heat without the involvement of oxygen. In fact, the well known *β-hydrogen transfer* is promoted by pure photolysis action (Norrish II) as well as by pure thermal degradation process at 280°C (Scheme 2).



Scheme 1. *α-H hydrogen abstraction* mechanism.



Scheme 2. *β-Hydrogen transfer* mechanism.

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DEGRADATION OF LOW MOLAR MASS PET/ORGANOCLAY NANOCOMPOSITES

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From an industrial point of view, preparation of thermoplastic nanocomposites by melt blending, using conventional plastic compounding tools is the best choice, due to its simple and versatile processing way. However, this method can cause thermal decomposition of commonly used alkyl ammonium ions in modified clays, which caused further degradation of polymer matrix[1-3]. Thus, the purpose of this work was to prepare a low molar mass PET/organoclay nanocomposites by melt extrusion, and to examine the influence of organoclay content on the PET degradation.

PET with low molar mass and intrinsic viscosity of 0.60 dL/g from Mossi & Ghisolph S.A., in pellet form was used. An organically modified montmorillonite (MMTO) with a cation exchange capacity of 90 mequiv/100 g and a real density of 1.98 g/cm^3 was purchased from Southern Clay Products, INC., USA. The ammonium cation of clay is reported to be methyl tallow bis-2-hydroxyethyl quaternary ammonium. PET and MMTO were dried under vacuum at 180 °C and 80 °C, respectively, for at least 12 h before use. PET was mixed with the desired quantity of organoclay (1, 3 and 5 wt %) and processed at one compounding step in a co-rotation twin-screw extruder. The characterization was made by the intrinsic viscosity measurements (IV), differential scanning calorimetry (DSC), thermogravimetric analyses (TG), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The pristine PET shows a slight reduction of intrinsic viscosity (from 60 to 54 mL/g) which can be considered as the result of a combination of temperature and mechanical shear encountered during processing[4]. Thus, the organoclay addition influenced on the polymer degradation during processing, which can be attributed to a consequence of an increase of the amount of Brønsted acidic sites on the platelet surface available for polymer degradation[2].

Compared with the pure PET, the maximum transitions peaks of the nanocomposites, containing different clay contents were virtually unchanged in the DSC thermograms. On the other hand, with the increased of 3 wt % of MMTO in the PET matrix occurred an increased of melting enthalpie and the degree of crystallinity, suggesting that the organoclay could interfere in the crystallizable material amount. To explain these results it can be hypothesized that a more pronounced degradation of PET matrix occurs when was added 3 wt % of MMTO. In this case, on decreasing of the molar mass, the chains become more mobile and more prone to form crystallites with lower regularity[5].

The decomposition temperature (T_d) at which there is 10 wt %, 50 wt % of weight loss and residues (R_e) at 650ºC can be seen in Table 1 and it is possible to observe that with the increase of organoclay in the PET matrix the T_d, for both temperatures, decreases suggesting that MMTO could cause the polymer thermal instability, which is attributed to the decrease on polymer molar mass, supported by the IV measurements, due to the presence of Brønsted acidic sites on the platelet surface available for polymer degradation during processing.

Table 1. Paramenters of TG curves of pure PET and nanocomposites under inert conditions at 650ºC.

Composition	$T_{10\%}$ (ºC)	$T_{50\%}$ (ºC)	R_e (wt %)
PET-0%	401	434	4
PET-1%	400	434	11
PET-3%	394	432	12
PET-5%	392	432	16

The XRD peak shifted from 4.9° for pure MMTO to 2.8° for PET nanocomposites filled with 5 and 3 wt % of organoclay, which suggests intercalation of the polymer molecules in the clay galleries. For the PET filled with 1% of organoclay, the absence of the clay diffraction peak suggested clay delamination. However, this could also be related to the low organoclay content and/or to the platelets disorganization in to the polymer matrix.

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THE INFLUENCE OF THE CLAY'S PRESENCE ON THE POLYPROPYLENE-MONTMORILLONITE NANOCOMPOSITES

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The development of nanocomposite materials, especially those using layered silicates, with polymeric matrices, provides an alternative to conventional composites with fillers[1]. One of the aspects shortly discussed in scientific literature of polypropylene-montmorillonite nanocomposites (PP/MMT) is about the influence the organoclay on composite thermal stability. In this work the nanocomposites were prepared by melt intercalation process in a twin-screw corotating extruder (operating at 120 rpm and at 170°C,) and were injected according to ASTM D-638 type 1, using a isotactic polypropylene (PPH105 - Braskem, Brazil) and an organoclay Cloisite® 20A (Southern Clay Products Inc.). The nanomposites were prepared with 1, 3 and 5% w/w. The materials were characterized by thermogravimetry and melt flow index.

Thermogravimetric analyses (TGA) were carried out until obtaining of inorganic and organic residues, and the decomposition profile of the nanocomposites. The samples of PP and the PP/MMT nanocomposites were heated from 25 to 600°C at 10°C/min under oxygen flow. The Table 1 shows the temperature values of 5% and 25% weight loss ($T_{5\%}$ and $T_{25\%}$) for the samples. This table reveals that PP/clay nanocomposites show an increase in both temperatures. The plausible reason is the intimate contact between the polymer molecules and the inorganic crystalline layers acting as diffusion barriers for the oxygen[2], causing a higher thermal stability than the pure PP.

Table 1. Values obtained by TGA for PP and for PP/MMT composites with different concentrations of an organoclay.

Samples	$T_{5\%}$ (°C)	$T_{25\%}$ (°C)
PP 0%	379.43 ± 2.055	271.90 ± 1.961
PP 1%	381.30 ± 8.885	335.89 ± 1.855
PP 3%	408.72 ± 2.961	387.57 ± 1.495
PP 5%	457.10 ± 5.445	417.80 ± 7.475

The analysis of the melt flow index (MFI) was used in this work because it is a simple method to study the relationship between composition and rheology of the nanocomposites[3]. The MFI was determined using a CEAST plastometer with temperature of 230°C and load of 2.16 kg according to ASTM D1238. All analyzes were performed in triplicate and are expressed as g/10 min (Table 2).

Table 2. Average melt flow index results for polypropylene and the PP/MMT composites with different concentrations of an organoclay.

Samples	MFI (g/10 min)
PP 0%	40.108 ± 0.049
PP 1%	36.546 ± 0.914
PP 3%	32.806 ± 0.025
PP 5%	27.018 ± 0.015

The thermal stability caused by the addition of an organoclay may be explained by the effect of barrier layers of the remaining silicate layers for the process of thermal decomposition. The rheological behavior of a nanocomposite polymer with inorganic filler is sensitive to the amount of filler used, especially at low shear rates, such as those found in a plastometer, where the effects of the direction of the flow are minimized[3]. In comparison with virgin PP, nanocomposites with 1, 3 and 5% organoclay have MFI lower or, in other words, higher viscosities. The decrease in MFI of composites may influence on thermomechanical degradation because of their lower capacity to change spacial conformation with mechanical stimulus, which may cause chain scission during processing.

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FIRE BEHAVIOR OF ISOPHORONE DIISOCYANATE BASED FLEXIBLE POLYURETHANE FOAMS

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Introduction: In this work a preliminary study of the fire behavior of a novel polyurethane foam obtained from isophorone diisocyanate (IPDI) is presented. The fire behavior was evaluated from thermogravimetric and limiting oxygen index (LOI) data.

Materials: The foams were prepared from isophorone diisocyanate (Vestanat IPDI, Evonik Industries) and a polyether polyol (Desmophen 4042 BT Bayer), using dibutyl tin diacetate, stannous octoate and 1,4-Diazabicyclo[2.2.2]octane (Aldrich) as catalysts and a silicon surfactant (Tegostab B 8110 Evonik Industries). Water was used as blowing agent. The foams were obtained by the one-step method at 70 ºC in a computerized foam qualification system (FOAMAT).

Methods: Thermogravimetric experiments were carried out in a TGA Q-500 (TA instruments). Samples were heated up to 550 ºC at a rate of 10 ºCmin^{-1} under nitrogen and air. Limited oxygen index and foam density were measured according to ASTM 4589 and ASTM D 1622-98 respectively.

Results and discussion: White foams with a density of 0.04 g/cm^3 were obtained. The foam presented open cells (Figure 1).

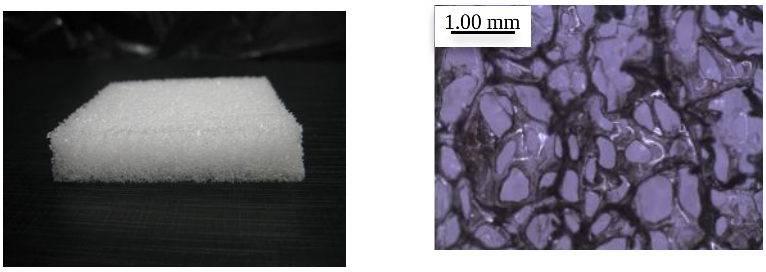

Figure 1: Photograph of the foam (left) and optical microscopy picture (right) of the cross-sectional surface of the foam.

Figure 2 shows the TG and DTG curves of the foams obtained under nitrogen and air atmosphere.

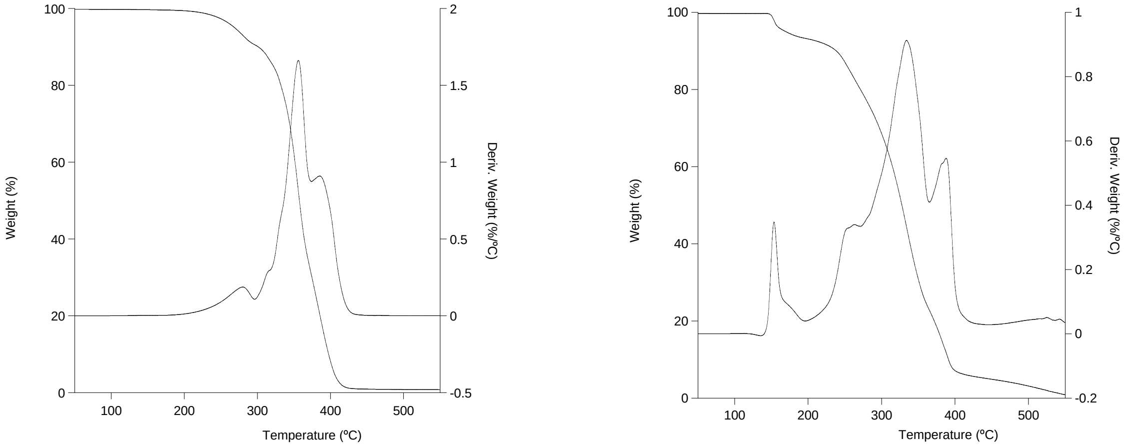

Figure 2: TG and DTG curves of the PU foam obtained under N_2 (left) and air (right).

The thermogram obtained under nitrogen showed two main steps of decomposition. According to literature[1] the mass loss of both steps corresponds to the decomposition of urethane and ether segments respectively. The pyrolysis occurred almost without any residue. In oxygen containing atmosphere the decomposition temperature was clearly lower than the obtained in nitrogen[2].

Limited oxygen index (LOI) is normally used as a qualitative method to evaluate the fire retardancy of polymeric materials. The IPDI based foam synthesized in this work showed a value of 20. Although this value means that the foam will support the burning in open air, aromatic isocyanate based foams show similar values before adding fire retardant additives[3,4].

Conclusion: IPDI based polyurethane foams were successfully obtained by the one step method. The material showed a thermal stability and LOI value similar to those of aromatic isocyanate based foams.

Acknowledgement: The authors thank the Basque Government (PhD scholarship), The University of the Basque Country (UFI 11/56) and the Ministerio de Ciencia e Innovación (MAT2010-16171) for the funding received to develop this work.

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ACCELERATED AGING TESTING OF HEAT STORAGE LINER MATERIALS USING MICRO-SIZED SPECIMENS

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A main goal of the basic research project SolPol-1 (www.solpol.at) is to develop accelerated aging methods for polymeric materials in solar thermal applications. In literature, sample thickness[1,2] and geometry[1,2] are considered to be two important parameters that strongly influence polymer oxidation. Hence, current work focuses on the evaluation of a testing approach based on micro-sized specimens with a thickness of 200 µm, which is a factor 10 below the nominal component thickness for polyolefin liner materials for heat storage tanks.

A Polyolefin (PO)-based model polymer system with systematic variation of the long-term thermal stabilizer packages (i.e., antioxidants (AO); s. Tab. 1) used as a liner for modular heat storage tanks was extruded to 2 mm thick sheets. 200 µm thick specimens were prepared by manual planing with a common planing tool running on a guide and aged at 135°C in circulating air. Specimens were removed in constant intervals and characterized by differential thermal analysis (DTA; aging indicator: oxidation temperature T_{OX}) and tensile testing (aging indicator: strain at break $\varepsilon_{B)}$.

The results of the aging tests (Fig. 1) show that for both T_{OX} and ε_B a clear distinction between the stabilizer performance of the 5 formulations under investigation is possible. The ranking of antioxidant performance for the formulations investigated is 01, 02 < 04 < 03 < 05. Stabilizer system 05 (time to embrittlement: 267 d) more than doubles the lifetime at 135°C oven-aging compared to the not additionally stabilized system 01 (time to embrittlement: 120 d). Comparison of T_{OX} and ε_B reveals that embrittlement occurs when T_{OX} values drop below 230°C to 220°C. Interestingly, with exception of formulation 03, the ranking of the long-term thermal stability (LTTS) of the different formulations as deduced from the completed aging tests can be derived from T_{OX} values after only three weeks. Thus, aging tests based on micro-sized specimens could allow for faster ranking of the LTTS of specific stabilizer systems.

Table 1 Investigated PO-based material formulations and designations (AO1 and AO2: Primary AO; AO3 and AO4: Secondary AO).

PO formulation no.	Additional stabilizer	
01	none	
02	AO1	AO3
03	AO1	AO4
04	AO2	AO3
05	AO2	AO4

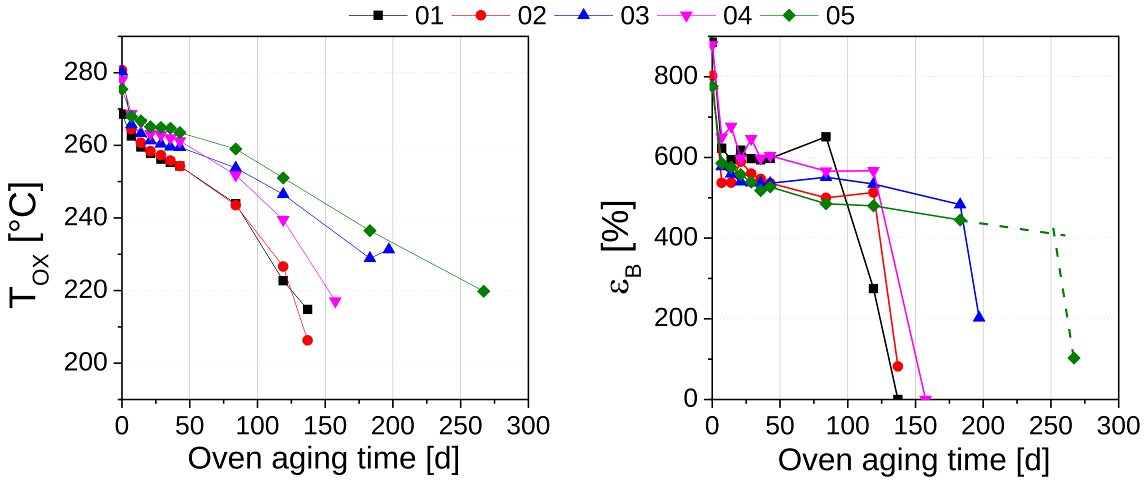

Figure 1 Graphs for oxidation temperature T_{OX} and strain at break values ε_B for investigated micro-sized specimens aged at 135°C in circulating air.

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BIODEGRADATION OF PLASTIFIED STARCH OBTAINED BY COROTATION TWINSCREW EXTRUSION

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The properties of obtained plastics strongly depend on mode and techniques of their manufacturing[1]. Earlier research showed[2] that mechanical degradation of starch prevailed over the thermal decomposition. Screw configurations of intensively acting plasticizing and mixing performance will probably drastically degrade the starch[3]. The results show that mechanical degradation mainly takes place in the so called “cooking” zone where the amylopectin chains break and the size of their molecules reduces.

The main objective of the present work was determination of extrusion conditions like rotation speed of screws and their configuration influencing degradation degree of plasticized starch and checking the influence of those parameters on its biological decomposition as a result of activity of typical microorganisms. For microbiological analyses following strains have been applied: Fusarium, Streptomyces, Bacillus.

To native starch has been added 25 weight percent of glycerol and mechanically mixed within 5 minutes. The mixture was extruded by corotating twinscrew extruder. Three samples: A, B and C have been prepared for tests. First sample A was extruded using screws of low intensity of mixing and shearing function. The process parameters were following: rotation speed of screws 160 min^{-1}, temperatures of extruder zones 80, 130, 150, 160, 180^{o}C (die head). Samples B and C were extruded using more intensity of mixing and shearing function that sample A. The processing temperatures samples B and C were the same as in case A. The sample B was obtained at the rotation speed 160 min^{-1}, sample C – 400 min^{-1}.

Relative humidity, ATR-FTIR spectra, SEC chromatography and microbiological analysis of starch and samples was determined

Low rotational speed and low intensive mixing do not cause strong degradation of polymer chain, but oxidizing processes of hydroxyl groups may arise. The intensity of mixing influences the formation of unsaturated links in polymer chain, which causes the yellowing. On the other side the enhancement of shearing speed when extruding causes the considerable polymer degradation connected with decrease of its molecular weight and formation of unsaturated ketone or aldehyde groups causing brownish look of the plastic. During activity of high shearing forces the starch crosslinking may cause lower solubility in water and lower susceptibility to biodegradation. All tested samples showed susceptibility to microorganisms (the rate of biodegradation - 4 after 7 days). The most susceptible to microorganisms was sample B which showed the highest moisture absorption and solubility in water. The quickest development was observed for actinomycetes as a most effective degrading factor for starch samples (Fig. 1). Plastification conditions of starch with glycerin in corotating twinscrew extruder have considerable influence on starch properties. However, the later biological decomposition is only slightly affected. This process is more effectively influenced by moisture absorption of the plastified starch.

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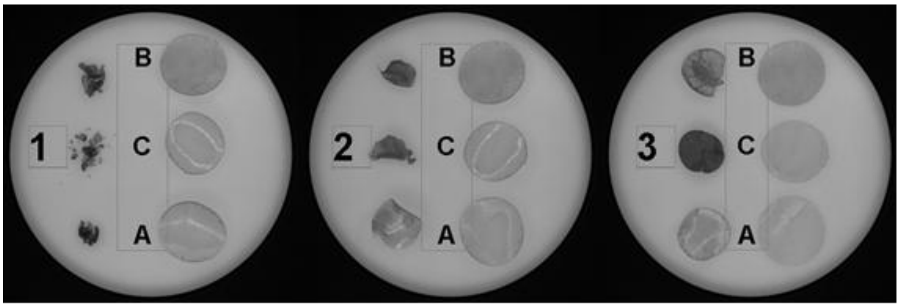

FIG. 3. Visual comparison of bacteria activity on samples A, B, C:
1 – *Streptomyces cyaneus*, 2 – *Bacillus subtillis*, 3 – *Fusarium culmorum.*
First column – after 28 days of activity, second column – referring samples

THE EFFECT OF NEWSPRINT PAPER MODIFICATION BY MAGNESIUM COMPOUNDS ON CELLULOSE DEGRADATION

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The degradation of cellulose is an important factor influencing its physical, mechanical, optical and chemical properties and the longevity of paper in stored paper and books. Several modification processes for the protection of lignocellulosic carriers of information are known, e.g. Bookkeeper process (MgO in perfluorheptane) or MMMK (methoxy-magnesium-methyl-carbonate in methanol). Some authors evidenced the correlation between degree of polymerization (DP) and the strength properties of paper, respectively cellulose.[1,2]

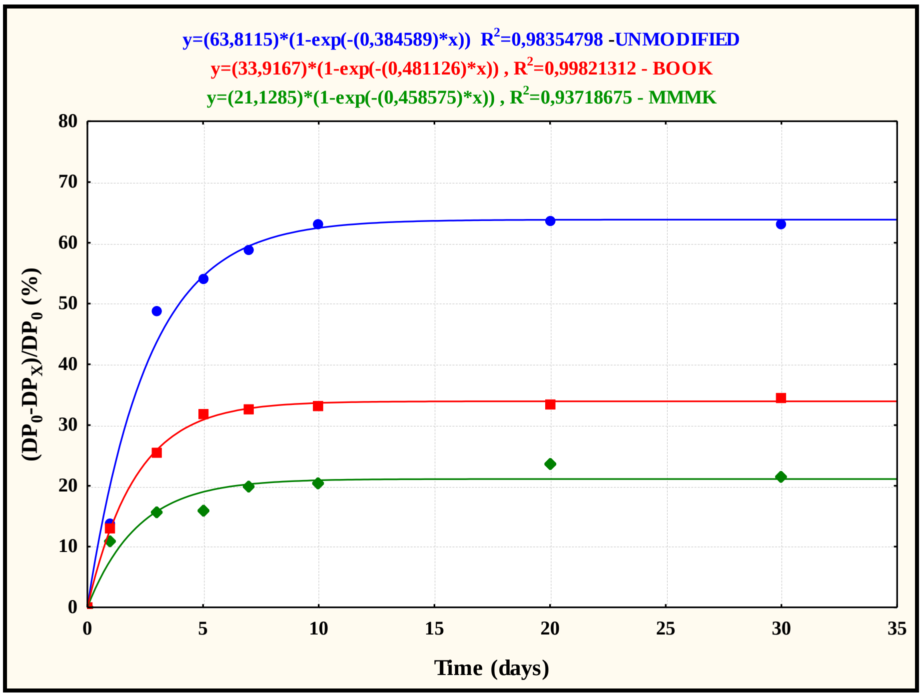

Fig 1 Change of degree of polymerisation (DP) plotted against time of ageing

Newsprint paper was modified by both magnesium compounds; accelerated ageing of sound and protected samples was performed at 98 °C and 50% RH during 1, 3, 5, 7, 10, 15, 20 and 30 days. The influence of treatment using MgO in perfluorheptane or a mixture dispersion of MgO in perfluorheptane and MMMK in methanol at cellulose degradation was evaluated by size exclusion chromatography (SEC) of cellulose tricarbanilates (CTC) prepared by adding of phenylisocyanate to dry sample in pyridine and the mixture was heated 6 h at 110°C.[3] The SEC analysis was carried out on PLgel MIXED B column in THF.[3]

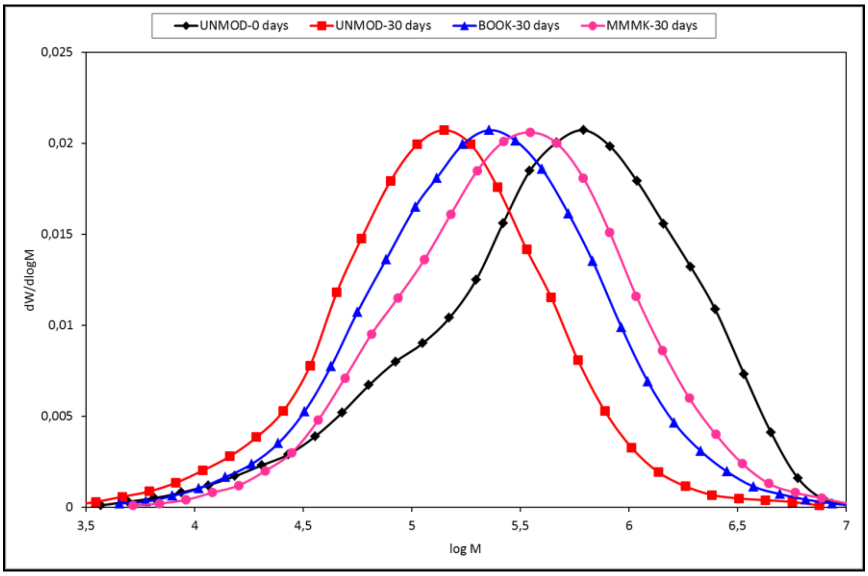

Fig 2 Molecular weight distributions of the tricarbanilates of the accelerated aged unmodified and modified newsprint paper at 30 days (UNMOD – unmodified, BOOK – Bookkeeper)

Cellulose degree of polymerisation (DP) of unmodified paper has decreased by 63%, sample modified by MgO by 35% and sample protected by mixture of MMMK and MgO by 22%, respectively. It can be concluded that modification by magnesium compounds has protective effect on cellulose degradation and thus for longevity of paper documents.

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THERMODEGRADATION OF PVB FILMS

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Abstract

In a previous work[1], the surface tension of PVB films (PVB copolymer and plasticizer) was evaluated as a function of temperature, for temperatures ranging from 180 to 260ºC, using the pendant drop method. This method involves the determination of the profile of a drop of one liquid suspended in another liquid (air in the case of surface tension measurement) at mechanical equilibrium. To evaluate the surface tension of the PVB film using the pendant drop, it was necessary to keep the film roughly five hours into the pendant drop apparatus, at the temperature at which surface tension is determined (in inert atmosphere). Moreover, prior to measurements, all samples remained under vacuum at a temperature of 120ºC for 2 hours. The results indicated that the surface tension decreases linearly with temperature but the variation of surface tension with temperature was shown to be more than ten times larger than the one of other polymers. In this work, in order to clarify the surface tension results, it was evaluated the chemical changes undergone by PVB films during the measurements using TG, FTIR and ESCA.

Results: Table 1 shows the surface composition (%) of PVB film drops, obtained by XPS. The quantitative analysis was performed using the ratio between the signal intensity of major peaks and a relative sensitivity factor (C1s).

Table 1. Results obtained by ESCA analysis.

Sample	*O=C-O*	*O-C-O*	*C-O*
PVB film	10.4	21.8	67.8
drop (120°C/2h)	10.2	22.6	67.2
drop (240°C/5h)	8	25.7	66.3
drop (260°C/5h)	3.7	29.0	67.3

Table 2 shows the results obtained by thermogravimetric analysis (TG) of PVB films. Figure 1 presents the infrared spectra of the samples for wavelengths ranging from 1900 to 1500 cm^{-1}. Absorption bands can be observed at 1735 cm^{-1}, corresponding to carbonyl group (C=O), and bands at 1652 cm^{-1}, relative to the axial deformation of the C=C double bonds[2].

Table 2 TG analysis of the PVB film drops and of treated PVB film (120ºC).

Sample	*Mass loss (film) (%)*
120 °C	0.9
240 °C	3.8
250 °C	21
260 °C	20

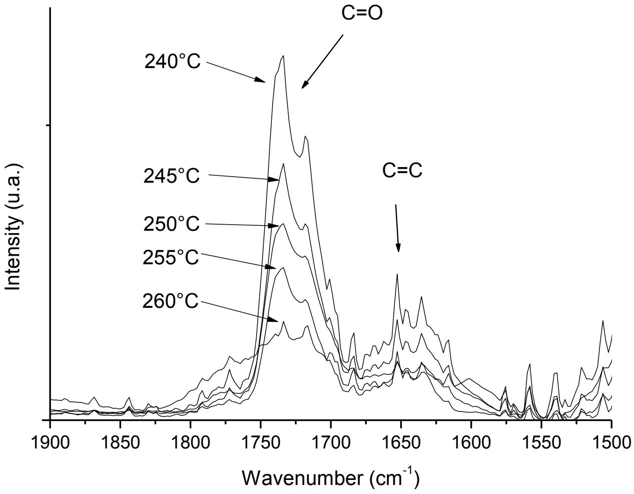

Figure 1 Infrared spectra of surface PVB drops.

Conclusion: The thermal degradation of the PVB film resulted in loss of polar groups present in its structure: there is a reduction in the absorbance of –OH and C=O bands. Also, during the pendant drop measurements the molecule of PVB suffers scission, leading to the formation of chains with C=C bonds[2].

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UV STABILITY OF POLYLACTIDE NANOCOMPOSITES REINFORCED WITH NANOCLAY

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In recent years biodegradable polymers have attracted more interest due to increasing environmental concern and decreasing fossil resources. Polylactide (PLA) is a biodegradable polymer well known for being a promising alternative to petroleum-based materials[1, 2]. Although PLA has good properties, it is known that it presents some disadvantages like poor thermal and mechanical resistance and limited gas barrier properties, which reduce the access to industrial sectors[3]. The incorporation of nanoclays has been used as a way to overcome this problem[4]. The degradation of polymers has a great influence on their behavior and a significant number of research papers have been devoted to the study of PLA and PLA/clay nanocomposites degradation[5].

The present work aims to compare the UV stability of PLA nanocomposites with 3 modified montmorillonite (Cloisite 30B, Cloisite 15A and Dellite 43B). The nanocomposites were prepared in a batch mixer with 3% clay incorporation and exposed to UV radiation in a Xenotest chamber.

The morphology of nanocomposites was evaluated by SEM and figure 1 shows the fractured surface the samples.

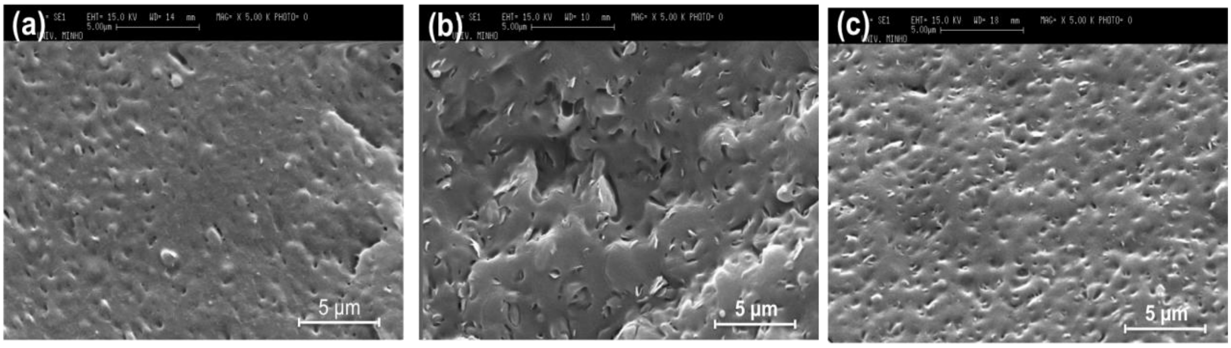

Figure 1 SEM micrographs of PLA with 3% incorporation of (a) C30B, (b) C15A, (c) D43B.

The micrographs reveal a good degree of clay particles dispersion with C30B and D43B and the presence of clay aggregates with C15A. Strong interactions of PLA chain and hydroxyl groups of C30B seem to improve the dispersion of this clay.

After 200, 400 and 600 hours of photo-degradation changes in intrinsic viscosity were observed (figure 2). Nanocomposites with C30B and C15A have a greater decrease in intrinsic viscosity than D43B and PLA without clay.

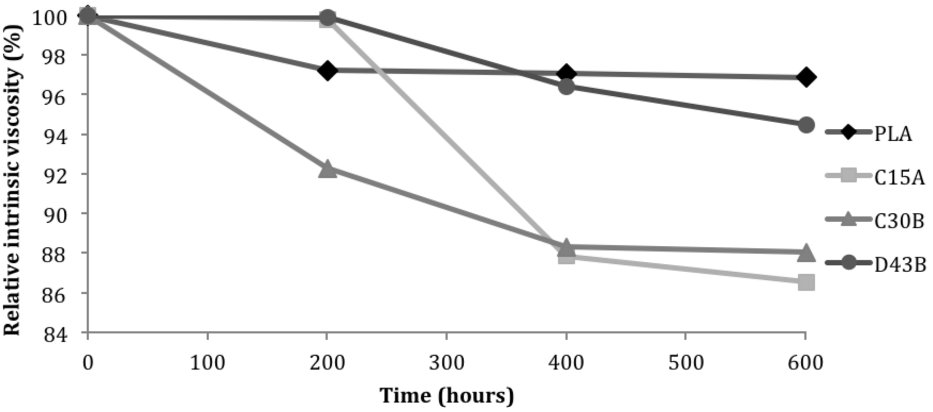

Figure 2 Relative intrinsic viscosity of PLA and PLA nanocomposites with 3% clay incorporation along photo-degradation time.

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POLYMERS AND ENVIRONMENT

Full Abstracts of Oral Presentations

SOLID STATE POLYMERIZATION OF POLY(LACTIC ACID): CRITICAL PROCESS PARAMETERS

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INTRODUCTION

Solid state polymerization (SSP) comprises an eco-friendly polymerization technique and a standard step for molecular weight build-up of PET and of PA 6.6. It involves heating the prepolymer to a temperature above the glass transition point but below the onset of melting; polycondensation progresses through chain end reactions in the amorphous phase of the semicrystalline polymers and reaction by-products are removed by maintaining reduced pressure or through convection caused by passing inert gas[1-3]. Poly(lactic acid) (PLA) comprises one of the most promising materials from renewable resources, serving as an alternative for polymers on fossil basis[4-5]. The current work aims to apply SSP on PLA prepolymers so as to limit melt polymerization time. The process parameters herein studied were prepolymer initial molecular weight, reaction temperature and time, in order to establish an optimized SSP profile.

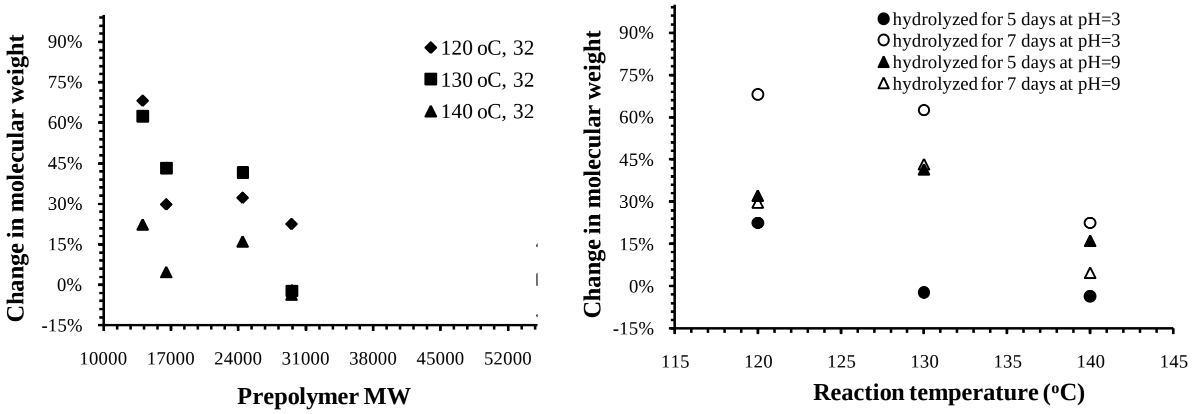
EXPERIMENTAL

Commercial PLA (NaturePlast) of 171500 g mol^{-1} was hydrolyzed at 60 ^{o}C under acidic (pH=3) and alkaline (pH=9) conditions for 3, 5 and 7 days in order to prepare suitable PLA prepolymers. The hydrolyzed grades were then submitted to SSP in a bench scale cylindrical stainless steel reactor at 120, 130 and 140 ^{o}C, for 16, 24 and 32 h under flowing nitrogen.

RESULTS AND DISCUSSION

PLA SSP under the studied conditions resulted in up to 68% increase of molecular weight. However, different trends were observed depending on the prepolymer starting molecular weight (MW), reaction temperature and time, as well as hydrolysis conditions.

In particular, it was found that PLA SSP at 120 and 130 ^{o}C occurred at a significant extent in the case of prepolymers with low MW, revealing a critical starting MW value at 30,000 g mol^{-1} for SSP efficiency (Fig.1a). On the other hand, at the highest SSP temperature of 140 ^{o}C, the SSP rate was kept low independently of starting MW, potentially due to accelerated side reactions.



(a) (b)

Fig.1. a) Change in molecular weight after 32 h of SSP of both grades, b) change in molecular weight vs. reaction temperature for prepolymers of MW<30,000 g mol^{-1}.

With regard to the influence of the reaction temperature (Fig. 1b), it was observed that the samples hydrolyzed under alkaline conditions (pH=9) showed the highest molecular weight change at 130 ^{o}C, while SSP at 120 ^{o}C was proved most efficient for the samples hydrolyzed under acidic conditions.

Finally, when comparing the prepolymers with the lowest starting MW, hydrolysis under acidic conditions favored post reaction compared to hydrolysis under alkaline environment.

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DURABILITY OF POLYLACTIDE-BASED NANOCOMPOSITES IN DIFFERENT ENVIRONMENTS

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Polylactide (PLA)-based nanocomposites have been successfully prepared by a melt intercalation method using Cloisite 30B (C30B) as organoclay. The material morphology obtained from this protocol indicates that the dispersion of mineral platelets within the PLA matrix is relatively homogeneous, as revealed by wide angle X-ray scattering, transmission electron microscopy, rheology and nanoindentation[1].

Thus, the aim of the present communication is to develop the influence of different kinds of environments (natural ageing, gamma-irradiation and biodegradation in compost) on the structure, the morphology and the thermo-mechanical properties of PLA/C30B nanocomposites. The results obtained are discussed on the basis of neat polymer. The degradation of the aged samples is evaluated as a function of clay contents (1, 3 and 5 wt.%) using several techniques as infrared spectroscopy, steric exclusion chromatography, nanoindentation measurements, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy and transmission electron microscopy[2].

The natural weather effect on PLA/C30B nanocomposites with respect to neat PLA has been studied up to 130 days. The FTIR results showed that the photo-oxydation mechanism of PLA was not modified in the presence of C30B, but only the degradation rates were accelerated. The decrease of molecular weights associated with an enhanced polydispersity of the nanocomposite samples indicated that chain scission was the most prominent phenomenon in natural weathering. Under natural weathering exposure, the PLA nanocomposites undergo photo-oxidative degradation by free radical process which can lead to a breakdown of the polymer backbone and to the formation of lower molecular weight species. These structural modifications are responsible for the deterioration of the physico-mechanical properties of the samples.

Then, the effect of the gamma-irradiation at low doses (up to 100 kGy) on the structure and properties of neat PLA and PLA nanocomposites containing 5 wt.% of C30B has been also investigated[3]. Results show the gamma-irradiation leads to a severe decrease in the molecular weight of PLA and nanocomposites as a function of radiation dose, suggesting PLA degradation due to chain scission mechanism. Nevertheless, thermal and mechanical properties are less affected in the case of nanocomposites than in the case of neat PLA. This behavior may be explained by the homogeneous dispersion of C30B platelets in the PLA matrix, leading to a relative inhibition of gamma radiation effect.

Finally, some results concerning the biodegradation rate of these materials, i.e. neat PLA and PLA-C30B nanocomposites filled up to 5 wt.%, have been obtained in compost at 58°C and the nanoclay role on the PLA biodegradation kinetic has been discuss[3]. The biodegradation curves clearly show improved biodegradability for PLA nanocomposites compared to pure PLA. The improved biodegradability of PLA after nanocomposites preparation may be due to a catalytic role of the nanofiller in the biodegradation mechanism as usually explained in the literature. The presence of residual hydroxylated groups at the C30B surface may be one of the factors responsible of this behavior.

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WOOD-FILLED LLDPE COMPOSITES WITH IMPROVED BIOCIDE PROPERTIES

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Introduction

The effects of the silica containing immobilized nanocopper (SiO_2-Cu) as well as maleated linear low-density polyethylene (MLLDPE) on the phase behavior, microstructure and mechanical properties of wood-filled linear low-density polyethylene composites (LLDPE/W) were studied using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetry (TGA) and dynamic-mechanical analysis (DMTA). Furthermore, the ability of SiO_2-Cu to give bactericidal properties was also investigated for the first time in such nanocomposites.

Experimental

Materials

The linear low-density polyethylene (LLDPE) was supplied by Dow Chemicals (Dowlex4056G). The soft wood fiber (Lignocel C 120) with particle size 70-150 μm was provided by J. Rettenmaier GmbH. Maleated linear low-density polyethylene containing 0.68 wt.% of grafted maleic anhydride was prepared by melt blending according to the procedure published elsewhere [1] and used as a compatibilizer at the concentration of 5 wt.%. Spherical silica containing immobilized nanocopper synthesized according to the developed sol-gel process [2, 3] was used as a nanofiller.

Preparation and methods

Prior to preparation of samples, wood fiber was dried at 65 ± 2 °C for 24 h. Then, LLDPE, wood fiber, MLLDPE and SiO_2-Cu were melt mixed using a Berstorff ZE-25x33D twin screw co-rotating extruder (D = 25 mm, L/D = 33) according to the process published elsewhere [4]. Samples for structural and mechanical tests were prepared by injection molding using Arburg 420M injection machine, type Allrounder 100-250.

Escherichia coli strain ATCC 8739, *Staphylococcus aureus* strain ATCC 6538 and *Salmonella typhimurium* strain ATCC 14028 were used as test organisms to check bactericidal properties. The exact initial concentration of bacteria was determined using microscopy method. Vitality of bacteria onto polymers was determined using ATP method. The HY-LiTE® (Merck) system based on bioluminescent method was applied to measure the ATP content on polymer surface.

RESULTS AND DISCUSSION

SEM observations showed that the addition of silica in the presence of MLLDPE improves adhesion between the LLDPE and wood fiber. DMTA measurements confirmed these observations, showing an enhancement of the storage modulus in the presence of MLLDPE and SiO_2-Cu. Moreover, higher silica content resulted in higher storage modulus, proving that the material became stiffer. Through DSC runs it was found that the MLLDPE and SiO_2-Cu increased crystallization temperature of wood-filled LLDPE. The thermal stability of the composites containing SiO_2-Cu was better in comparison with pure and wood-filled LLDPE. The gradual enhancement in tensile and flexural strengths of the wood-filled composites containing MLLDPE was observed. The addition of silica nanoparticles to the wood-filled LLDPE composites increased tensile and flexural moduli, pointing to a synergistic effect arising from the presence of the reinforced LLDPE phase, containing high amounts of the finely dispersed wood fiber. Wood-filled LLDPE composites modified with SiO_2-Cu were found to be active against *Escherichia coli*, *Staphylococcus aureus* and *Salmonella typhimurium* whereas unmodified composite did not show this efficacy. Thus wood-filled LLDPE composites containing SiO_2-Cu are effective bactericidal materials.

Acknowledgments

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NANO-STRUCTURE AND PROPERTIES OF BIOSYNTHESIZED MEDIUM-CHAIN-LENGTH POLY(3-HYDROXYALKANOATE)S

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Polyhydroxyalkanaotes (PHAs) are biodegradable polyesters produced by bacteria and are recognized as candidate materials for sustainable development. Based on the structure of monomeric units, PHAs are divided into two groups; short-chain-length (scl) PHAs consisting of hydroxyalkanoate units with 3 to 5 carbon atoms, and medium-chain-length (mcl) PHAs containing hydroxyalkanoate with over 6 carbon atoms. In this study, we synthesized the medium-chain-length poly(3-hydroxyalkanoate)s (mcl-P(3HA)s) with different side-chain-length ranging from C3 to C9 carbon atoms and investigated the effect of side-chain length on the physical properties and solid-state nano-structure of mcl-P(3HA)s.

Mcl-P(3HA)s with different side-chain length ranging from C3–C9 were synthesized from 2-alkenoic acids of C6–C12 by using a metabolically engineered strain of *Escherichia coli*. Thermal properties and crystallization behaviors of synthesized mcl-P(3HA)s was examined by DSC and X-ray analyses.

All mcl-P(3HA)s formed a chain-packed crystalline structure in the solvent-cast films. As shown in Figure 1, melting temperatures of solvent-cast film of mcl-P(3HA)s first decreased from 59 °C to 45 °C with the change of side-chain from C3 to C4 and thereafter increased to 69 °C with an extension of side-chain to C9. The X-ray diffraction patterns indicate the formation of a layered structure aligned the main-chains in planes involving side-by-side packing of side-chains with a periodic distance of 1.6–2.8 nm for the mcl-P(3HA)s with over C4 side-chain. The interlayer distance increased proportionally to the length of side-chain for the mcl-P(3HA)s with over C4 side-chain, while the corresponding value of mcl-P(3HA) with C3 side-chain was apparently deviated from the extrapolated line plotted the distance against side-chain length (see Figure 1). These results indicate that the changeover in crystallization manner occurs between P(3HA)s with under C3 side-chain and with over C4 side-chain. For the mcl-P(3HA)s with side-chain carbon number over C7, two distinct phase transitions were happened during heating process from a melt-quenched amorphous state (Figure 2). At lower temperature region, the mcl-P(3HA) molecules formed a smectic liquid-crystalline structure from a melt-quenched amorphous state owing to the side-chain interactions, and the structure was disrupted at temperatures between 20–50 °C. After the disruption of smectic aggregates, the crystallization of mcl-P(3HA) chains immediately occurred with participation of both main- and side-chains. In the crystallization process of mcl-P(3HA)s, the main-chains are arranged with helical conformation, and the packing of alkyl side-chains progresses to play a role in stabilization of the crystalline. The finding of phase transition from liquid-crystalline to crystalline state for mcl-P(3HA)s with over C7 side-chain promises to use them as thermo-responsive biomaterials.

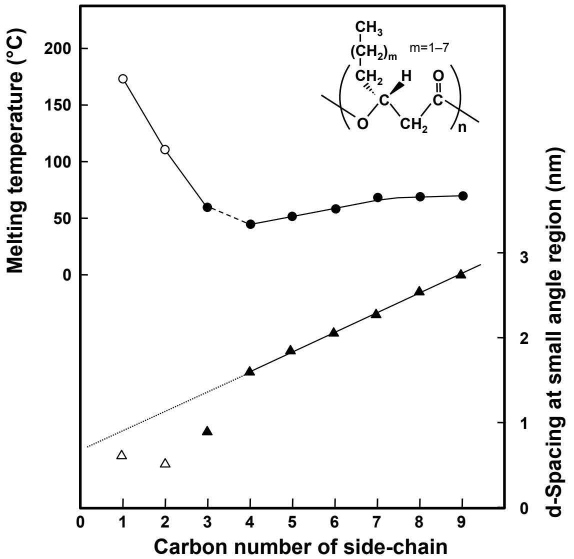

Figure 1. Melting temperature and distance of reflection detected at small angle region for mcl-P(3HA)s.

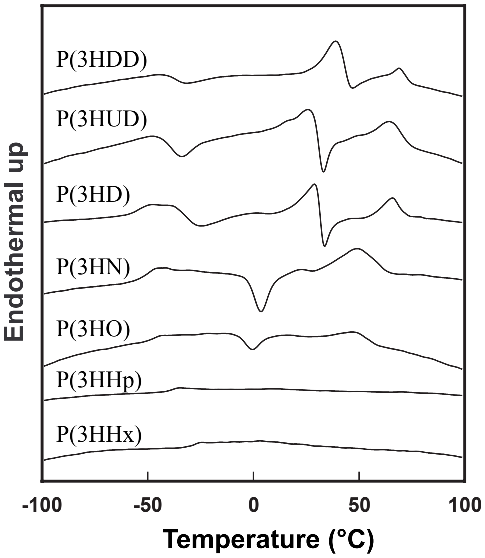

Figure 2. DSC thermograms of mcl-P(3HA)s recorded at second heating scan after melt-quenching.

RECYCLING OF VEGETAL FIBERS REINFORCED POLYMERS

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The manufacturing of plant fiber-reinforced composites is a growing sector for many environmental reasons. The production of vegetal fibers needs lower energy than synthetic fibers: they have a low density allowing to reduce the transport costs [1], they reject lower quantities of green house gas [2] and they offer several end of life ways (combustion, recycling or composting with a biodegradable matrix [3]). These environmental advantages are combined to interesting mechanical properties showing that vegetal fibers are good candidates for the substitution of glass fibers in thermoplastic reinforcement.

In the first part of this work, we have been focusing on the recycling of thermoplastic-matrix composite materials made of polypropylene (PP) and polylactic acid (PLA) resins reinforced with plant fibers such as flax, sisal and hemp [3-5]. These materials were processed by extrusion and injection moulding then crushed and grounded using an industrial cutting mill. Despite a degradation of fiber wall properties evidenced by in-situ nanoindentation measurements [6], we highlighted a good stability of the composites mechanical properties. This phenomenon could be explained by the stabilization of the fiber aspect ratio with the recycling, due to the division of bundles during the process and to the decrease of the fiber length. The aspect ratio plays a key role in the reinforcement mechanisms of a composite. In the same time, we could notice a decrease of the composites viscosity due to the conjugated effect of the process shear rate and of the PP chains drop.

The second part of this study is dedicated to the evolution of the main characteristics of a PP/hemp composite elaborated with a PP coming from automotive wastes after multiple injection mouldings. We have investigated, after each cycle, the mechanical, viscoelastic, impact and rheological properties. As evidenced in the figure 1, these results show, despite some differences induced by the first life of the PP, a good stabilization of these properties after several injection cycles.

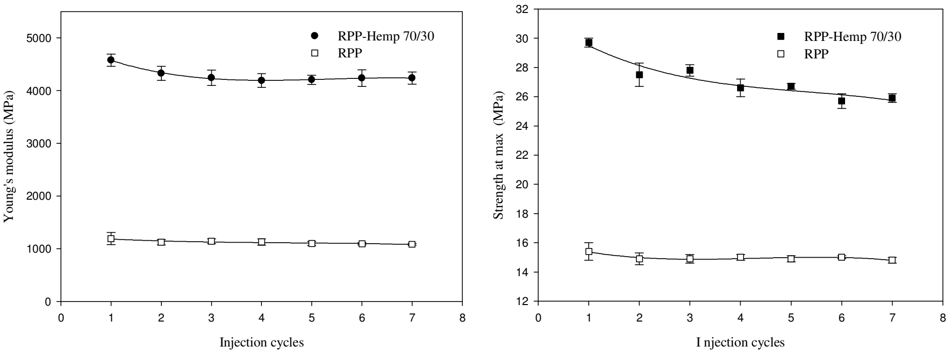

Figure 1: Evolution of the Young's modulus and strength at max for recycled PP and RPP-Hemp 70-30 with injection cycles

To conclude this work, we have carried out a simplified life cycle analysis to estimate the environmental interest to use a recycled matrix and hemp fibers to reinforce composites.

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EFFECT OF PAINT CONTAMINANT ON THE RECYCLING OF AUTOMOTIVE BUMPERS

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Introduction

According to the European directive 2000/53/EC, the automotive industry will have to meet recycling targets of 95% by an average weight per vehicle and year for all end-of-life vehicles (ELV) by January 2015. As plastic components are increasingly being used to replace metal, the problem of their recycling is raised[1]. Among automotive parts, bumpers are easily to remove because of their size and relatively simple composition (mainly polypropylene) but the paint covering some of these bumpers is detrimental to their recycling. In fact, the presence of paint leads to the formation of surface defects and to the decrease of the mechanical properties of the recycled material compared to conventional bumpers. In particular, evaluation of painted bumpers coming from ELV have shown that the main change in the properties compared to newly produced bumpers was due to a decrease of the elongation at break[2]. Thus, the aim of the work is to understand the influence of the paint on the mechanical properties of the recycled material and then to find an additive which could compatibilize the paint particles and the polymeric matrix.

Results and discussion

The paint coating deposited on the bumpers is composed of three layers: a primer, a base and a varnish[2]. To understand the influence of each ingredient of the paint on the mechanical properties of the recycled material, blends composed of polypropylene (PP) and of one selected component of the paint have been done and tensile tests have been carried out using an Instron 4466 universal testing machine at a speed of 50mm/min. Figure 1 shows the elongation at break (EAB) obtained for the three samples compared to the value of PP alone and of PP + the whole paint including the three components.

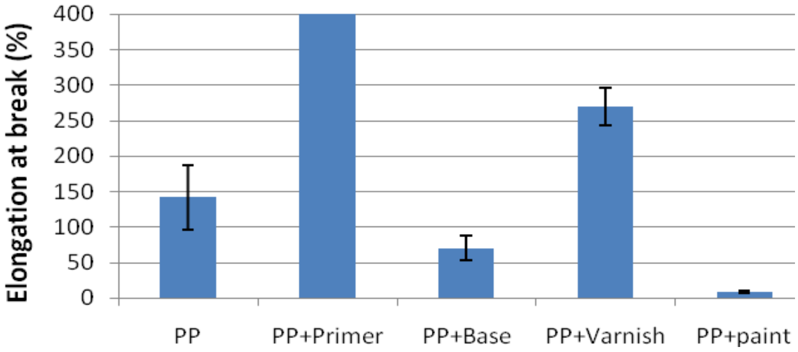

Figure 1. Elongation at break of PP and PP containing the different components of the paint at a speed of 50mm/min.

If a comparison is made between the behavior of the blends containing only one component of the paint and PP alone, it can be seen that two components, namely the primer and the varnish, lead to a huge increase in the EAB of the polymer. It has to be noted that the samples containing only the primer did not break which means that the EAB is higher than 400% in that case. On the contrary, a decrease of the EAB is observed when the base is added to the PP matrix. When the three components of the paint are added simultaneously, a sharp decrease in the mechanical properties is obtained showing that the behavior of the whole system was governed by the base.

On the other hand, SEM analyses on samples coming from ELV have shown that the failure during the tensile tests occurred precisely at the interface between the paint particles and the polymeric matrix. Thus, the compatibility between the two has to be improved.

Conclusion

Tensile tests on the different components of the paint have shown that the fragile behavior of the blend containing the whole paint is mainly due to the base. Moreover, there is no compatibility between the paint particles and the polymer. Thus, different additives have been tested in the PP matrix to improve the compatibility between those two phases. One of them has proved to be very efficient to improve the EAB of the blend and SEM analysis has shown that this additive surrounded the paint particles.

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BIODEGRADATION OF EXPANDED POLYSTYRENE MODIFIED WITH A NOVEL POLYMER ADDITIVE

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In 2010, the global production and use of polystyrene was approximately 15.4 million tonnes [1]. With the widespread use of PS in transient packaging applications, it is not surprising that around 70% is disposed to landfill after use [2]. Recycling options for PS are limited with recycling rates in Australia for 2010-2011, for example, at 27.1% for high impact PS (HIPS) and only 8.4% for expanded PS (EPS) [3]. Moreover, the structure and inherent stability of PS contribute to the persistence in the landfill environment and these materials are not recognized as biodegradable [4]. Some recent research has focused on the modification of PS with additives in attempts to impart degradability. Examples include the use of oxo-degradables for foamed PS [5], the addition of modified carbohydrates for biodegradability [6], and the use of zinc oxide for enhanced photocatalytic degradation [7].

A new polymeric additive based on polyamide has been recently developed to initiate the biodegradation of EPS [8]. This biodegradable additive is electrostatically coated on the surface of pre-expanded PS beads thereby introducing a mechanism that can support microbial growth and activate the microbial decomposition of the EPS beads. Figure 1 shows a scanning electron micrograph image of a sample of a modified EPS cup that has been incubated under standard anaerobic test conditions (ASTM D5511) [9] for 25 days. This image shows microbial growth on the surface of the EPS suggesting the additive effectively contributes to the establishment of microbial colonies that may eventually aid in the decomposition of the EPS bead cells. Figure 2 shows a plot of the volume of biogas evolved from the anaerobic reactor vessels over the 25 day test period. In comparison with a standard untreated commercial EPS cup, the product treated with the additive produced significantly more biogas over the test period.

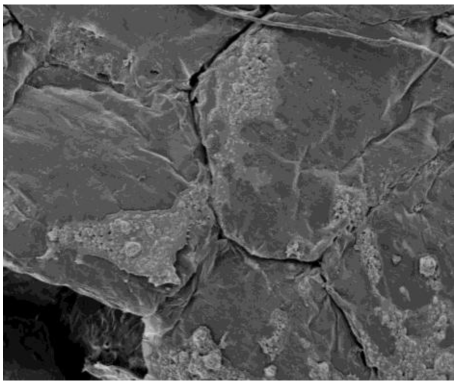

Figure 1. Scanning electron microscope image of EPS at 54 × magnification.

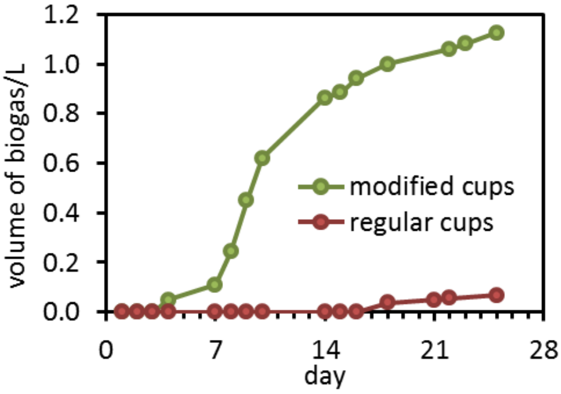

Figure 2. Volume of biogas evolved during anaerobic incubation of modified and standard EPS.

This work reports the results of biodegradation tests on treated and untreated EPS under standard anaerobic test conditions [9]. The results suggest that the EPS modified with the additive has the potential to undergo biodegradation at a rate that would be adequate in a managed landfill. Results of tests using new additives under development to assist the biodegradation of HIPS and EPS will also be presented.

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IS THE SOIL TYPE INFLUENCING THE ABOVE-GROUND DEGRADATION OF OXO-DEGRADABLE POLYETHYLENE THIN FILMS?

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In some applications, such as agricultural crop propagation films, it is necessary to control the rate of degradation of the film above ground to enable a healthy crop growth. Several studies have investigated the photo- and/or thermo-oxidation of polyethylene (PE) in sunlight [1,2] and buried in soil or compost [3,4]. The rate of PE degradation can be influenced by the grade of polymer as well as the concentration or type of pro-degradants and also by environmental factors, such as type of soil [5], UV spectral irradiance and dose, air temperature and humidity. Evaluation of the impact of all these environmental factors including the effect of soil type on the above-ground degradation of PE has not previously been addressed and needs to be defined to allow the development of PE films with predictable and reliable above-ground degradation.

The above-ground degradation of oxo-degradable PE thin films containing TiO_2 or Fe (II) stearate pro-degradants has been investigated over a range of soils with varying organic matter (OM) concentrations as well as humic and fulvic acids, which are the most active component of the organic matter. The characteristics of the soils used in the study are shown in Table 1. Samples were aged using a Q-Sun accelerated weathering device. This device simulates day & night cycles, whilst controlling the air temperature and humidity. FTIR-ATR was used to measure the extent of oxidation by characterization of the carbonyl index. Films containing TiO_2 were also analyzed by UV-Vis spectroscopy and SEM to monitor changes in film opacity and topology during oxidation.

Table 1: Soil Characteristics

Soil	**OM 4.5**	**OM 6**
Colour	Red Brown	Grey
pH (water)	7.2	7.1
% organic matter	4.5	6

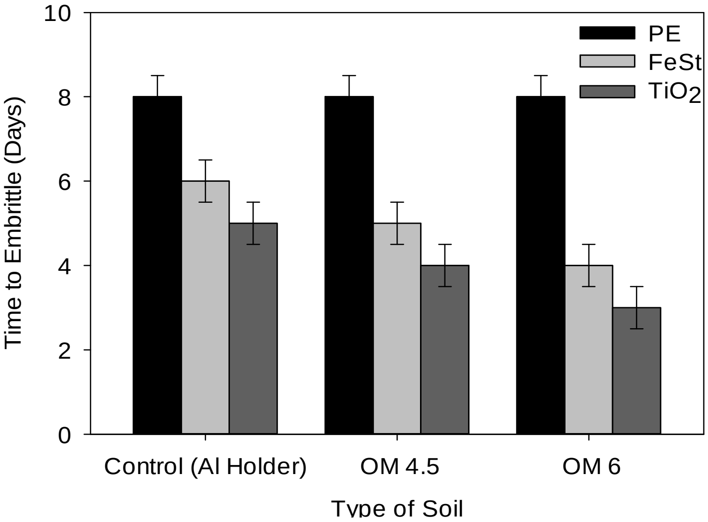

Figure 1. Time to embrittle for oxo-degradable PE films over soil.

Fig. 1 presents the time to embrittlement for all films over soils containing different concentration of organic matter. The rate of degradation of oxo-degradable PE films was increased when the amount of organic matter in the soil increased. These results suggest that organic matter within the soil may impact on the rate of above-ground degradation of PE. From preliminary results, the humic acids present in the organic matter when exposed to the sun are degrading, forming volatiles species [6], that might be responsible for this increase in rate of above-ground degradation of PE. Possible mechanisms and other results will be presented.

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SYNTHESIS AND CHARACTERIZATION OF XYLAN AND GLUCOMANNAN ESTER DERIVATIVES AND THEIR CRYSTALLIZATION EFFECTS FOR POLY(LACTIC ACID)

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Xylan is the most abundant hemicellulose with mainly beta-(1→4) linked xylose and it gains increasing importance for the basis of new biopolymeric materials. On the other hand, glucomannan is one of natural polysaccharides and can be isolated from konjak. In this paper, we synthesized xylan and glucomannan ester derivatives and investigated thermal and mechanical properties of solvent-cast and melt-pressed films of these ester derivatives. Furthermore, in the case of xylan ester derivatives, we demonstrated a possibility of xylan esters as bio-based nucleating agents for PLLA and PDLA.

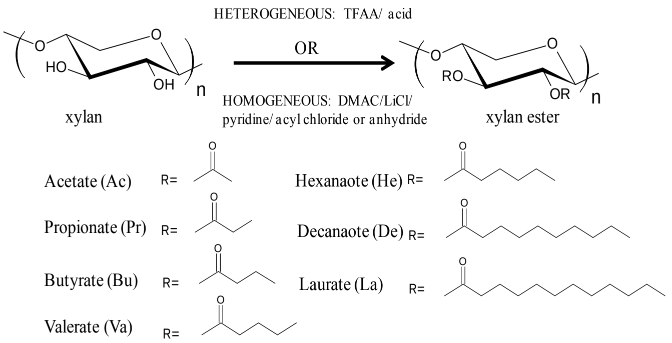

Fig 1. Esterification of xylan.

Xylan was first extracted from eucalyptus hardwood pulp by alkaline treatment with different concentrations of NaOH solutions. Xylan ester derivatives were synthesized as shown in Figure 1.

Xylan was esterified with different acyl groups and products were analyzed by NMR, DSC, TG, GPC and WAXD analyses. Films can be processed resulted to an improvement in thermal stability.[1]

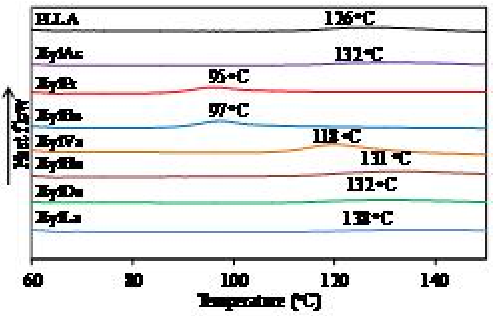

Fig 2. Endotherms of PLLA and its blends containing 1% xylan esters.

The xylan esters were screened for their effect on the crystallization behavior of PLLA. Figure 2 shows the DSC traces of PLLA and PLLA blend films with 1% xylan esters. XylPr and XylBu showed an excellent effect on the crystallization behavior of PLLA. The exothermic peak, which is attributed to the crystallization of PLLA, was shifted to a lower temperature with the addition of these xylan esters.

Figure 3 presents the plots of $t_{1/2}$ values of the PLLA and PLLA blends at different T_cs. Results revealed that the $t_{1/2}$ is dependent on the T_c. In the case of PLLA, the rate of crystallization was fastest at 100 °C ($t_{1/2}$= 1.8 min) and slowest at 130 °C ($t_{1/2}$=13.6 min). The same trend was observed for the PLLA blends. The $t_{1/2}$ values of the PLLA blend with XylPr and with XylBu at 100 °C were 1.0 and 0.8 min, respectively. Based on these results, XylPr and XylBu are effective in enhancing the crystallization rate of PLLA during isothermal crystallization.

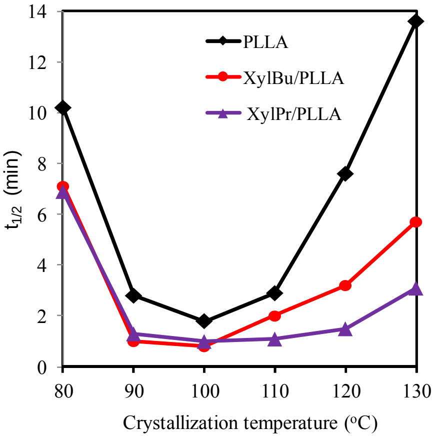

Figure 3. Plots of $t_{1/2}$ values and T_cs of PLLA and its blends with 1% xylan esters.

Spherulites of xylan ester/PLLA grown after isothermal crystallization were observed to be smaller and denser compared to that of PLLA. These results indicate that xylan propionate and xylan butylate act as excellent bio-based nucleating agents for PLLA.

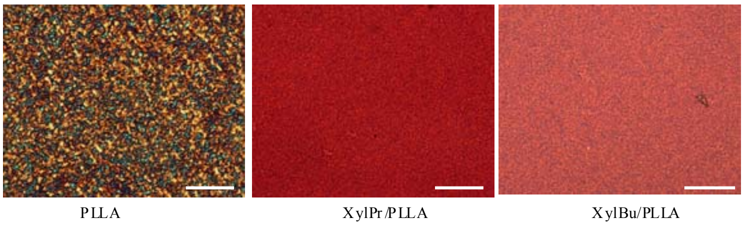

Figure 4. Spherulite images of PLLA and its blends isothermally grown at 100 °C (Scale bar= 100 μm)

In the case of glucomannan ester derivatives, tensile strength and elongation at break depend on acyl groups. Glucomannan esters have not Tm as same as xylan esters, however, melt-pressed films could be processed by hot-pressing at the temperature above Tg.

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SYNTHESIS OF BIODEGADABLE COPOLYMERS OF ETHYL VINYL ACETATE AND POLY(E-CAPROLACTONE)

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Grafted copolymers, EVA-g-PCL, were synthesized by reactive extrusion, through transesterification reaction between ethylene-vinyl-acetate copolymer (EVA) and poly(e-caprolactone) (PCL) using titanium propoxide (Ti(OPr)4) as catalyst. The effect of EVA molar mass on the amount of grafted copolymer and materials properties was evaluated. The prepared materials were characterized by several analytical techniques and the biodegradability was evaluated based on biochemical oxygen demand method. The results evidenced that the amount of copolymer increases as the amount of catalyst increases. Furthermore, using EVA with high molar mass, allowed to obtain a material exhibiting properties similar to conventional polymers with higher biodegradability.

NATURAL FIBER REINFORCED BIO-BASED EPOXY RESIN COMPOSITES DEVELOPED FOR AERONAUTICAL APPLICATIONS

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Introduction

The tendency of the replacement of traditional mineral oil based resins with bio-based systems is nowadays characteristic for many segments of the industry. In case of polymer composites, not only the matrix materials are available or can be synthesized from renewable sources, but also natural fibres can be applied as reinforcement to replace the traditionally used glass or carbon fibers in order to obtain an all bio-based composite. For aeronautical applications (interiors and/or structures) the challenge is much larger than elsewhere, therefore it is a common practice to combine the bio-based components with synthetic ones[1] to approach the characteristics of aeronautical benchmark materials. The aim of this study was to examine the mechanical property changes caused by the application of epoxidized soybean oil as renewable component in natural fiber reinforced epoxy resin composites.

Materials and methods

As composite matrix materials epoxidized soybean oil (ESO) (Drapex 39, Galata Chemicals, Lampertheim, Germany) from renewable sources was combined with a glycerol based epoxy component (ipox MR 3012, ipox chemicals, Budapest, Hungary), which is currently synthesized on mineral oil basis, but could be possibly synthesized from plant-based glycerol as well. In this study 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0 of ESO - ipox MR 3012 mass mixing ratios were investigated. As curing agent an aliphatic amine, triethylene-tetramine (TETA) (ipox EH 2291, ipox chemicals, Budapest, Hungary) and an aromatic one, 4,4’-diaminodiphenylmethane (DDM) (Sigma-Aldrich) were used. Based on mechanical properties and worldwide production, jute fibers were chosen as natural reinforcement[2]. Woven jute fabric with 309 g/m^2 surface mass provided by Műszaki Konfekció Kft. Szeged, Hungary was used. Based on earlier studies[3] the fibers were preliminary treated with alkali solutions.

The effect of mixing synthetic and renewable epoxy resin components on the mechanical and morphological properties of jute fabric reinforced composite materials was investigated by Differential Scanning Calorimetry (DSC) and Differential Mechanical Analysis (DMA).

Results and discussion

Based on the tensile and bending test results, by changing the mixing ratio of the synthetic and renewable epoxy resin components, the glass transition temperature and the mechanical properties could be customized according to the requirements of different aeronautical applications as aircraft interior panels or body fairing. The fiber treatment was necessary to optimize the mechanical properties of the composites.

Conclusions

In this study bio-based and partially bio-based thermoset matrix composite materials were investigated in different compositions with jute fabric reinforcement. Optimal mixing ratios of the synthetic and renewable epoxy resin components have been selected based on the DSC and DMA results for further investigations. The effect of fiber treatment on the mechanical properties of the prepared composites has also been characterized.

Acknowledgement

This work is connected to the scientific program of the "Development of quality-oriented and harmonized R+D+I strategy and functional model at BME" project supported by the New Széchenyi Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002). The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Clean Sky Joint Technology Initiative under grant agreement n° 298090.

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NANOMATERIALS INCINERATION AND PARTICLES RELEASE

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Abstract

INNANODEP is a cooperative project between LNE and ARMINES, supported by ADEME in France, targeting specifically a research on Nanocomposite, Environment and Recycling. The objective of the project is to study current nanocomposites for which there is no recycling or revalorization solution, the only alternative being incineration[1]. The applications under consideration are mainly products from the field of sport, high performance technical equipment or aeronautical/naval area. For such applications, mechanical performances are increased by the incorporation of nanocharges. The polymer matrices that are most often used are thermoplastics such as polyamide-6 (PA6-), polycarbonate (PC) and thermoset (TS) like epoxy resins. Within the framework of this project, we will focus on nanocomposites made of these matrices,and target on those nanocharges which could potentially have an impact on health when released during incineration. The two main interests of this study are: a) to establish the specific emissions of fine particles resulting from the nanocomposite incineration which are not taken into account at the end-of-

life of the incinerated nanocomposites, b) to produce a knowledge complementary to that of projects already carried out, such as in NanoFeu[2,3,4] implementing original methodologies and experimental techniques.

1. Description of the project

1.1. Position of the project

Many National and European programmes devoted to the study of risks related to the production or use of nanoparticles, are under way.

These studies can be considered as specific work on:

- the risks linked to the exposure of populations, especially when nanoparticles are being manufactured;
- the intrinsic toxicity of emerging nanoparticles;
- the understanding of interactions between nanoparticles and the human being;
- the design of specific detection methods;
- the enhancement of experimental procedures aiming at determining the toxicity level;
- the provision of regulations and recommendations.

However, there is no specific programme dedicated to the assessment of potential hazards linked to the release of particles produced at the end of the cycle of life of nanoparticle-based materials.

In Europe, no project considers hazards related to the release of ultrafine particles during intentional burning by incineration of nanocomposites.

Recently, A. Morgan[5] reported the current available knowledge related to the flammability of nanocomposite polymers and flame retardants. Nevertheless, no knowledge on the dissemination of particles through accidental or intentional burning of nanoparticle-based materials is reported.

1.2. General objectives

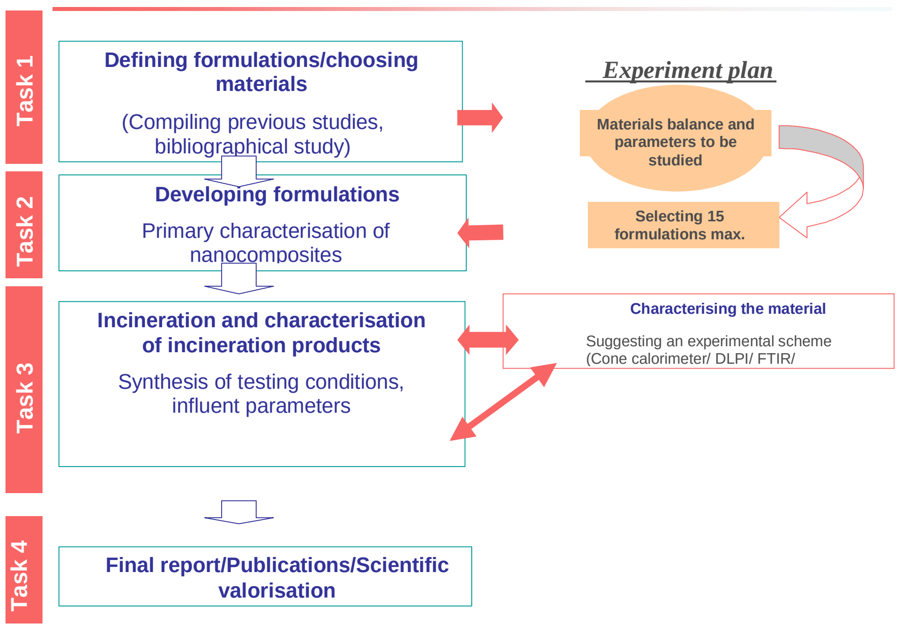
One of the main objectives of the present research consists in understanding the impact of the nanocomposites characteristics on the structure and composition of ultrafine particles that are released during the incineration process. Different incineration scenarios simulated with a cone calorimeter and characterised by different radiation levels and flammable atmospheres will be followed.

The behaviour of nanocomposites will be compared with that of virgin polymer-matrix ones to determine whether the structure of the released particles is significantly different in function of the incorporation level, and whether nanoparticles are released or not into the flammable atmosphere as a function of their surface or functionalisation treatments. The goal is to draw a precise material balance between the amount of nanoparticles that are released in aerosol compared to that of the burnt residue..

Another objective is to determine whether specific dispersion states of nanoparticles contained in polymer-matrices (state of aggregation or agglomeration for nodular particles, inserted structure) can modify the composition as well as the granulometry of the released fractions.

Since previous work has shown that the presence of nanoparticles might modify the degradation process of polymers, the project intends to understand the structure and composition of the released particles in relation to nanoparticles/polymer interactions (or associated degradation products) during the degradation process. Some authors succeeded in understanding the nanoparticles/polymer interactions during the degradation process, especially with carbon nanotubes in fire scenarios. However, this is a novel procedure for incineration scenarios. On the basis of the results, recommendations might be made in terms of compositions and optimal surface or functionalisation treatments in order to limit the amount and toxicity of particles that are released during the incineration of the nanocomposite.

The 30-month study programme is made up of four tasks.



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CHEMICAL DECOMPOSITION OF PLASTICS IN MICROWAVE FIELD – NEW WAY HOW TO RECYCLE PLASTIC WASTE

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In spite of numerous ways of chemical recycling of plastic waste, only a very limited number have been used in industrial scale. The reasons for this phenomenon are quality problems, economy of the process and the environmental balance of the process in comparison to the production of virgin raw-materials. Microwave reactors seem to be a way how to overcome the problem of high energy demanding recycling processes. The origin of the microwave heating lies in the ability of the electric field to polarize the charges in the material and the inability of this polarization to follow extremely rapid reversals of the electric field[1].

Recently we have developed recycling processes for several kinds of waste plastics (PUR, PET and PC), which utilize a microwave (dielectric) heating and significantly reduce operating costs of the whole process. These processes always consist of three main steps: i) mechanical pre-treatment of plastic waste to a form suitable for feeding to a reactor, ii) chemical decomposition in the microwave-heated reactor and iii) purification of a recycled polyol product obtained.

The basic physico-chemical properties of polyol products obtained by chemolysis of various plastic wastes (PUR, PET and PC) as well as their further applications are given in Table 1. The application possibilities for the polyols depend on the type (structure) of original polyol but can be also adjusted by suitable selection of a decomposing reagent.

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Table 1 Properties of prepared recycled polyol products

Source of plastic waste	*Appearance*	*Viscosity, 25 °C [mPa.s]*	*Hydroxyl number [mgKOH.g^{-1}]*	*Water content [wt.%]*	*Application*
PUR	Brown liquid	2 400	430	0.3	Rigid PUR foam
PUR	Yellow liquid	1 100	133	< 0.1	Flexible PUR casts, Aerosol PUR foam
PET	Yellow liquid	1 300	100	< 0.1	Flexible PUR casts
PC	Yellow liquid	3 700	350	< 0.1	Rigid PUR foam

SYNTHESIS OF PLA-PEG COPOLYMER AND ITS CHAIN EXTENDING WITH DI-ISOCYANATES. STRUCTURE, DEGRADATION AND POTENTIAL UTILIZATION.

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Introduction

Lactic acid (LA) polymer (PLA) and copolymers are recognized for their biocompatibility and biodegradability and have wide used in many fields.

In this work, poly(lactic acid)/poly(ethylene glycol) (PLA/PEG) copolymer predominantly terminated with OH groups was prepared and subsequently reacted with di-isocyanates to produce poly(ester-urethane) (PEU). The properties of the products and their potential utilization as nano fibers and nano/micro capsules were investigated.

Materials and Methods

PLA/PEG – LA was dehydrated 4 h at 160 °C, p = 20 kPa. Then, 0.4 % of $Sn(Oct)_2$ +7.5 % PEG (4000) was added. Reaction continued 24 h, 0.1 kPa.
PEU – 30g of PLA/PEG was melted (N_2, 160 °C). Then, MDI (CAS 101-68-8) or HMDI (822-06-0) was added and reaction continued for 30 min.
Electro spinning –12% DMF solution on PP nonwoven substrate.
Nano particles – Formed by solvent evaporation method according to [1].

Results and discussion

In Fig. 1 (upper part) the weight average molecular weight of products are shown. It can be seen, that after addition of di-isocyanate the M_w increased significantly. This was more dominant in case of HMDI, where the highest M_w ~ 225 000 kg/mol was achieved. This showed on successful reaction between chain end groups and di-isocyanate compounds. In the lower part of Fig. 1 the degradation behavior in buffered solution (pH=7.4, 37 °C) is presented. It can be seen, that the type and concentration of di-isocyanate compound play a significant role during hydrolysis. Enhanced hydrolysis was observed in case of HMDI at the lowest concentration, while MDI

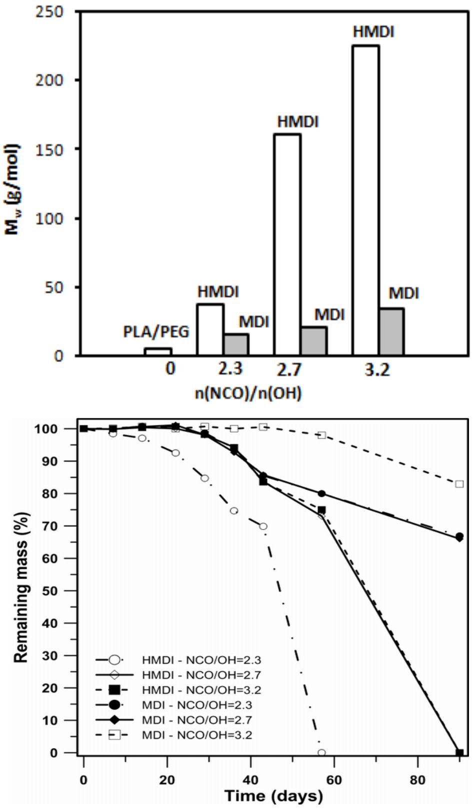

Figure 1 – The M_w (up) and degradation profiles (lower) of PEU products.

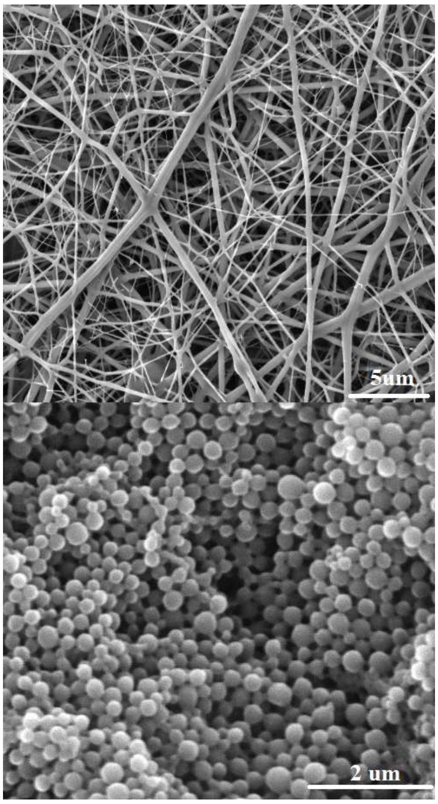

Figure 2 – SEM images of nano fibers (up) and particles (down).

provided more stable products (compact even after 90 days). Fig. 2 depicts nano fibers and particles successfully formed from prepared PEU. It can be seen, that in case of fibers (10 layers) the combination of nano and micro structures was achieved, which can be beneficial for example in filtration technology. In case of microparticles, the average diameter was found to be about 200 nm (light scattering, not presented) and they can be utilized in the area of encapsulation.

Conclusions

Poly(ester urethane) based on PLA/PEG copolymer was prepared. It can be successfully utilized in nano/micro fabrication like, fibers and particles.

Acknowledgements

The study was supported by project IGA (Grant IGA/FT/2012/005).

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FEASIBLE PATHWAY TO DEVELOPED MULTIFUNCTIONAL HYBRID LOW-COST MATERIALS BASED ON BACTERIAL CELLULOSE

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Bacterial cellulose has been recently investigated as an attractive environmentally friendly material for the preparation of low-cost nanocomposites. The functionalization of cellulose with inorganic materials opens new pathways for the fabrication of novel multifunctional hybrid materials with promising properties. Bacterial cellulose was used as template for preparation of novel hybrid composites that gather together excellent properties of bacterial cellulose with the ones displayed by typical inorganic nanoparticles like optical, magnetic and electrical properties, luminescence, ionic conductivity and selectivity, as well as chemical or biochemical activity.

In this work bacterial cellulose was used as template for generation hybrid materials by the addition of titanium or vanadium oxides nanoparticles. These nanoparticles are of particular interest taking into account their properties which offer wide range of potential application; titanium dioxide nanoparticles with their electric and photocatalytic properties and vanadium oxide nanoparticles with their widely recognized photo-electrochromic properties.

We proposed a simple, rapid, low-cost pathway based on a diffusion step of sol-gel nanoparticles into swollen bacterial cellulose mat via orbital incubator. This alternative pathway allows to keeping intact the 3D network of the bacterial cellulose mat while sol-gel nanoparticles are formed *in situ* and anchored on the nanofibrils surface.

The morphology of designed hybrid materials was investigated by AFM and SEM. In order to characterized obtained materials from the point of view of future applications different techniques were employed. On the one hand optical properties were analysed by UV-vis spectroscopy and spectrofluorimetry and on the other hand electrical properties were studied at nano and macroscale using electric force microscopy (EFM) and Keithley semiconductor analyser, respectively. Additionally XRD, FTIR and TGA techniques were also performed.

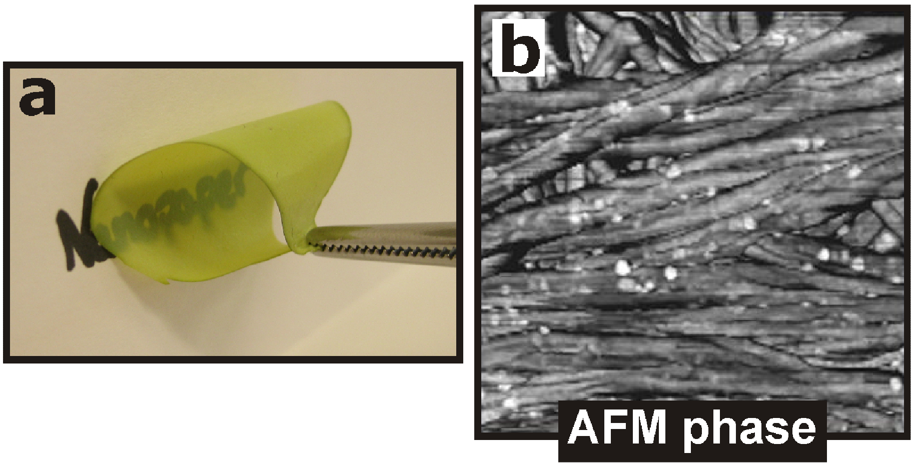

Figure 1. (a) Digital image and (b) AFM phase image (1 μm x 1 μm) of green vanadium oxide nanopaper.

Acknowledgements

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KAWABATA ANALYSIS AND X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS PLASMA TREATED COTTON

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Plasma treatment of cotton fabrics were performed under O2, Air, NH3 atmosphere at specified pressure and power. Oxygen and air plasma treatments of cotton increased wettability and uniformity due to surface oxidation while ammonia plasma treated cotton decreased wettability significantly. Air and oxygen plasma treatments had relatively little effect on shear and bending properties. Ammonia plasma treated cotton showed a small reduction in shear and bending properties.

XPS analysis of ammonia plasma treated cotton showed nitrogen was incorporated into cotton surface due to formation amine/amides species. XPS analysis of air/oxygen plasma treated cotton showed a mixture of oxidation and gaseous fixation. SEM treatment with oxygen and air plasma produced rougher, etched/pitted surface relative to untreated while ammonia produced a smoother surface.

EFFECTS OF REPROCESSING OF OXOBIODEGRADABLE AND NON-DEGRADABLE POLYETHYLENE ON THE DURABILITY OF RECYCLED MATERIALS

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Plastics play a very important role in our daily lives. Throughout the world the demand for plastics, particularly plastic packaging, bags, thin films etc. continues to grow rapidly and consequently the fastest growing component of the waste stream. Although the efficiency of plastic recycling is increasing, plastics are often seen as a permanent environmental problem due to littering. The introduction of oxo-biodegradable polyolefins (OBD), containing pro-degradant additives, reduces this problem by enabling a significantly faster degradation of the plastic by oxidation. The pro-degradant additives form radicals that attack the polymer chains causing chain scissions and generation of low molecular mass oxidation products that can be consumed by microorganisms. There is however a concern that the pro-degradant additives, that act as catalysts and are therefore not consumed in the process, will present a problem when OBD materials end up in the conventional plastic recycling streams. The present study therefore highlights the effects of mixing OBD-materials with conventional polyethylene in order to evaluate the impact on the remaining service life of the recyclates.

The study included the use of two different OBDs, mixed in different proportions (10 and 20%) in a conventional polyethylene. The remaining service life of the mixtures was evaluated by monitoring the reduction in tensile strain at break after exposure to thermo-oxidative degradation at elevated temperatures, compared to a pure polyethylene. The oxidation process was monitored by Fourier Transform Infrared Spectroscopy (FTIR) as an increase in carbonyl index. Furthermore, the impact of stabilizer content in the mixtures was evaluated together with the effect of mixing partially degraded OBDs into the recyclate.

The effect of reprocessing of OBD materials with conventional materials is exemplified in Figure 1. It is shown that unstabilized LDPE without any prodegradant starts to degrade immediately and after about 38 days at 70 °C the elongation at break is reduced to 50 % of the original value. Of course the rate of degradation of the OBD materials is much faster and depends on the type and amount of prodegradant system. Addition of 1000 ppm Irganox 1010 to the LDPE material extended the time to 50 % reduction of elongation at break from 38 days to 224 days at 70 °C. The interesting result is that the addition of 10 % of the OBD material to the stabilized LDPE did not affect the thermooxidative stability of the material.

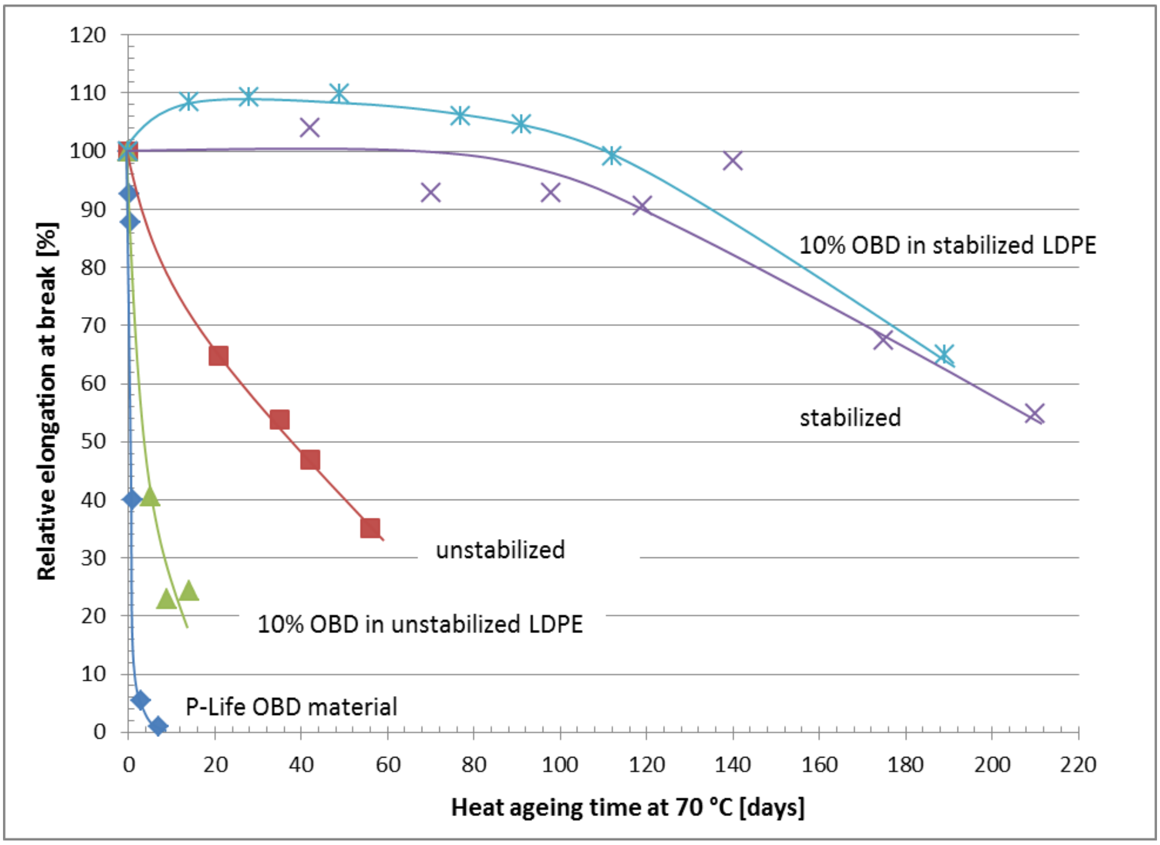

Figure 1. Elongation at break as a function of aging time at 70°C.

Our results lead to the conclusion that the incorporation of minor fractions, although a significantly higher fraction than expected in the real life, of OBD materials in the existing recycling streams will not present a severe effect on the service life of the recyclates as long as the polymer mixture possess a reasonable degree of stabilization.

EFFECT OF REPROCESSING ON BAMBOO FIBER REINFORCED POLYPROPYLENE COMPOSITE PROPERTIES

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Sustainable eco-efficient practices and products have gained increasing attention and the use of natural fibers as reinforcement for polymers has been rapidly expanding [1]. In certain composite applications biofibers have shown to be competitive in relation to glass fiber [2]. To assess recyclability of these composites bamboo fiber filled polypropylene composites were submitted to eight reprocessing cycles. Polypropylene composite specimens containing 40wt % bamboo fibers and 4wt% compatibilizer (maleic anhydride grafted polypropylene) were manufactured by extruding a blend of the composite components in a co-rotating twin-screw extruder, with subsequent pelletizing and injection molding. Composite specimens were then ground in a cutting mill and re-injected. For control neat PP was also submitted to the same processing and reprocessing conditions. Heat deflection temperature (HDT), tensile, bending, impact and fatigue (F_{max}=1400N, f=6Hz) testing were performed. After eight reprocessing cycles HDT showed a drop of around 3%, tensile modulus 8%, flexural strength and modulus 10%, tensile strength 13%, Charpy impact strength and strain at break 30%, and fatigue life under cyclic tension-compression loading about 90%. SEM analyses revealed fiber breakage with reprocessing, however no significant differences have been observed between virgin and reprocessed composites regarding fiber-matrix adhesion. For most properties the drop was more pronounced after the first reprocessing cycle, likely because of more intense fiber breakage in this cycle with fiber size stabilizing afterwards. It has thus been shown that natural fiber composites can be reprocessed without great losses in property for applications not subject to fatigue and/or impact loading.

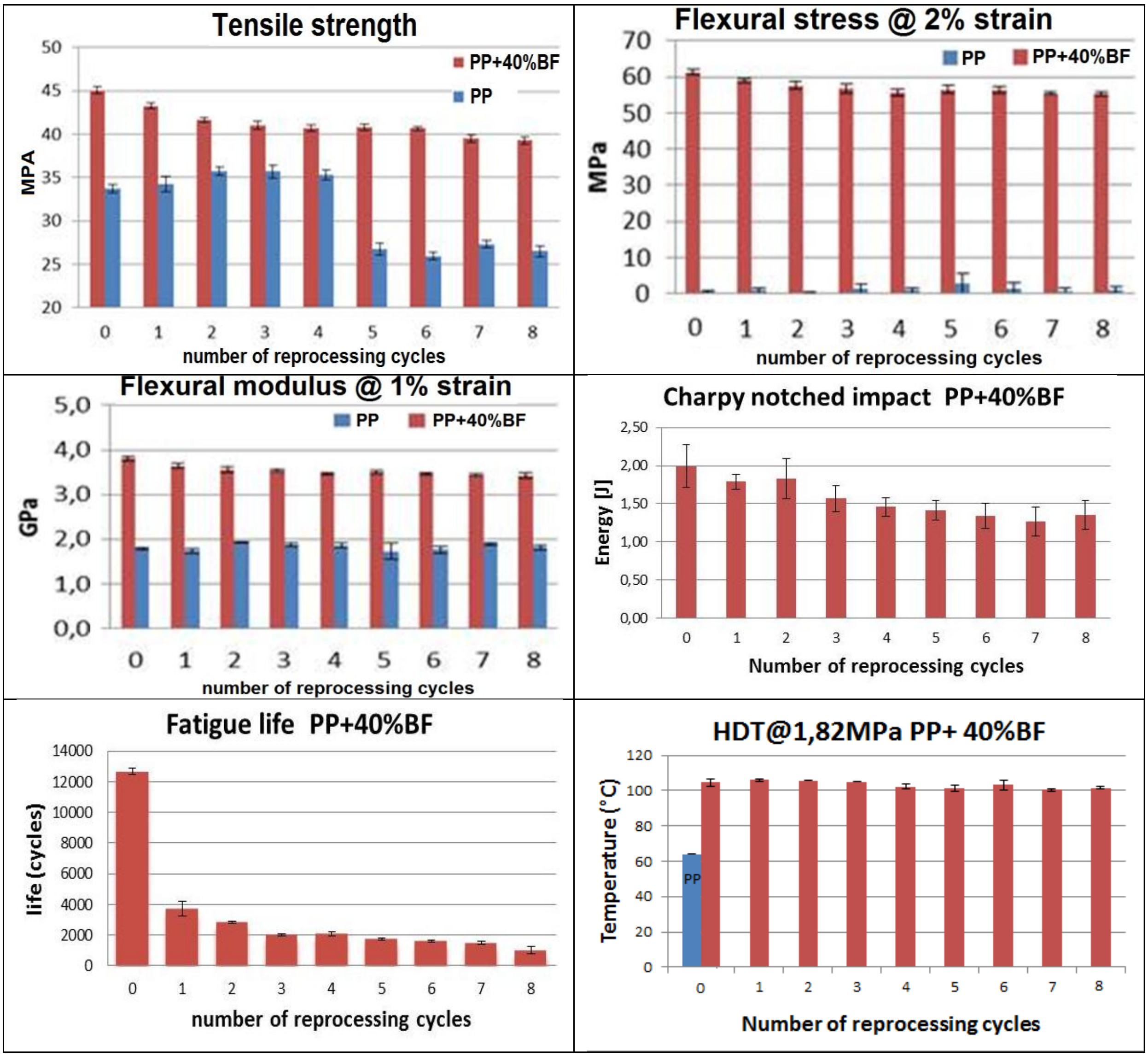

Figure 1 Variation in assessed properties of neat PP and PP reinforced with 40wt% bamboo fiber (BF) as a function of reprocessing cycles.

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POLYMERS AND ENVIRONMENT

Full Abstracts of Poster Presentations

NATURAL OIL-BASED REAGENTS FOR RECYCLING OF WASTE POLYCARBONATE

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Polycarbonates (PC) have become important commercial materials and have found wide applications in the electronic sector, in optical data storage media, in the construction industry, in automotive engineering, in food and beverage containers and other fields. High market consumption of PC products leads to the production of high amount of PC waste. Methods of physical recycling are not always suitable for the PC waste, which is prone to degrade during the reprocessing. Alternatively, we have developed the method of chemical recycling utilizing natural oils as reagents for PC depolymerization.

In the first step, castor oil was reesterified with trimethylol propane (TMP) in order to increase a number of reactive hydroxyl groups needed for reaction with carbonate groups of PC. Consequently, higher hydroxyl number enabled to improve the whole depolymerization process of PC (more efficient, faster, consumes less energy and catalysts, larger yield). The reesterified castor oil had viscosity 1603 mPa.s and hydroxyl number 471 mg KOH.g^{-1}.

In the second step, the reesterified castor oil reacted with PC in the microwave reactor at constant power (250 W) and temperature (220 °C). The best product was obtained when a molar ratio of carbonate / hydroxyl groups 1 / 7 and zinc acetate catalyst (0.5 wt.%) were used. After 20 min of the reaction, the PC was completely decomposed into a liquid polyol product having viscosity 6314 mPa.s and hydroxyl number 365 mg KOH.g^{-1}.

The product was used for preparation of water-blown rigid polyurethane (PUR) foams. The PUR foams were prepared by mixing of polyols, isocyanate: trimer of hexamethylene-1,6-diisocyanate, water and catalysts (DBTL + DABCO). Three different types of PUR foams based on: i) just the recycled polyol, ii) the combination of recycled polyol and castor oil, and iii) the combination of recycled polyol and modified CO, were prepared. For all types of foams, various molar ratios of urethane / urea (6/1, 4/1, 2/1, 1/1, 1/2, 1/4, 1/6) were examined. Structures of tougher foams without bubbles (molar ratios of urethane / urea: 2/1, 4/1, 6/1) were examined using scanning electron microscopy and measuring their values of free rise density. The best foams were obtained when the combination of recycled polyol and modified CO was used.

Acknowledgement: the authors thank the UNESCO/IUPAC Postgraduate Course in Polymer Science 2011/12, for financial support of this work.

OBTAINMENT AND CHARACTERIZATION OF ORGANIC ACID MODIFIED STARCH/PLASTICIZED CORN STARCH COMPOSITE FILMS

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Organic acid-modified corn starch microparticles (ASM) were obtained by the dry preparation technique from corn starch (S) and malic acid (A). ASM was used as filler within glycerol plasticized-corn starch, at different concentration values (4, 8, and 12% based on the corn starch amount), the composites being prepared by the casting process. Structural changes in the corn starch were studied by X-ray diffraction, and FTIR spectroscopy. The effects of ASM concentration level on the water sorption, and thermal properties of starch films were investigated. The values of water uptake decreased through addition of ASM. Thermal parameters decreased in the presence of ASM. The addition of ASM reduced the weight loss rate and improved the thermal stability of the starch films.

Corn starch microparticles modified with organic acid (ASM), were obtained first by precipitating starch with ethanol for starch microparticles synthesis, and further these were mixed with malic acid solution, being finally washed, dried and ground.[1] ASM was used as filler within glycerol plasticized-corn starch based matrix, at different concentration values (4, 8, and 12% based on the starch amount), the composites being prepared by the casting process. X-ray diffraction was performed at a speed of 2° min^{-1} and at ambient temperature by means of Bruker AD8 ADVANCE X-ray diffractometer equipment. FTIR-ATR spectra were recorded using a spectrophotometer Vertex 70 model (Bruker-Germany) in the range of 4000-400 cm^{-1} with 4 cm^{-1} resolution. The spectrophotometer is equipped with MIRacle^{TM} ATR accessory designed for single or multi-reflection attenuated total reflectance (ATR). Corn starch produced a typical crystalline X-ray diffraction pattern, while there was no crystalline peak of

SM or ASM, which suggested that the crystalline structure has been destroyed during gelatinization and chemical modification.[2]

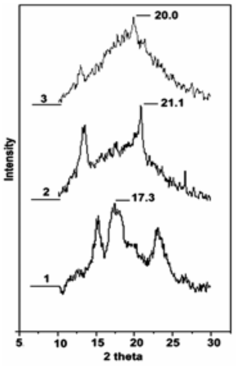

Figure 1. XRD diffractograms recorded for corn starch (S), SM, and ASM powders

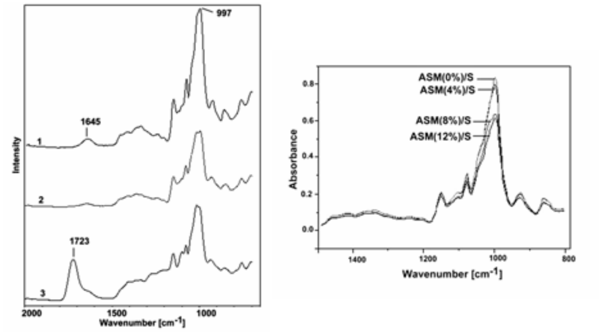

Figure 2. FTIR spectra recorded for the S, SM, ASM, and ASM(0%)/S, ASM(4-12%)/S films

The characteristic peak of ASM was located at 1723 cm^{-1}, corresponding to the C=O stretching ester carbonyl group. In the region between 1200 and 800 cm^{-1}, several strong absorption peaks assigned to C–C and C–O stretching modes appeared.[3, 4] The characteristic peak occurred at 1650 cm^{-1}, being a feature of tightly bound water present in the starch.[5] The water uptake of ASM/S films decreased with the increasing of ASM content level. The addition of ASM reduced the weight loss rate and improved the thermal stability of the starch films.

Acknowledgements

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EVALUATION OF DIFFERENT EXTRUSION PROCESSES FOR CLEANING THE RECYCLED POLYPROPYLENE REMOVING NON-VOLATILE SURROGATES

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Abstract In this work contaminated PP was recycled using extrusion processes. Non-volatile surrogates were quantified in the polymer after of the processing. To evaluate the decontamination of the samples, the extractability tests were performed under different conditions of time and temperature. The extractables were quantified using chromatographic method.

Introduction Polypropylene (PP) is one of the most used polymers, especially by the disposable packaging industry, and it has also been one of the largest sources of environmental problems. An alternative would be recycle these material, however there are still some restrictions regarding its use as packaging for direct food contact [1-4]. Therefore, focusing on the need to reuse it in this market, the contaminated PP, with non-volatile contaminants, was studied by doing extraction tests, which the contaminants were quantified in each recycling process.

Experimental PP was contaminated with benzophenone and tetracosane [4]. After, it was recovered (washed and dried). The sample was processed in a single-screw extruder and in a co-rotating twin-screw extruder with forced degassing. Terminology used for identification of the samples was: PPc (contaminated), PPrs (contaminated and recovered – processed by single screw extrusion) and PPrd (contaminated and recovered – processed by twin-screw extrusion). For the extraction tests, the samples were grinded and after, the samples and the food simulant (isooctane) were conditioned at 40°C for 10 days and 150 ºC for 30 min. So, the contaminants present isooctane were extracted by GC-MS [5]. Calibration curves showed correlation coefficients (r)>0.9974.

Results and Conclusions

Table 1. Concentration of benzophenone and tetracosane ($\mu g \cdot g^{-1}$) using isooctane

Isooctane	**Test Condition**		**Benzophenone**		**Tetracosane**	
			40 °C/10 days	150 °C/30 min	40 °C/10 days	150 °C/30 min
	Samples	PPc	671.1 ±0.4	484.3 ± 1.0	60.3 ± 1.4	568.1± 2.4
		PPrs	534.6 ± 1.9	402.6 ± 0.8	58.5 ± 0.9	496.9± 3.7
		Prd	428.6 ± 0.3	134.4 ± 0.2	0.0 ± 0.6	170.0± 0.6

As seen in Table 1, it was noticed that the release of contaminants and the decontamination of the PP in removing the contaminants were based on the factors: chemical affinity, time, temperature and type of process used in the mechanical recycling. The results showed that the chemical affinity between compounds was the main factor to migration of contaminants. The higher chemical affinity led to a higher extraction of the contaminants. So, there was the greater amount of the migrated to the food simulants. The effect of time and temperature conditions showed that, in general, the released of non-volatile contaminants in the simulant increased more in higher temperature instead of longer time. About the decontamination, the best results were achieved with the twin-screw extruder. High shear, the parameters during extrusion (temperature and screw rotation speed) and the use of a degassing system resulted in the greatest forced removal of contaminants from the PP. The use of conventional washing proved not to be used as efficient in removing the non-volatile contaminants, suggesting the use of more stringent washing conditions, or other washing procedures.

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STUDY OF THE CHEMICAL MODIFICATION OF POST-CONSUMED GROUND TIRE RUBBER AFTER DEVULCANIZATION BY MICROWAVES

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In order to make possible reusing and recycling post-consumed ground tire rubber (GTR), it was exposed to microwaves. This treatment with microwaves makes the cross-links breaks, making possible for the material to be reprocessed. From this point, this study evaluates the influence of time of microwave exposure, the number of stages of treatment and the characterization of the different samples using the techniques: Differential Scanning Calorimetry (DSC); Thermogravimetric Analysis (TG); Fourier Transform Infrared – Attenuated Total Reflectance (FT-IR/ATR); and Soxhlet Extraction. The results showed that the longer the exposure to microwaves, the higher the structural change of molecules, leading to higher devulcanization.

CHARACTERIZATION OF IRRADIATED WOOD AFTER CHEMICAL MODIFICATION WITH ORGANIC ANHYDRIDE AND COATING WITH EPOXIDIZED VEGETABLE OIL

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Wood originating from a softwood species was subjected to chemical modification by reaction with succinic anhydride (SA) in dimethylformamide (DMF). Modified wood samples were coated with epoxidized soybean oil (ESO), an epoxidized glycerol fatty ester in the presence of triethylamine (TEA), as catalyst, and further extracted with DMF to remove the excess of reagent. The light stability of ESO coated wood was investigated. Analysis of the color changes in wood surfaces during artificial light irradiation was carried out by measuring CIELAB parameters. Fourier transform infrared spectroscopy was used to study chemical changes caused by photo-degradation. The color difference, yellowing index, and weight loss were also evaluated.

Chemical modification of wood, [1-3] was shown to improve the weathering and coating performance. Wood was extracted with DMF, dried, and dipped in succinic anhydride (SA) dissolved in DMF (120% w/w) and heated at 100°C under continuous stirring for 1h. Dried wood specimens were immersed in ESO with 5% TEA, and were heated at 100°C for 7h. The wood samples were irradiated in air, in an accelerated weathering rotative device equipped with a middle pressure mercury lamp HQE-40 type, having a polychrome emission spectrum in the field of 240–570 nm, with a 30 mW/cm^2 light intensity. Each sample was analyzed for colour changes according to ASTM D 2244 and for chemical degradation of the surface by FT-IR spectroscopy.[4-6] FT-IR spectroscopy of wood samples was performed on a Bruker spectrometer (Vertex 70), at a spectral resolution of 4 cm^{-1}, the scanning range being from 400 to 4000 cm^{-1}. The L*, a* and b* parameters were measured with a colour comparison device

(Pocket Spec Color QA, SUA). These values were used to calculate the colour change ΔE_{ab} as a function of the UV irradiation time.

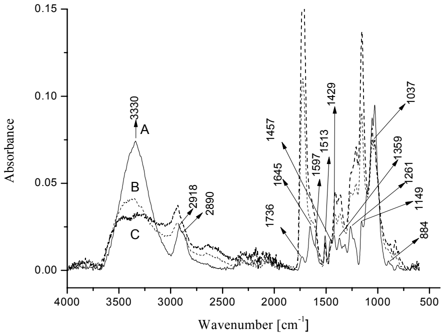

Fig. 1. The FTIR spectra of non-modified wood sample (A), of the wood sample modified with succinic anhydride (B) and of the wood sample modified with succinic anhydride and coated with epoxidized soybean oil (C).

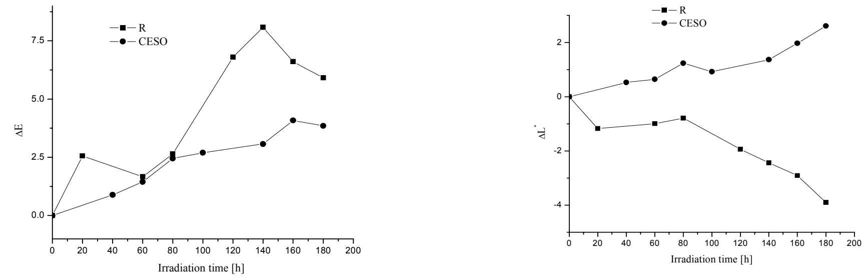

Fig. 2. Total colour difference (a) and lightness factor (b) of non-modified (R) and modified wood coated with ESO (CESO) as a function of irradiation time.

The rate of colour change is very high during initial period of exposure. Yellowing of wood surfaces indicates modification of lignin (formation of carbonyl groups and degradation) and hemicelluloses with occurrence of chromophores depending on the irradiation time and coating with ESO.

Acknowledgements

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NOVEL LOW-TEMPERATURE CHEMOENZYMATIC APPROACH FOR THE PRODUCTION OF CONDENSATION POLYMERS

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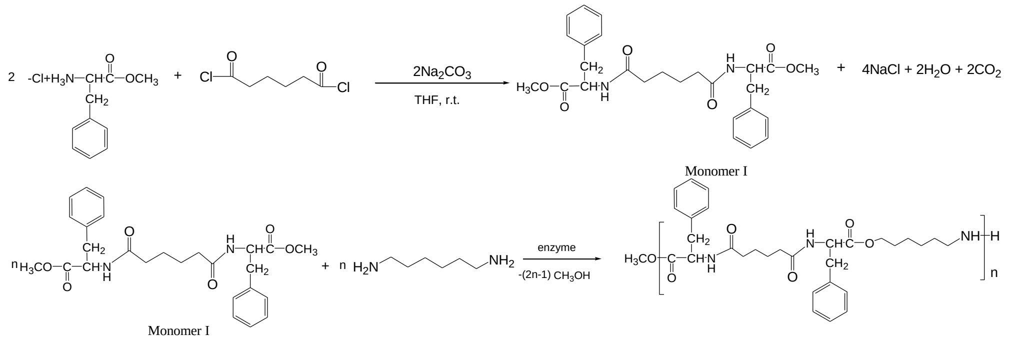
INTRODUCTION

Conventional polyamidation and polyesterification processes require high reaction temperatures and chemical catalysts based mainly on Ti, Sn, Mn, Zn and Pb. However, the use of these harsh conditions may be problematic for certain product end-uses; indicatively, metal catalysts may impart acceleration of side and decomposition reactions and often increase polymer yellowness and haziness[1-3]. A new approach to bypass the traditional chemical polymerization routes is the use of enzyme-catalyzed polycondensation reactions. Aliphatic polyesters and polyamides bearing a biodegradable chemical linkage were prepared in the current work through biocatalysis. Even more, a low-temperature post polymerization cycle[4-5] was applied for the production of biopolyesters.

EXPERIMENTAL

Regarding **polyesterification reactions**, stoichiometric amounts of the reactants and 10 % wt. immobilized lipase from *Candida antarctica* (*Novozym*® 435) were dispersed in toluene and reacted under stirring at 75°C. The procedure yielded polyester prepolymers as colorless solids. Post polymerization followed in a small scale reactor under nitrogen flow at temperatures 60-70 °C for 16 and 24 h[6].

Regarding **polyamidation reactions**, monomer I containing l-phenylalanine ester at both ends was synthesized using a Scotten–Baumann reaction. Stoichiometric amounts of monomer I and 1,6 diaminohexane were dissolved in chloroform in the presence of the protease α-chymotrypsin and polymerization was conducted for 48 h at 37°C under stirring.



RESULTS AND DISCUSSION

The **enzymatic polyesterification** was successfully applied for the preparation of poly(octanediol adipate) (PE 8.6), poly(octanediol dodecanediate) (PE 8.12) and poly(octanediol tetradecanediate) (PE 8.14) with intrinsic viscosity of 0.115-0.189 dL g^{-1} and mass yields 75-90 %, indicating first of all the lipase effective catalytic performance at 75 ^{o}C in toluene. In the comparison between biobased 1,12-dodecanedioic acid and petroleum-based adipic acid, rates were higher for PE 8.12 which can be associated to its higher hydrophobicity and thus its favored diffusion into the hydrophobic active centers of the enzyme. The melting points of the aliphatic polyesters were in the range of 57.6–75.5 ^{o}C (Fig.1) with enthalpy of fusion 76.7-102.7 J g^{-1}, both increasing with the number of carbon atoms in the diacid segment and demonstrating higher compound cohesive energy.

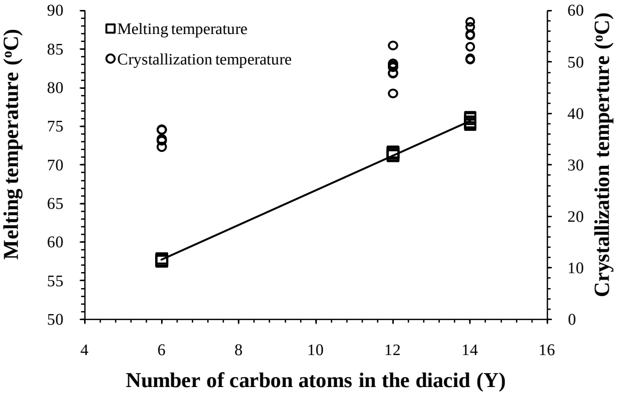


Fig.1. Melting and crystallization temperatures of synthesized polyesters.

The polyesters prepared through enzymatic prepolymerization were submitted to post polymerization at temperatures in the vicinity of their melting points. The intrinsic viscosity increase was restricted to low values (up to 12 %), which was attributed to slow by-product removal through convection caused by passing inert gas. The need for process optimization particularly regarding application of a more vigorous by-product removal step was indicated and the pertinent parameters are currently studied by the authors.

Regarding **enzymatic polyamidation**, the FTIR spectrum verified the prepared polyamide structure: strong absorption at 3277 cm^{-1} was assigned to the N-H stretching vibration of the secondary amide, at 1641 cm^{-1} to the carbonyl stretching vibration and at 1529 cm^{-1} to the N-H deformational vibration. A low vibration at 1734 cm^{-1} was also observed for chain-ends (-C(O)OCH$_3$).

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IN-SITU UPGRADING OF POLYCARBONATE PYROLYSIS PRODUCTS IN THE PRESENCE OF BASIC CATALYSTS

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1. INTRODUCTION

Polycarbonates and the most representative member of this group poly(bisphenol A carbonate PC), consist a group of important polymers, mainly due to a series of desirable properties, a variety of uses and an increase in the annual world consumption[1]. In the current study, pyrolysis, as a thermo-chemical recycling process of polycarbonate-based plastics, was investigated in a fixed bed reactor. Pyrolysis reactions have been performed in the presence of a series of basic catalysts in order to identify the most active catalyst(s) on the PC degree of degradation. In addition, a comparison of liquid, gas and solid products distribution without an active catalyst(s) as well as in the presence of an acidic catalyst were also investigated.

2. EXPERIMENTAL

Pyrolysis of model poly(bisphenol A carbonate) (PC) was investigated through a laboratory-scale fixed bed reactor. A detailed description of the reactor set-up and the experimental procedure can be found elsewhere[2]. All experiments were performed at 600°C.The gaseous and the liquid products obtained from the different pyrolysis runs were characterized by GC and GC/MS analysis. A commercial PC (Aldrich) was used for the experiments (Tg 149.0 °C and melt index 7.00 g/10 min). Catalysts MgO-70 (SSA: 62 m^2/g, SiO_2: 1.2 wt.%) and MgO-71 (SSA: 47 m^2/g, SiO_2: 5.9 wt.%) are natural products derived by calcination of magnesite rocks, while MgO is a commercial chemical produced by Fluka.

3. RESULTS AND DISCUSSION

The aim of the current study was the pyrolysis of a PC sample in the presence of basic catalysts with varying textural properties and purity.

Experiments in the absence of a catalyst (silica sand) and in the presence of an acidic catalyst (ZSM-5) are presented for comparison.

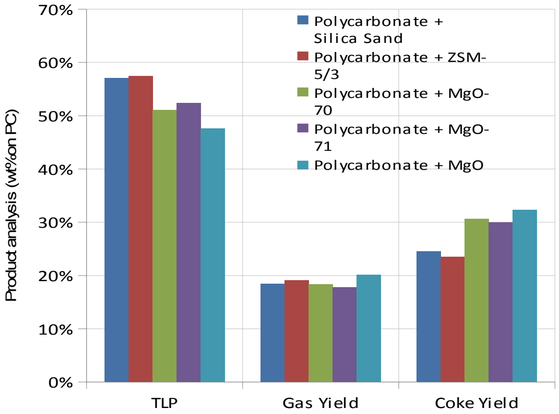

Figure 1: Products yields (wt. % on PC)

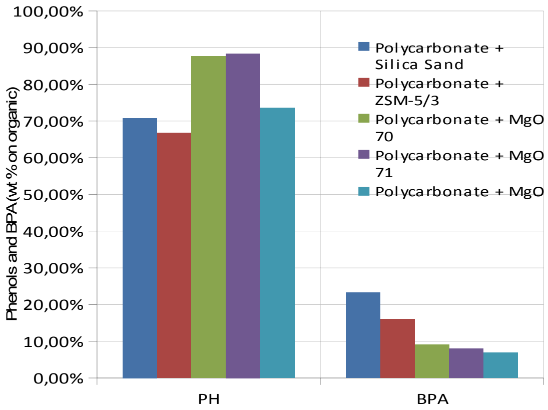

Figure 2: Phenols yields (wt. % on organic)

The main findings from the Figures 1 and 2 indicate that the three basic catalysts decrease the liquid (TPL) compared both to the non-catalytic and the ZSM-5 catalytic runs, indicating extended decomposition of the polymer with the basic catalysts. This is also verified by the decrease in the amount of monomer (BPA) detected in the liquid fraction as shown in Figure 2. This fraction consists mainly of phenols and substituted phenols, which indicates that basic catalysts favor decarboxylation reactions and enhance degradation. Gases were almost unaffected while coke was increased by the use of the basic catalysts.

4. CONCLUSION

All three basic catalysts seem to favor the PC pyrolysis in terms of producing fractions of lower molecular weight and richer in phenols, compared to the non-catalytic and the acid-catalyzed pyrolysis.

Acknowledgements

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SYNTHESIS OF ION-EXCHANGE POLYHIPE NANOCOMPOSITE FOAM FOR REMOVAL OF NITRATE IONS

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One of the applications of polyHIPEs (polymerized high internal emulsions) foams is their uses as ion-exchange membranes [1]. The ion-exchange membrane can be used for many applications such as purification of water, recovery of metal ions, and fuel cells. There are anion exchange membranes with hydroxide (OH^-) and chloride (Cl^-) functional groups. In the chloride type, the preparation of anion-exchange membrane consists of two chloromethylation and amination steps. Nevertheless, the use of chloromethylating agents, such as chloromethylmethyl ether or bischloromethoxy butane is strongly carcinogenic and expensive. The use of functionalized monomers such as vinylbenzyl chloride is the goal of this research work to provide the chloromethylating polyHIPE membranes which are free of the aforementioned drawbacks. In addition, the mechanical properties of the foams were improved by adding Cloisite 30B (C30B) into the organic phase of the foam emulsion. SEM micrographs illustrated that the neat and C30B-reinforced polyHIPE foams exhibited similar open-cellular morphology with a highly interconnected pore structure. On the other hand, the addition of various levels of organoclay to the copolymer foam significantly decreased the mean void diameter as compared to the polyHIPE prepared without any reinforcement. However, the subsequent treatment of the prepared polyHIPE foams with amine agents, e.g. trimethyl amine or triethyl amine, introduces the porous membrane with ion-exchange capability (Fig. 1). The amination of the resulting neat and reinforced foams was carried out using different amounts of trimethylamine (TMA) agent. The ion-exchange capacity (IEC) of the ion-exchange membranes depends on number of ion-exchange groups present in the membrane surface. The IEC variation of the membranes versus TMA and organoclay levels is shown in Figure 2. As it is shown, increasing the TMA concenteration up to 5% increased the IEC value. Further increase of TMA concenteration caused the IEC reached to a plateau region with no significant IEC changes. In addition, the increase of organoclay content up to 1 wt% increased IEC, when further additional organoclay lowered the IEC value. This behavior can be attributed to the effect of organoclay on the morphology and specific surface area of the resuting reinforced memberane. In fact, increasing the organoclay level decreased the size of voids and windows, and consequently reduced the penetration of amine solution inside the foam.

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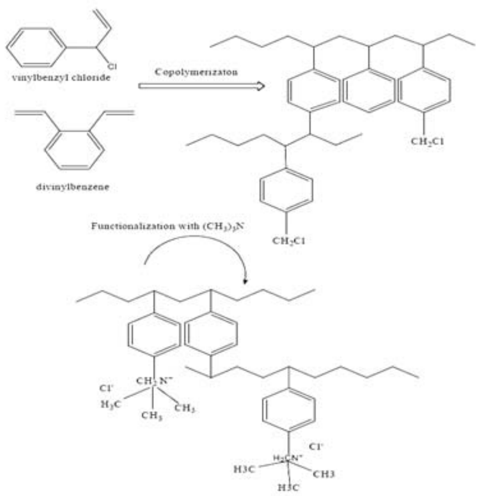

Fig. 1 Polymerization of functional monomers and the amination of resulting copolymer.

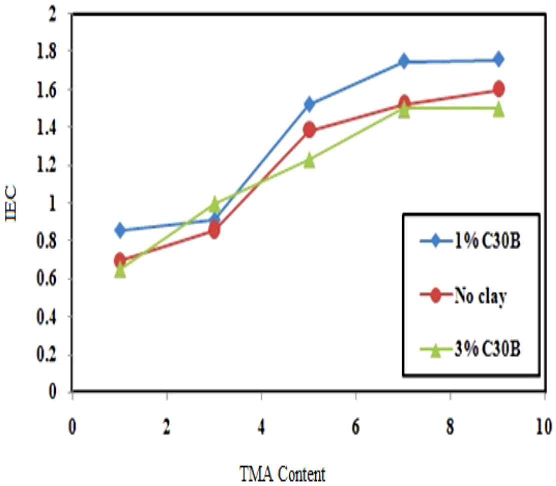

Fig. 2 The effect of TMA and organoclay levels on the IEC of resulting polyHIPE membranes.

STUDY OF THE NANOCOMPOSITE ECOVIO/MONTMORILLONITE CLAY

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The Ecovio, a blend of polylactic acid and Ecoflex, was extruded with 10 wt.% of three different types of clays: Cloisite 20A, Cloisite Na^+ and Cloisite Na^+ treated with Praepagen salt (distearyldimethylammonium chloride). The biodegradability of the materials was evaluated and the mechanical and morphological properties were characterized.

Figures 1 and 2 present the mechanical properties of the nanocomposites. It can be seen that the nanocomposites present higher Young's modulus values than the ones for pure Ecovio. It can be also seen that the Izod impact strength values decrease when the clay is added to Ecovio. However, interesting impact strength results were obtained for the composite containing Cloisite Na^+, and, surprisingly[1,2], with improvement in modulus. These results can be explained in light of the morphologies of the nanocomposites. Figure 3 shows optical images of Ecovio/clay nanocomposites. The nanocomposite with Cloisite Na^+ presents a better dispersion of the clay particles in the matrix than the one with Cloisite Na^+ treated with Praepagen salt. Similar results were obtained when comparing the nanocomposites with Cloisite Na^+ and Cloiste20A.

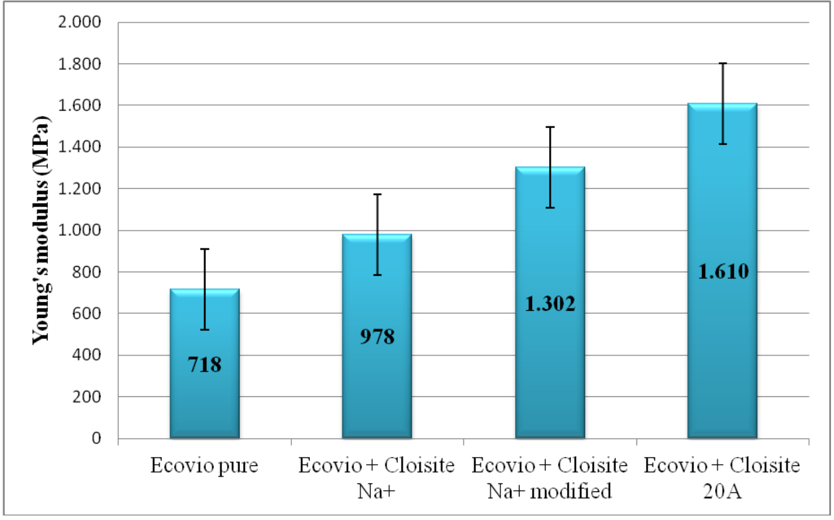


Figure 1 - Young's modulus of the Ecovio and the nanocomposites (Ecovio + Cloisite Na^+, Ecovio + Cloisite Na^+ modified, Ecovio + Cloisite 20A).

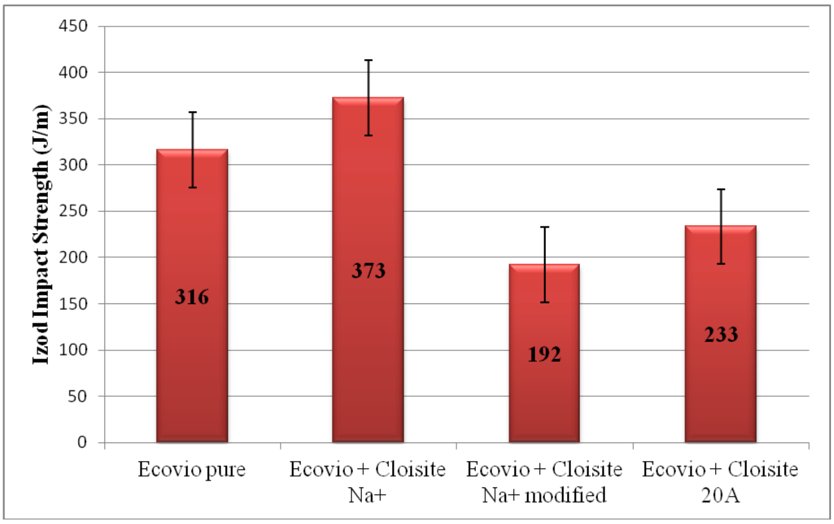
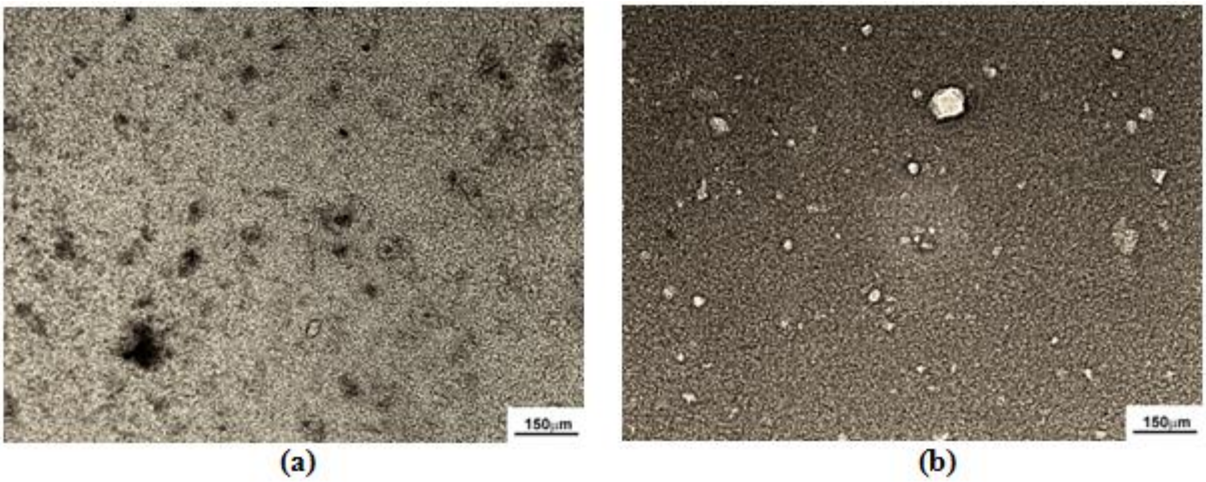


Figure 2 – Izod Impact Strength of the Ecovio and the nanocomposites.



(a) (b)

Figure 3 – Optical images of Ecovio/clay nanocomposites: (a) Ecovio + Cloisite Na$^+$; (b) Ecovio + Cloisite Na$^+$ modified.

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THERMOPLASTC STARCHS: PREPARATION PARAMETERS VERSUS PROPERTIES

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This work presents a systematic study about thermoplastic starch preparation methods. Mixtures of starch and 30 wt.% glycerol, to which citric acid (CA) was added, were obtained by melt blending using an internal mixer. Five parameters were evaluated: the starch water content; CA concentration; and three process parameters: temperature, time and rotor speed. The water and CA contents ranged from 10 to 30 wt.%, and 0 to 10 wt.%, respectively. The variation of the process parameters was as follows: temperature, 100 to 150ºC, time, 8 to 15 minutes, and rotor speed, 100 to 150 rpm. The materials were characterized by torque required to process, FTIR and thermal analysis (DTA/TG).

The evaluation of process parameters, was done using a factorial design 2^2x3^{3-1}. The various treatment combinations of high, low, and intermediate values generated 36 factorial experiments. These were separated in 9 mixtures, listed in Table 1.

Table 1 2^2x3^{3-1} factorial design to study the influence of five variables in the processing of starchs:glycerol:citric acid

Mixture	%H_2O	Citric Acid – CA (%)	Temperature (ºC)
1	10	0	100
2	10	4	125
3	10	10	150
4	20	10	100
5	20	0	125
6	20	4	150
7	30	4	100
8	30	10	125
9	30	0	150

Figure 1 shows some of the curves obtained for mixtures processed under different conditions. Initially, the torque presented overshooting, indicating the gelatinization of the starch. After gelatinization, when the mixtures did not contain citric acid, the torque increasesd. This can be explained by the retrodegradation phenomenon. When citric acid was added to the mixtures the torque decreased. Dueto a reduction of intermolecular forces.

Furthermore, the more water content in compositions with citric acid, the less will be the torque. And for a higher rotor speed, the torque decreases.

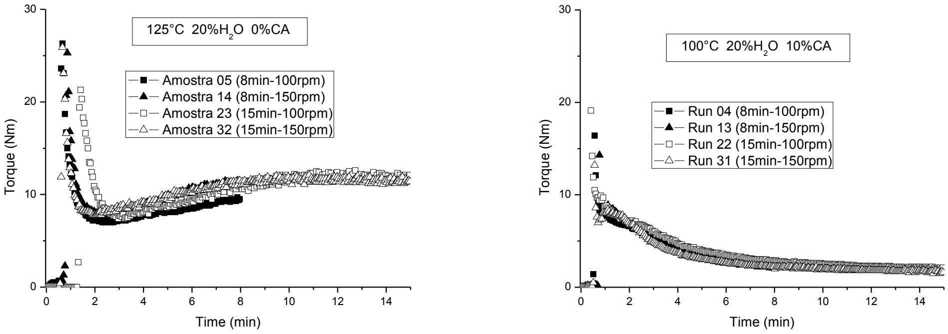

Figure 1. Torque obtained during the mixing process in a torque rheometer (a) Mixture 5 without CA and (b) Mixture 4 with CA.

Table 2 showed the FTIR peak's area in 1729cm^{-1}. This peak is the C=O stretching vibration peak, and it is probably a coalescence peak which is caused by the ester bond and carboxyl groups of citric acid and starch. This peak will indicate that the citric acid reacts with the hydroxyls of starch creating, therefore, ester groups. Is possible to verify that increase the citric acid concentration the area of peaks increase too. It was showed that citric acid is incorporated in the mixture. Although, we have to consider the temperatures are different for each mixture.

Table 2 Peak's area in 1729cm^{-1} in FTIR.

Blend 1		**Blend 5**		**Blend 9**	
1	0.2349	**5**	0.1065	**9**	0.1054
10	0.3749	**14**	0.2185	**18**	0.2265
19	0.2727	**23**	0.1818	**27**	0.2240
28	0.3007	**32**	0.1780	**36**	0.2590
Blend 2		**Blend 6**		**Blend 7**	
2	0.3474	**6**	0.3615	**7**	0.2449
11	0.2016	**15**	0.2750	**16**	0.2871
20	0.1561	**24**	0.5655	**25**	0.1771
29	0.2469	**33**	0.8502	**34**	0.2192
Blend 3		**Blend 4**		**Blend 8**	
3	0.4017	**4**	0.2447	**8**	0.3620
12	2.0256	**12**	0.3213	**17**	0.5041
21	0.4290	**22**	0.2648	**26**	0.4375
30	0.5543	**31**	0.4130	**35**	0.2715

Analyses of TG/DTA showed that CA starts to degrade at 250°C and starch at 330°C. Although in these mixtures without CA there is just one temperature of degradation, in the mixtures with CA there are 2 temperatures of degradation (280 e 330°C). Changing the process parameters the degradation temperatures didn't modify.

Conclusion: The water and citric acid contents, rotor speed and temperature were important parameters to control the properties, while the time wasn't so important.

POLYMERS FOR INNOVATIVE TECHNICAL AND MEDICAL APPLICATIONS

Full Abstracts of Oral Presentations

POLYMER MODIFICATIONS FOR PHARMACEUTICAL EXTRUSION

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The **pharma-extrusion** shows similarities to biopolymer processing, but the peculiarities, required by the drugs, need special attention. Structure-property design and in line control is required aiming mainly to control the polymorphism/amorphization of the drug embedded and thus its dissolution. A complex approach is called "process analytical technology (PAT) technology. The continuous pharmaceutical processing, involved by this approach, is most straightforward in the case of extrusion. Stability is, however, a critical aspect to be considered. Plasticising methods and their role in stabilization efficiency are more important for pharmaceuticals than for conventional polymer systems, while the choice of relevant additives is limited by the authorities. In order to perform gentle processing and still achieve efficient amorphization **supercritical extrusion** was used. Supercritical technique, using supercritical CO_2 (sc-CO_2), is well known in the (nano)pharmaceutical technology, but the most productive way is the sc-extrusion. The amorphization can be well controlled this way because drugs of poor water solubility can be dissolved, at least partially, in CO_2. Than it can be mixed with the polymer matrix in the extruder and the expansion of the bubbles enhance the surface available by the dissolution medium. The results of such as process in the case of Carvedilol can be seen in **Figure 1**.

The drug dissolves from the extrudate very rapidly comparing to the reference.

Porous extrudate can be formed also utilizing the internal pressure of some residual water as proposed by a recent patent (1). Depending on their size and wall thickness, which limit the size of growing crystalline particles, the morphology of drug in the polymer matrix (above T_g) can be affected. An example is the extrusion of spironolactone in presence of hydroxypropyl cyclodextrine (HPβCD).

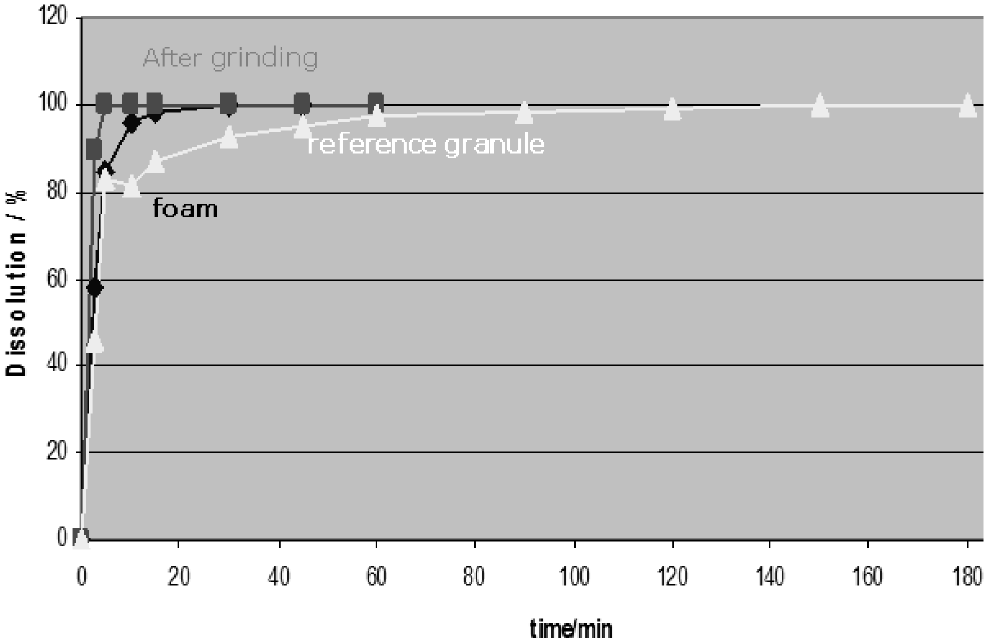

Figure 1 Dissolution of Carvedilol drug from sc-extrudate (♦), from sc-extrudate after grinding (■) and from reference (non-sc-ex) granule (Δ)

Another continuous method for amorphization is the formation of nanofibres by means of **electrospinning**. This method was introduced into the pharmaceutical technology recently. Polyvinyl pyrrolidone (PVP) and Carvedilol drug of poor water solubility were dissolved in methanol for performing electrostatic spinning. All measurements, including XRD, SEM, micro-Raman and DSC, confirmed that the drug is in amorphous state. With PVP K30 the sample dissolved immediately. This is a huge improvement compared to the crystalline Carvedilol dissolution, which took 2 hours.

Methods for forming nanostructured extrudates have a big prospect for pharmaceuticals. Their advantages include the good balance between stability and rapid dissolution.

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EFFECT OF COLD DRAWING ON THE ANTIMICROBIAL AND PHYSICAL PROPERTIES OF PCL/CHX MONOFILAMENTS

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Bacterial contamination is a problem that concerns a wide variety of materials used for biomedical applications. Commonly, inserting an alien material in the body provokes an immune and/or inflammatory response at different intensity levels. This is particularly true for surgical suture threads. In order to contrast these processes, appropriate therapies (antibiotics, anti-inflammatory) must be assumed even if their systemic action is often scarcely tolerated. Alternatively, the active drug could be part of the suture thread, being effective on-site with no systemic consequences. Providing a suture thread or, generally, a polymeric article with antimicrobial properties can be achieved by different routes, including or less the modification of the polymer structure

Polycaprolactone (PCL) is synthetic biodegradable aliphatic polyester widely used for biomedical applications, such as controlled-release drug delivery systems, absorbable surgical sutures and three-dimensional scaffolds for use in tissue engineering.

Chlorhexidine (CHX) is a broad-spectrum antimicrobial agent belonging to the bis(biguanide) family. It is used primarily as a topical antiseptic/disinfectant in wound healing, at catheterization sites, in various dental applications and in surgical scrubs.

In this work we prepared PCL monofilament with antimicrobial properties for surgical suture applications by incorporating CHX during the melt extrusion of the PCL monofilament. The effect of CHX content and of the cold drawing on antimicrobial and mechanical properties of the prepared monofilaments was investigated. Moreover, the possibility to control the release of CHX from the fibres was investigated too.

PCL has been compounded with CHX at different concentrations (1%, 2%, 4% by weight) by using a counter-rotating twin screw compounder. The fibres were spun by using a capillary rheometer operating under a constant extrusion speed; under these conditions the final diameter of the as spun fibres was about 250 µm.

The antimicrobial activity of filaments was determined by agar diffusion method to evaluate the presence of inhibition zones against two Gram-positive and a Gram-negative. Moreover, bacterial growth in presence of the antimicrobial fibres was determined by plate counting test.

All the filaments containing CHX showed a clear zone of inhibition against both Gram-positive and Gram-negative bacteria as shown in figure 1.

The measurements of the bacterial growth revealed, in full agreement with the agar diffusion tests, that pure PCL did not show any antibacterial activity. On the contrary all the samples added with CHX inhibited the growth of the bacterial mass.

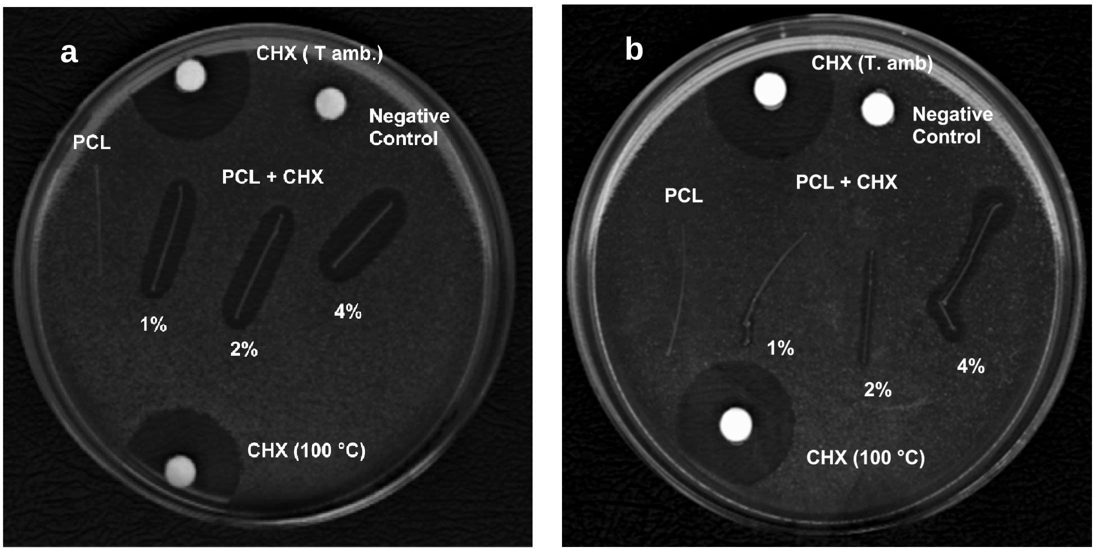

Figure 1 Agar diffusion test performed on *M. luteus* overlay: a) as spun fibres; b) drawn fibres.

The off-line cold drawing of the fibres induced an obvious decrease of their diameter and an increase of the mechanical properties with particular reference to the load at break. Both inhibition tests showed that also the drawn fibres clearly exhibit a strong antibacterial activity.

The evaluation of CHX release showed that, as expected, the amount of released antimicrobial agent raised on increasing the content added to the fibres. Moreover, the drawn fibres released a lower amount of CHX if compared with as spun ones.

TIME-DEPENDENT STRUCTURE CHANGES OF POLYMERS FOR MEDICAL APPLICATION DURIMG THEIR LIFE CYCLE

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As for all polymers, polymers in medical applications must fulfil demanding safety requirements and withstand various influences, such as mechanical, biological or chemical stress. The demands with regard to durability are highly dependent on the specific application. Beyond this, performance with respect to durability is not only determined by the practical application, but is also influenced by the life-cycle history. The oxidative attack at increased temperatures during processing and storage must be considered, as well as irradiation during the sterilisation process and the influence of humidity during the use in vivo [1].

The goal of the work is to evaluate the different aging-relevant parameters for individual polymeric products for medical application. Catheter tubes and syringes based on poly (urethane ether) (TPU) and poly (propylene) (PP) were analysed for their durability against aqueous solutions (TPU) and against oxidation processes (PP) at various temperatures. The changes were characterised by macroscopic and molecular tests methods, such as, mechanical tests, chemical composition analysis (FTIR, TG-FTIR, EDX), changes in morphology (DSC) and oxidation behaviour (ICOT, OIT).

TPU exposure in the autoclave tests under wet and dry conditions does not affect the chemical structure of the material significantly (hydrolysis, oxidation etc.). Beside the continuous loss of processing morphology (short to long-range ordering of hard segments) after 1 d of immersion in a wet environment the material morphology changes significantly. TPU probably incorporates water during immersion, resulting in changed flexibility of the polymer chains. Consequently the microstructure of hard and soft segments transforms to higher-ordered phases or structures [2].

PP syringes exposure to high oxygen concentration in the autoclave result in a significant degradation of antioxidants (Irganox 1010, Irganox

1076, Irgafos 168) (Figure 1). It could be shown that independent on the temperature the major part of the antioxidant is consumed during the first 10 days of immersion. After this time the presence of Irganox 1076 plays the major role in the stabilisation of the polymer due to mechanic stability and carbonyl formation. Under the used aging conditions in autoclave ICOT and OIT measurements detect the major decomposition of antioxidant at the beginning of tests, but both methods alone are not functional to predict the life time of the polymer product.

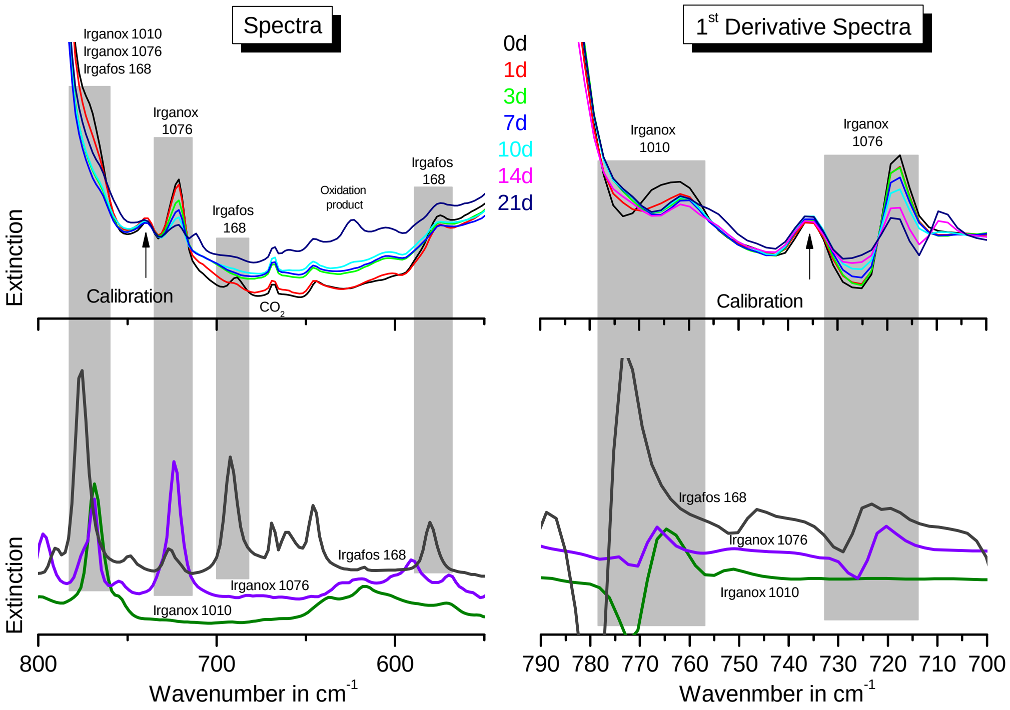

Figure 1 Details of FTIR spectra and derivatives of FTIR spectra of PP syringe and reference spectra in transmission mode at various aging times in autoclave (80°C, 50 bar).

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SYNTHESIS OF NOVEL BIOCIDAL POLYMER BASED ON POLY(HYDANTOIN-METHYL-*p*-STYRENE) AND CHARACTERISTICS OF ITS PROPERTIES

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Recently the great interest is devoted to biocidal polymers which can be applied for obtaining of products able to kill pathogenic microorganisms or at least characterizing by the high resistance to microbial attack. Such promising properties have polymers based on *N*-halamine, particularly hydantoins containing N-Cl bond (the term *N*-halamine signifies a compound with *N*-halogenated imide, amide or amine).

Hydantoins represent the group of compounds which over the past few years have attracted a great attention because of their diverse biological activities including antibacterial, antiviral, fungicidal, herbicidal etc.

A special kind of hydantoins are spirohydantoins which have hydantoin moiety chemically bonded to alicyclic ring condensed with aromatic group. Spirohydantoins were found to have high biological and anti-inflammatory activities[1,2].

The aim of this work was to synthesize a new polymer containing spirohydantoin, desired from 2-tetralone, (**Fig.1.)** and investigation of its physicochemical properties.

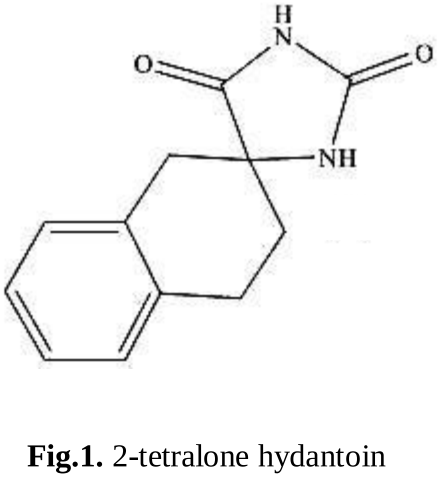

Fig.1. 2-tetralone hydantoin

To synthesize this polymer, firstly a chloromethylated polystyrene via bulk polymerization of 4-vinylbenzyl chloride has been prepared. In the next step, polymer containing spirohydantoins moieties with N-H bond was obtained by *N*-alkylation reaction at the room temperature. Finally, this polymer has been chorinated, during which N-H bond was transformed onto N-Cl[3]. The obtained polymer was totally insoluble in common organic solvents.

Polymer with 5,5-dimethylhydantoin has been also prepared as a model compound.

For confirmation of expected structures of polymers, ^{13}C NMR in solid state and FTIR (in HCB) spectra have been done. The polymer was insoluble either in chloroform, dimethylsulfoxide or tetrahydrofuran even on heating.

Thermal stability of polymer before and after chlorination was studied using TA Instrument SDT 2920 Simultaneous DSC-TGA. It was found that the obtained methylstyrene-based polymer containing the spirohydantoin derivative in para-position is more thermally stable than chloromethylated polystyrene[4]. However, this stability decreased after chlorination.

A novel polymer was synthesised with high purity by new, efficient method. This compound are designed to obtain the materials with biocidal properties. The broad application of such polymers is predicted in textile industry, in production of water or air filters, hygienic articles and protecting coatings in hospital equipments, bathroom accessories or covers of ships.

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Synthesis of functionally modified polyetherimides by reduction using sodium borohydride.

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Polyetherimide (PEI) is an aromatic polyimide patented by the General Electric Co. in 1973[1]. This amorphous thermoplastic polymer combines high strength retention at elevated temperatures, coupled with good resistance to fuels, lubricants, and coolants account for PEI's use in electrical and aerospace applications[2-3].

Polyetherimide Ultem 1000 was functionalized by reduction of phtalimide groups using sodium borohydride as a mild reducing agent. The new chemical structure of the polymers has been fully analyzed by nuclear magnetic resonance, attenuated total reflectance Fourier transformed infrared, gel permeation chromatography and thermal analysis. The degree of chemical modifications induced more colorful polymers with lower thermal stability. However the surface modification of polyetherimides by reduction appeared as a new and interesting way to prepare more hydrophobic PEI suitable for coating or biomedical applications[4-5]. The contact angle measurements and infrared spectroscopy mapping confirmed the successful reduction of the upper layer of PEI films.

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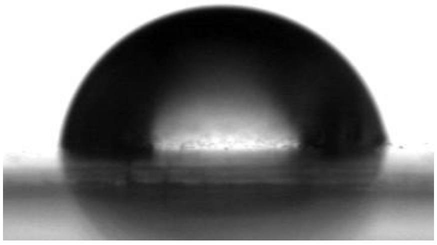
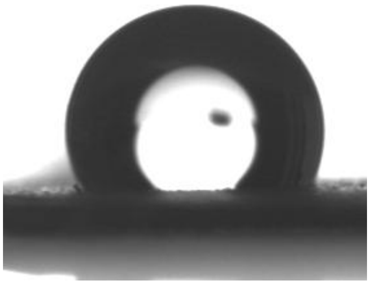
Table1. Average contact angle data obtained from drops of distillated water for pristine PEI and its derivatives.

			
Contact Angle (°)	83°±1°	134°± 4°	162°± 3°
Polymer	PEI	PEI-OH2	PEI-OH4

INFLUENCE OF GRAPHENE NANOPARTICLES ON THE THERMAL STABILITY OF POLYCARBONATE NANOCOMPOSITE FOAMS

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Graphene-based nanocomposites is an important subject of interest nowadays.[1] Knowledge of foams made from these materials is still pretty scarce, mainly due to their multiphase nature, direct result of the combination of a complex developed cellular structure and polymer microstructure.[2] So far, only a few works have investigated the thermal degradation of graphene-based foamed composites.[3-4]

In the present communication, a thermogravimetric study under both nitrogen and air atmospheres was carried out on unfilled and graphene-reinforced solid and foamed polycarbonate composites. The polycarbonate (PC) foams with graphene were prepared using a sc-CO_2 dissolution process. It was found that the decomposition occurred in a one-step decomposition process under nitrogen and in a three-step degradation process in air (Fig. 1). The thermal stability of PC increased with foaming, with the lower relative density materials being the ones that delayed decomposition the most during the first stage in both atmospheres, which was related to their higher thermal insulation. A linear relationship was found between the temperature of maximum mass loss and relative density. In addition, the well dispersed graphene nanoparticles improved the thermal stability of polycarbonate due to their barrier effect, delaying both the escape of volatile decomposition products as well as the thermo-oxidative degradation of the material.[5] Finally, a complete thermo-oxidative decomposition of the char formed in the first process was observed in air, accelerating the degradation process and resulting in zero residues obtained at the end of the process.

The results presented in this work demonstrate that the combination of incorporating small amounts of graphene nanoparticles to a polycarbonate matrix and later foaming significantly improves the thermal stability of polycarbonate, opening up a wider range of applications of this material as thermally-improved lightweight component.

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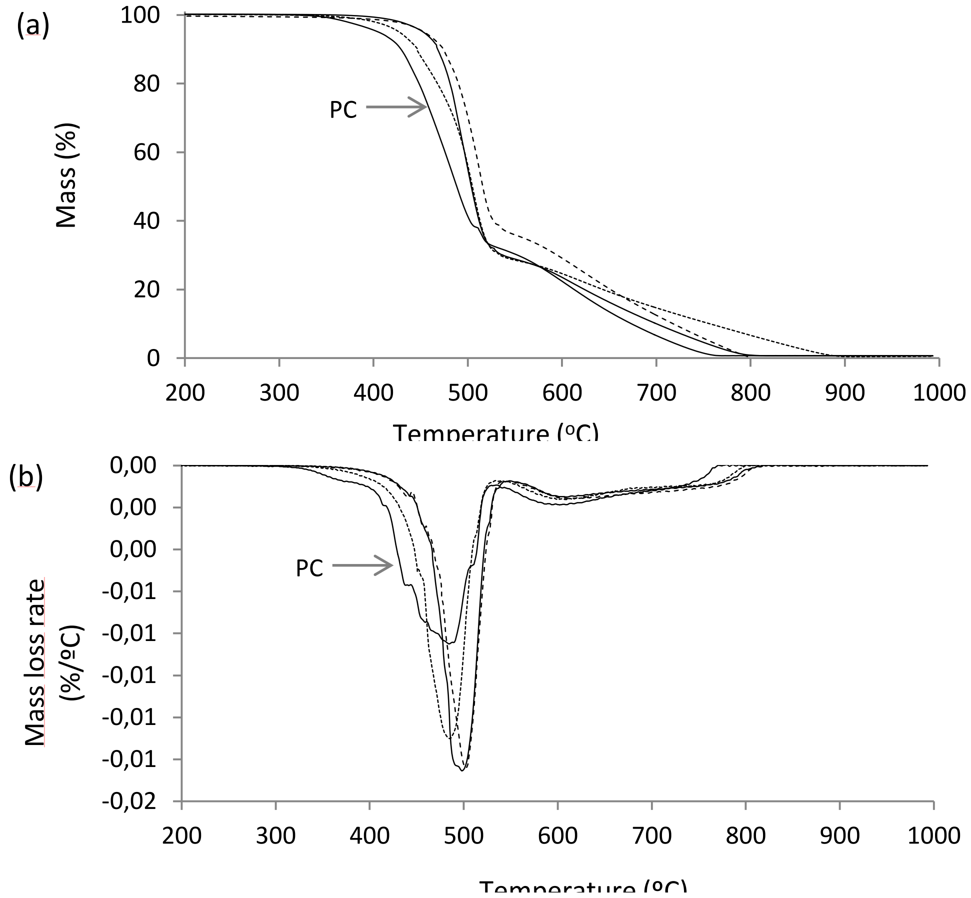

Figure 1. (a) TGA and (b) DTG curves under air atmospheres for the unfilled solid (PC), the foamed PC (PC-f, dotted line), the graphene-reinforced solid nanocomposite (PCg, continuous line) and the foamed nanocomposite (PCg-f, dashed line), obtained at a heating rate of 10 ºC/min.

PHOTO AND THERMAL DEGRADATION OF POLYLACTIDE / ZINC OXIDE NANOCOMPOSITES: EVOLUTION OF THERMAL AND MECHANICAL PROPERTIES

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To limit environmental impact of plastic waste and to ensure low cost of raw materials, development of biosourced biodegradable polymers such as polylactic acid (PLA) receives great interest. Recently, an awareness of general sanitation has led to the development of antimicrobial materials, e.g., using nanoparticles with photocatalytic properties such as zinc oxide (ZnO). For these reasons, PLA/ZnO nanocomposites are potential candidates for applications in packaging and in medical applications[1]. The impact of temperature and/or UV-light can provoke dramatic modifications of the chemical and physical structure of the polymer, with a degradation of the properties. The main objective of this work was to correlate the local modifications provoked by thermal/UV exposure of PLA and PLA/ZnO nanocomposites with the evolution of the mechanical and thermal properties, in the bulk and at the surface.

Changes in bulk mechanical and thermal properties were characterized by Differential Scanning Calorimetry (DSC), Dynamical Mechanical Thermal Analysis (DMTA) and MicroHardness tester. Surface evolution of films of PLA and PLA/ZnO nanocomposites was investigated using an Atomic Force Microscope (AFM) and techniques derived such as nano indentation and nano thermal analysis (Vita mode). Accelerated artificial ageing of the samples was performed either by irradiation at λ>300 nm and 60°C in SEPAP 12-24 or in an oven at temperatures between 60°C and 100°C.

Photo- and thermal ageing provoke bulk crystallization, as observed by DSC and DMTA analysis, and chain-scissions that are evidenced by Size Exclusion Chromatography.

ZnO nanoparticles strongly absorb in the UV domain, which provokes heterogeneous degradation resulting from light absorption profile[2] within the PLA/ZnO nanocomposites films. At the surface of the samples, a progressive crystallization is evidenced by AFM images. As an example, after 300h of UV light-irradiation, glass transition temperature of PLA-3 % ZnO disappears, and the transition temperature detected at 103°C should be the melting temperature (Figure 1). By transition temperature analysis with the AFM Vita mode, we are able to discriminate crystallization and crosslinking reactions. Correlation between surface thermal transition temperature and nano hardness will be discussed.

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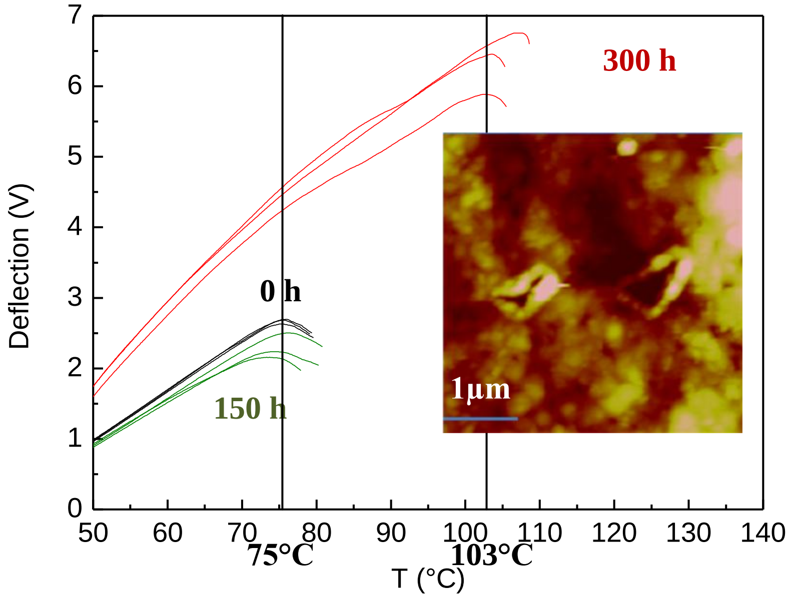

Figure 1: Evolution of the surface thermal transition temperature of PLA – 3% ZnO nanocomposite film during photo ageing in SEPAP 12-24 using an Atomic Force Microscope at various irradiation times (a) 0 h (b) 150 h (c) 300 h (inset) AFM image showing two holes obtained after surface thermal analysis of PLA – 3% ZnO photo irradiated 150 h.

STYRENE/ACRYLIC ACID COPOLYMERS MODIFIED BY CROSSLINKING AND SULFONATION REACTIONS FOR THEIR USE AS MEMBRANES IN FUEL CELLS

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Abstract

Proton permeation membranes used in hydrogen fuel cells need to have mechanical resistance, hydrophilicity to work in a humid environment but insoluble to water and ability to transport protons from the anode to the cathode side of the cell. Such properties are almost covered by Nafion (DuPont), which has some disadvantages as high cost, and unsatisfactory proton conductivity, as well as some permeation to oxygen and hydrogen. In this work styrene/acrylic acid copolymers were prepared for their use as economic membranes for fuel cells expecting to have mechanical and proton permeation properties through several concentrations of crosslinking and sulphonation and sulphonation reaction time.

Introduction

Aromatic polymers are thermally and chemically stable and are therefore potentially useful for making membranes due to its excellent mechanical properties[1]. However it is also necessary that the membrane contains a certain degree of moisture in order to perform the proton conduction phenomenon[2]. One way to achieve this moisture is by copolymerization of acrylic acid with styrene, the carboxylic groups help the swelling of the membrane on contact with water. Subsequently the copolymer is subjected to sulphonation reactions to incorporate -SO_3H groups to the benzene ring, which readily ionize it and thus provide the proton conductivity[3]. The water absorbed by the membranes decreases mechanical properties acting as a plasticizer, reducing Tg and modulus of the membrane[4]. However, this phenomenon can be compensated by decreasing the molecular mobility of the material by crosslinking, e.g. divinyl benzene (DVB) for the formation of networks[5].

It is also advisable to select carefully the conditions and agents to prevent crosslinking through sulphone formation[6,7], from sulphonic acid groups, as well as undesired side reactions, especially when using strong sulphonation agents[1].

Experimental

Polymerization. The radical copolymerization in solution of crosslinked styrene-co-acrylic acid was carried out under a nitrogen atmosphere in a glass reactor. Reaction involved introducing the styrene, acrylic acid, benzoyl peroxide (BPO) and divinylbenzene (DVB) into the reactor with diethyl benzene. Considering stirring (200 rpm) and reaction temperature of 90 °C, the polymerization was performed during 120 min. The reaction was stopped and the copolymer recovered by precipitation into methanol. The copolymer was purified dissolving it in acetone and recovered by precipitation into boiling distillated water and finally dried under vacuum at 65-70 °C for 48 h. Copolymers were confirmed by FTIR and RMN.

Copolymer sulphonation. The styrene/acrylic acid copolymer sulphonation was carried out at 40 °C in dichloromethane using an equivalent molar quantity of H_2SO_4 conc. or fresh acetyl sulfate as sulphonation agents, at 1 and 2 hr of reaction time.

Membrane preparation. The copolymer and sulphonated copolymer solutions were dissolved in THF and passed through a 0.45 μm filter. Films were cast from solutions onto a glass mold. The resulting films possessed thicknesses of about 83-93 μm.

Characterization. Gel permeation chromatography (GPC) was carried out with a Hewlett Packard chromatograph, using copolymer solutions of 1mg/1mL. The instrument had three Ultrastyragel columns (105, 104, 103 Å) with THF as eluent at a flow rate of 1 mL/min (40 °C) and polystyrenes as standard. Glass transition temperatures of the copolymers were measured by differential scanning calorimetry (DSC) using in a 2920 TA Intruments. Samples were first heated up to 170 °C, cooled rapidly to room temperature and then scanned again at a rate of 20 °C/min. Dynamic mechanical analysis (DMA) was carried out with a TA instruments Q800 using a tensile mode, heating ramp of 2 °C/min and frequency of 1 Hz. Samples were heated from ambient to 130 °C.

Results and discussion

Table 1 lists experimental conditions, T_g, molecular weights and PDI of the copolymers obtained as well as the E’ obtained by DMA.

Table 1. Experimental conditions and characterization results from the non-sulphonated styrene/acrylic acid copolymers.

Reaction	*BPO (% molar)*	*DVB (% molar)*	*T_g [a] (ºC)*	*Mw (g/mol)*	*Polydispersity index (PDI)*	*E’ [b] (MPa)*
A	0.045	0.25	119.4	182,799	3.1	2922
B	0.045	0.30	119.2	245,590	3.6	2061
C	0.050	0.00	91.8	93,662	1.9	N.F.
D	0.050	0.05	111.9	87,155	2.6	N.F.
E	0.050	0.20	120.4	156,048	3.1	1482
F	0.050	0.30	118.8	248,100	3.5	2569
G	0.175	0.15	116.9	100,371	2.3	N.F.
H	0.300	0.00	107.8	44,923	1.7	N.F.
I	0.300	0.05	112.4	41,509	1.9	N.F.
J	0.300	0.10	93.6	47,658	2.0	N.F.
K	0.300	0.30	113.1	128,606	3.4	N.F.

[a] Tg by DSC, [b] E’ by DMA, value at ambient temperature, NF= Unable to make film

We can observe that there is only one Tg value for each copolymer, indicating that in fact we have a random copolymer, instead of a block copolymer, which would result in two separated Tg values.

Only four copolymers were able to make films (A, B, E and F), which are the ones with the largest molecular weights and PDI from among all samples, except K reaction. The latter suggests the reason for feasibility to make films by casting, unlike the other copolymers with more brittleness. It is also clear that E’ values has a linear relationship with Mw[8,9]. Figure 1 shows E` traces and the results in a 3D graph showing clearly the effect of the variables evaluate (Concentration of BPO and DVB) into Mw.

Copolymers prepared with 0.05 % BPO were selected for sulphonation reactions with concentrated sulphuric acid and acethyl sulfate. From FTIR data it was observed that long sulphonation time with acethyl sulphate enhances the signal at 1064 cm-1 (stretching S=O) corresponding to sulphonic acid, but reduce it when treating with sulphuric acid. The latter suggests two possibilities: high sulphonic acid formation that make the material highly soluble in water (lost by washing) or decomposition of the structure by the strong acid treatment.

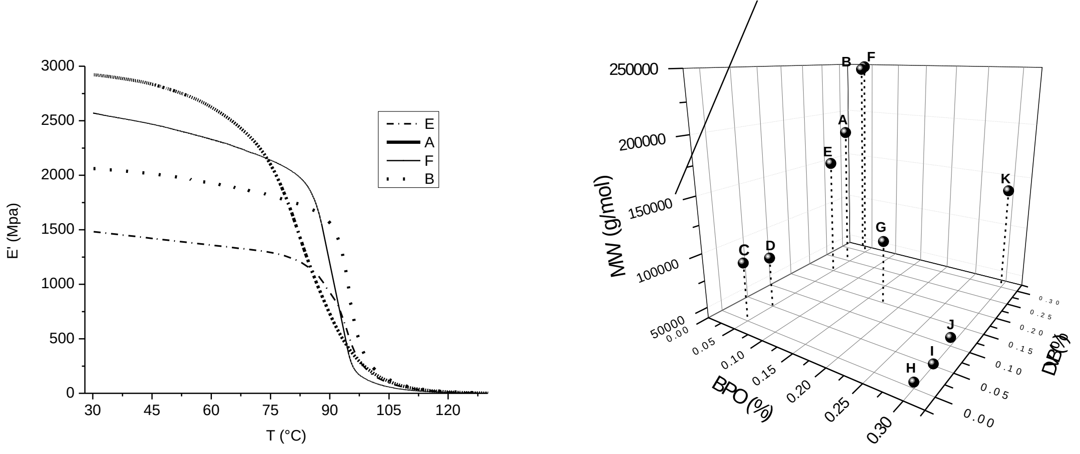

Figure 1. DMA results for films and effect of experimental conditions on Mw.

A noticeable effect observed for long sulphonation time (both agents) is the formation of a cyclic ketone as remanent after nucleophilic aromatic substitution over the carbonile with water elimination.

Conclusion

Copolymers were prepared in a random sequence and high concentration of initiator and low level of DVB reduce Mw and availability to make films as a consequence. Sulphonation reaction can be carried out by using sulphuric acid or acetyl sulphate, specially the latter, with some effect in loosing wettability when loosing acrylic acid through ketone formation.

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IMPACT OF OPERATING CONDITIONS AND MEMBRANE DEGRADATION ON PERFORMANCES OF PEMFC

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From ecological and economical points of view, there is a strong urge to use sustainable energies and at the same time to decrease the pollution impact of human activities. Fuel cells by converting chemical energy (hydrogen) into clean electrical power can be part of the solution[1]. However, costs and performances of the polymer electrolyte found at the heart of the cell still have to be improved (durability[2], ability to withstand both higher operating temperatures and dryer gases…), and are the subjects of intense research.

Polyaromatic membranes, like sulfonated poly(Ether Ether Ketone) (sPEEK), used as polymer electrolyte for fuel cells offer a better thermomechanical stability than perfluorosulfonic membranes like Nafion (reference membrane) but a much lower chemical stability. Our goal was to understand the impact of fuel cell operating condition on the chemical stability of this alternative membrane and on the device performances.

In a first step focused on the impact of operating conditions on the device performances, we observed when increasing gas stoichiometries, a much important decrease of the performances for sPEEK than for Nafion, as illustrated in Figure 1. Electrochemical Impedance Spectroscopy (EIS) was used to understand the origin of the performances drop observed for sPEEK[3]. This technique highlighted a very high spatial heterogeneity of hydration and therefore of performance, due to slower water transport in the polyaromatic membrane. Chemical degradation was not responsible for the fast drop of performances observed after few hundreds of hours of operation, as we demonstrated that performance could be recovered, at least in part, after rehydration of the membranes. However a non-reversible ageing was noticed through the slight decrease of the molecular weight observed for sPEEK 3/1.5, and the drop of the initial output voltage, not recovered after rehydration of the membrane.

In order to test the impact of chemical and structural modifications resulting from oxidative ageing (H_2O_2 can be produced during fuel cell operation) the second step of this study was focused on ex-situ ageing tests. These tests highlighted the correlation between a decrease of the sPEEK molecular weight observed during ageing and an improved swelling and conductivity of the modified membranes. In conclusion we have shown that a pre-oxidation of the membrane, using a H_2O_2 solution, improves sPEEK in-situ performances to such an extent that it could reach those of Nafion.

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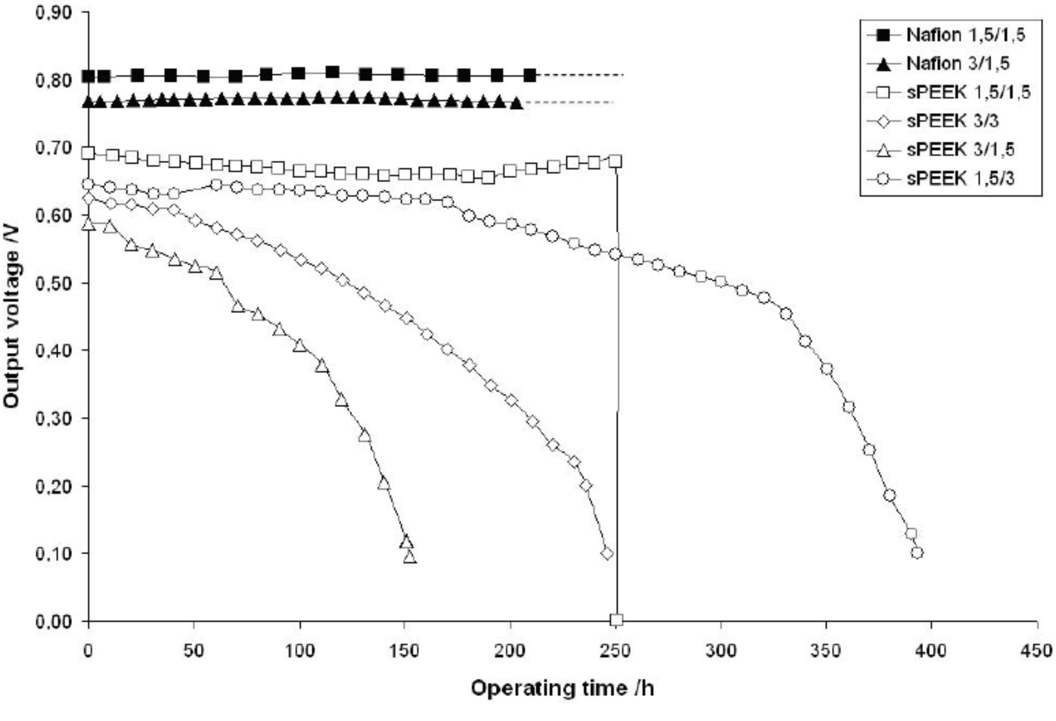

Figure 1: Evolution of output voltage as a function of operating time, for different gas stoichiometry configurations for both Nafion and sPEEK membranes.

CHEMICAL STABILIZATION OF POLYMER ELECTROLYTES USED IN PEMFC

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Proton exchange membranes (PEM) are key components in fuel cell (FC) systems as they allow proton transport between the two electrodes, without any gas mixing. However, the enhancement of the durability of the PEM lifetime is critical to viability for the FC. The aging of the membrane is due to a chemical / electrochemical and a mechanical degradation. Hydrogen peroxide and its products of decomposition (HO• and HO_2•) generated during the fuel cell operation are considered as one of the important vectors of the membrane degradation[1,2].

The first works devoted to a strategy of chemical stabilization of membranes appeared only very recently (2003). These works are based on a radical scavengers approach[3, 4]. Following a different strategy, our work intends to develop sacrificial stabilizers able to decompose hydrogen peroxide formed in fuel cell operation. Two stabilizers based on thiourea (THP) and tetrasulfide (TS) groups were synthetized. In order to avoid leaching of the stabilizer induced by membrane swelling in the fuel cell, the stabilizer were grafted onto SiO_2 nanoparticles (figure 1). Nanoparticles dispersion in the membrane is expected to have a strong impact on both conductivity and mechanical properties of the membrane, and was thus thoroughly studied.

AFM analyses performed on the cross section of cryo fractured membranes have shown an excellent dispersion of functionalized THP loads whereas the formation of aggregates was observed with functionalized TS. (figure 2a). The ability of stabilizers to limit the membrane degradation was evaluated with a sPAEK membrane, for different aging times in an H_2O_2 environment. The most efficient stabilizer appears to be the one based on THP groups. However, this stabilizer cannot be used because strong acid base interaction with the sulfonic groups of the polymer reduced the proton conductivity of the membrane and as a consequence the performances of the FC. On the other hand, the oxidation of the TS stabilizer leads to the formation of sulfonic groups and consequently to an increase of the ionic conductivity of the membrane (figure 2b).

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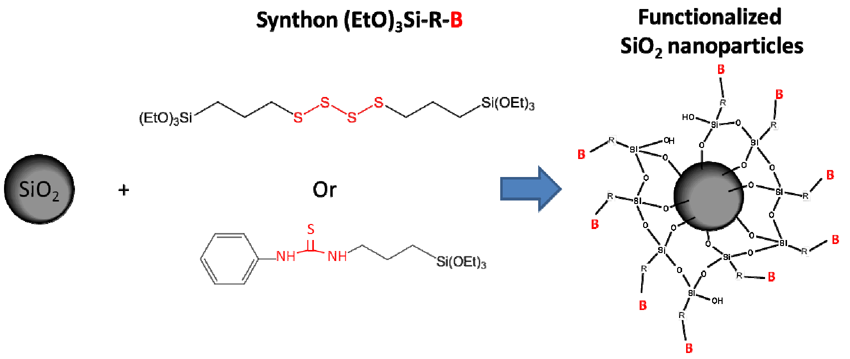

Figure 1: Synthons grafted on SiO_2 particles to produce stabilizing nanoparticles

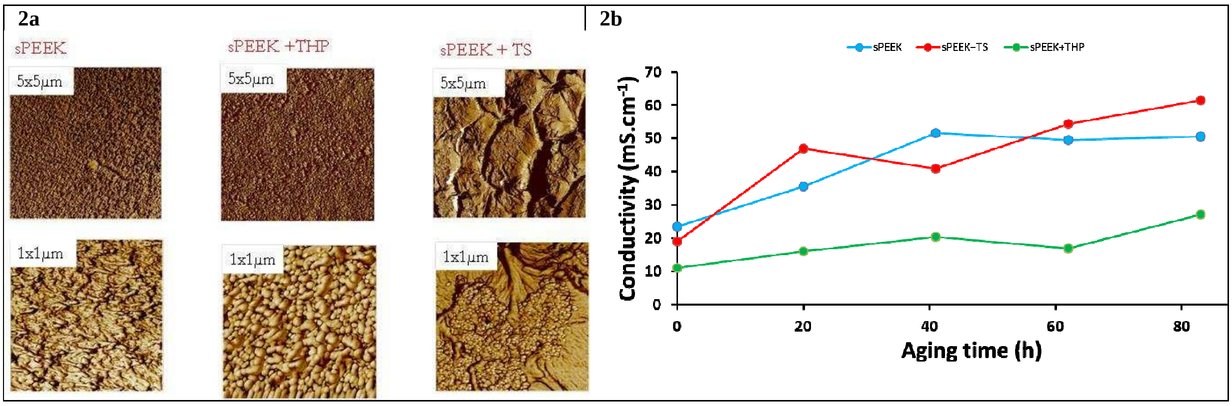

Figure2: a-AFM image of cryo-fractured membranes (tapping mode/phase contrast) and b-Ionic conductivity of the composite membranes versus aging time in H_2O_2 vapor at 70°C

PHYSICAL PROPERTIES OF CROSS-LINKED CHITOSAN ELECTROSPUN FIBER MATS

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Chitosan is the deacetylated derivative of chitin, which is the second most abundant polysaccharide found in nature, after cellulose. Chitosan has several interesting properties such as biodegradability, lack of toxicity, antifungal effects, and acceleration of tissue regeneration, hemostatic nature and immune system stimulation that make it an attractive material for medical applications[1].

Chitosan fiber mats were successfully processed by electrospinning. The as-spun fiber mats were neutralized with ethanol and cross-linked with glutaraldehyde. It was observed that the mean fiber diameter decreases from 243 ± 43 nm down to 215±53 nm and that the processing conditions do not alter the initial deacetylation degree of the polymer.

Polymer crystallinity index shows a decrease from 61 % for the Protasan material down to 17 % for the cross-linking fiber mats. A swelling index up to 1000 % was observed for the cross-linked samples. Preliminary MC-

3T3-E1cell culture showed good cell adhesion and proliferation in the cross-linked chitosan fiber mats.

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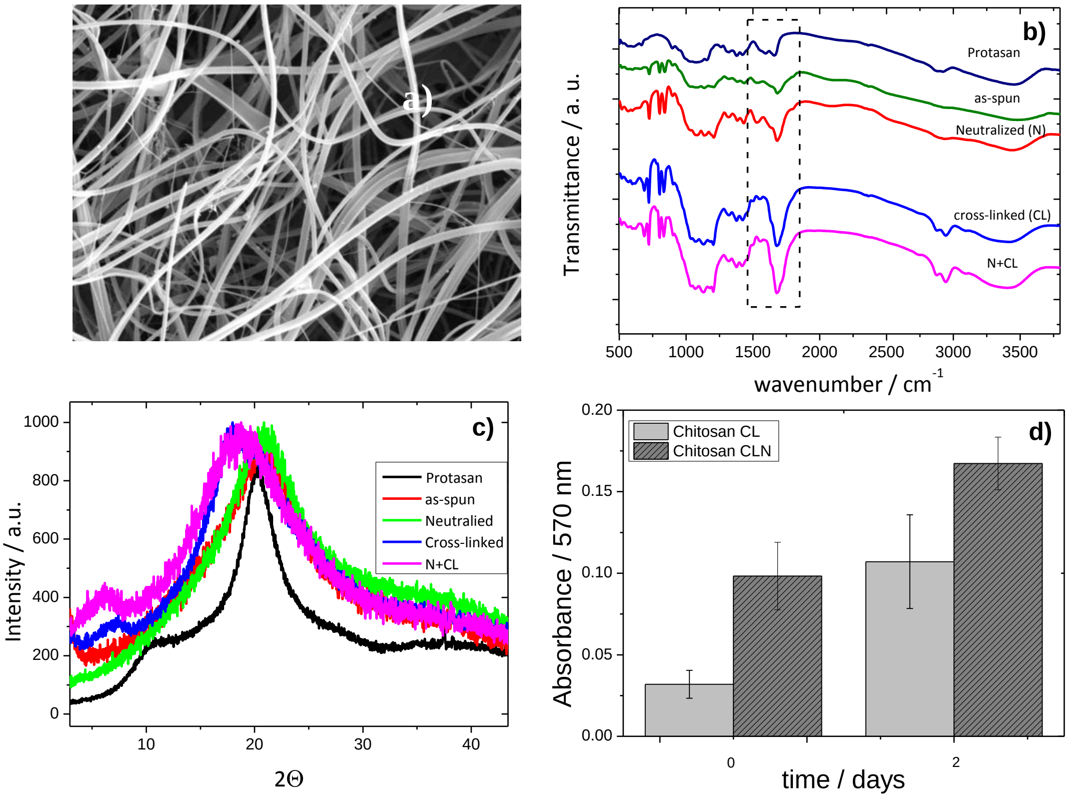

Figure 1: a) Chitosan electrospun membrane after neutralization and cross-linking, b) FTIR spectroscopy results for the different chitosan membranes, c) Evolution of crystallinity index after different processing conditions and d) MTT absorbance results after cells seeded for 0 and 2 days on neutralized and cross-linked chitosan fibers. Values are mean ± SD.

WATER-THINNABLE UNSATURATED POLYESTER RESINS WITH HYDROPHILIC SULFONATE GROUPS FOR COATING APPLICATIONS

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An emission of volatile organic compounds (**VOC**) is an important problem, related to the production of polymers for paints, lacquers, pigments and other coating materials. The legislation of European Union restricts the content of **VOC** in coatings composition. Our research concerns reducing the emissions of **VOC** from polyester composition.

The main subject of presented works is investigations on UV-curable polyesters binders for water-borne coatings compositions for different kind of applications. Water-thinnable unsaturated polyester resins (**WTUPR**) are usually obtained by using carboxylic polyfunctional monomers in the process of polycondensation and afterwards the neutralization of the resulting carboxylic groups with volatile tertiary amines [1]. Moreover, other volatile organic compounds are often used in the manufacture of **WTUPR**, for example co-solvents and other additives supporting dispersion. A different concept of the **WTUPR** synthesis is the introduction of highly hydrophilic sulfonate groups ($-SO_3Na$) into the polyester chain [2,3].

In our laboratory we have been working on this subject for many years. We have developed a new method of obtaining **WTUPR** with sulfonate groups using specially synthesised aliphatic sulfonate comonomers. This monomers can be incorporated into the polyester chain by polycondensation [4] or copolymerization [5] process. Elaborated methods are very sensitive to precipitation of sulfonate monomers in non-polar environment. This is a result of a strong hydrophilic character and a very low solubility of sulfonate monomers in non-polar reaction medium in the time of synthesis process. New solutions related to different types of sulfonate monomers and their incorporation into polyester chain are necessary. Innovative sulfonate monomers in polyesters synthesis environment should be more compatible.

Our present studies are focussed on the sulfonation of organic compounds which can be included into the polyester chain as hydrophilic monomers. The methods of the sulfonation of organic monomers were elaborated and optimized. Hydrogensulphate (IV) sodium was used as a sulfonating agent. The following hydrophilic monomers were obtained: trimethylolpropane ether with a sulfonate group, sodium salt of 2,3-dihydroxypropane-1-sulfonic acid (a new manner of synthesis), sodium salt of 3-hydroxypropane-1-sulfonic acid, sodium salt of 1,4-dihydroxybutane-2,3-disulfonic acid, sodium salt of 1,4-dihydroxybutane-2-sulfonic acid. The individual steps of the processes were elaborated. Particulars products of the reaction were isolated. The most effective way of the synthesis of each sulfonate monomer was suggested. All products were analyzed by ^{1}H HNM and ^{13}C NMR spectrums. Occasionally, mixtures of some products were obtained. It does not disqualify the application of mixtures of monomers in the syntheses of **WTUPR**.

The preliminary works on the practical applications of monomers for the syntheses of **WTUPR** with hydrophilic sulfonate groups were done. The pilot syntheses of polyesters were carried out. Selected **WTUPR** was diluted in water. The composition containing photoinitiator and other additives was applied by means of an applicator onto the glass plates. The film was cured by UV irradiation in air atmosphere. There was no emission of harmful organic compounds during hardening. In this manner coatings with high pendulum hardness and good properties were obtained.

The aim of further work will be focussed on the optimization processes of the synthesis of polyester resins with sulfonate groups and on the processes of obtaining their water dilution for practical applications as covers for different materials.

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POLYMERS FOR INNOVATIVE TECHNICAL AND MEDICAL APPLICATIONS

Full Abstracts Of Poster Presentations

INFLUENCE OF POLYAMIDE (PA 6) DURING STERILIZATION OF BIOMEDICAL DEVICES

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In order to protect operators and patients during handling and everyday use of biomedical products, special attention has to be paid to sterility during and after manufacturing. Unfortunately, conventional sterilization methods can accelerate the aging process of polymer products during the applied very high temperatures in steam sterilization, the exposure to beta or gamma beam radiation or the use to toxic chemicals, such as ethylene oxide or formaldehyde. Finding a more ideal method for sterilization of biomedical polymer products is advantageous and important for safe application.

Steam and ethylene oxide sterilized products could show polyamide-marks not expected to be there. It was found, that the sources can be polyamide parts in the product or the blister pack of the product. This suggests that during the sterilization process, polyamide, or rather ε-caprolactam, dissolves and deposits subsequently. This assumption has to be proved in further research.

The scope of our investigation comprises a search of PA 6 segments and an estimation of the solubility of this material related to sterilization conditions. In this investigation PA 6 granulate, PA 6 containing blister packs and PA 6 containing medical products are stored in water or steamed at different temperatures. These experiments were performed at RT, 40, 60, 80, 100, and 120 °C respectively in oven (Figure 1). Alternatively experiments in autoclave were carried out. Afterwards the dry samples are examined more closely using thermo-analytical (TA) methods like differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). Furthermore some structural analysis methods as Infrared spectroscopy (FTIR) were used.

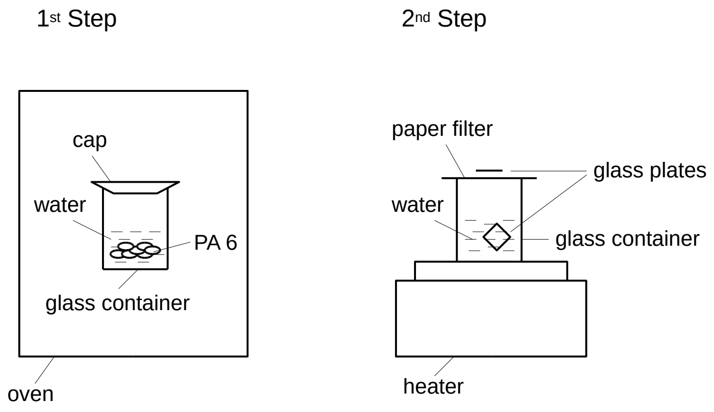

Figure 1 Construction of the evaporation experiment

First investigations shows that in the experiments the polyamide granulate, the polyamide containing blister package as well as the polyamide containing medical products degradate, resulting in polyamide films on small glass plates. These were located in and on the above the evaporating water mixture in which the polyamide containing things were stored.

The intensity of the polyamide film, detected by FTIR shows a clear dependency on the applied temperature (Figure 2). However, TGA investigation reveals no significant mass change or degradation behavior of the polyamide species. In DSC investigation no clear evidence for a changed molecular distribution was observed.

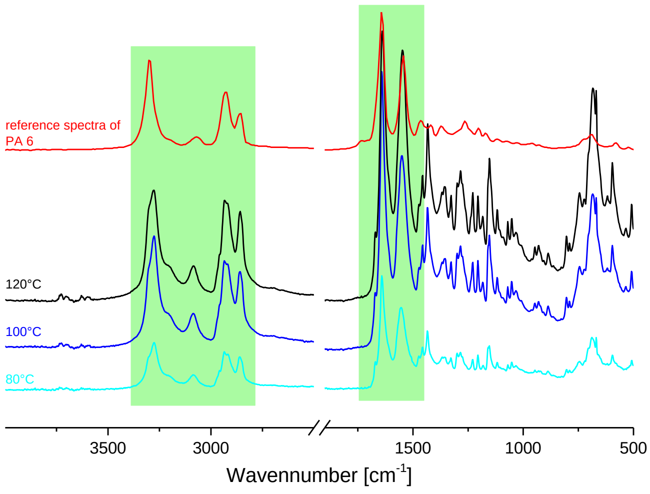

Figure 2 FTIR spectra of condensed polyamide films, produced by experiments described in figure 1

Characterization of biomedical devices based on polycarbonate urethane for orthopedic applications.

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Introduction. Thermoplastic polyurethanes (TPU) are a popular choice for use in medical devices, thanks to their combination of excellent biocompatibility, versatility and mechanical properties [1] Poly(ester urethanes) were the first generation of polyurethanes used in medical devices, but were found unsuitable for long-term implants because of rapid hydrolysis of the polyester soft segment. Later on, poly(ether urethanes), more resistant to hydrolysis, replaced poly(ester urethanes), but again several studies demonstrated that the polyether soft segment is susceptible to oxidation after extended periods *in vivo.* In the last years poly(carbonate urethanes) *(*PCU) were proposed as a more biostable alternative in long term implants. PCU, as all TPU, typically shows a two-phase structure in which hard segment micro domains, are dispersed in a matrix of soft segments. Modulating the ratio of the building blocks allows to obtain materials with different hardnesses, which can be used in different applications.

In the present work, three devices were investigated: Dynesys™ (Zimmer Inc.), non-fusion implant system for spine, based on a harder PCU (Bionate 55D) and TriboFit® hip system and NUsurface™ tibial implant (Active Implant Corporation, Memphis, TN), based on a softer PCU (Bionate 80A).

Experimental. Three TriboFit® acetabular component (A) and two NUsurface™ tibial plateau (T) were tested and compared with the pristine resin (Bionate 80A, DSM PTG Berkeley CA). Two of the acetabular components (A2 and A3) had been implanted for different periods (40 days and 4 months), while the others were new, as received from the manufacturer.

Five Dynesys™ system cylindrical spacers, based on Bionate® 55D, were also analyzed. All these medical devices were implanted for different period ranging from 0,7 to 7 years (avg. 2,5).

A differential scan calorimeter (DSC Q200, TA Inc.), provided with a cooling system RCS90, was used to investigate the microphase morphology of the prosthetic devices. The DSC measurements were performed with a closed aluminium pan under nitrogen atmosphere (50 cm^3/min) and with a 20°C/min heating rate, from -75°C up to 230°C cyclically, on 10-15 mg samples. The surface of the prosthetic devices was observed by scanning electron microscopy (SEM) on a Zeiss EVO 50 microscope. The samples were gold-coated using a sputter coater (Bal-tec SCD 050) for 60 s under vacuum at a current intensity of 60 mA. Micro ATR-FTIR spectra were recorded on a FT-IR microscope (Perkin-Elmer, Spectrum Spotlight 300), in the attenuated total reflectance (ATR) mode with a germanium crystal, using 16 scans per spectrum and a resolution of 4 cm^{-1}.

Results and Discussion. MICROPHASE MORPHOLOGY – DSC measurements were used to compare the morphology of TriboFit® and NUsurface™ samples with that of the pristine material, Bionate® 80A. The observed thermal transitions are summarized in Table 1, while more details on the attribution of these signal are given elsewhere [3]. The glass transition temperature of the prosthetic samples were found to be slightly shifted, with respect to that of the original resin, indicating a slightly different phase separation. The first endotherm, related to the degree of short range order, is significantly changeable, ranging from 80°C to 120°C, suggesting a quite different thermal history of the samples. The second endotherm, related to the mixing of the hard and soft segments, was detected around 160-166°C for all the samples.

On the contrary, DSC measurements performed on Dynesys™ system shows a good reproducibility among different samples. The glass transition temperature was detected at -5 (±2)°C, the first endotherm at 104 (±4)°C and the mixing signal at 177(±1)°C. These prostheses were probably subjected to a similar thermal history, resulting in a more reproducible morphology.

SURFACE DEGRADATION – All the prosthetic samples show a visible yellowing with respect to the colourless pristine material. Moreover, wear marks were visible on the external surface of all the retrieved samples
SEM micrographs of the retrieved acetabular cups showed the presence of branched fissure on the bearing surface The back surface exhibits a “spongy” aspect and the presence of some attached micro-aggregates.

ATR-FTIR analyses of the retieved acetabular components indicate the presence of species absorbed on the surface. Further analyses are in progress in order to clarify their nature.
The ATR-FTIR spectra of Dynesys™ after implantation are reported in Figure 1. New bands are observed at 1645 and 1174 cm^{-1}, along with a decrease in the 1737 and 1249 cm^{-1} peaks intensity, which was attributed to the degradation of the soft carbonate-based segment, probably resulting in chain scission.[2]

Conclusions. The heterogeneous thermal characteristics of TriboFit® and NUsurface™ may be probably a consequence of variable manufacturing, processing and storage conditions. A high thermal sensitivity was already observed in the pristine resin, Bionate® 80A.
The presence of absorbed species was found at the surface of the retrieved samples. Long-term implanted devices show evidences of probable degradation. Further studies are in progress to clarify this issue.

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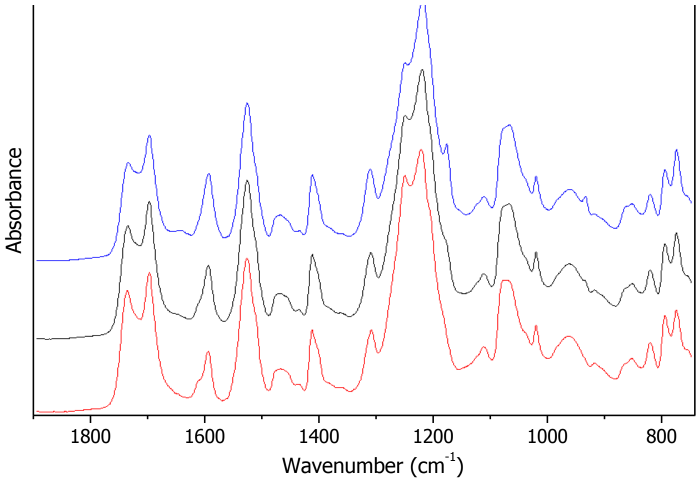

Fig.1. ATR-FTIR spectra of different area of Dynesys™ system.

Table 1. Thermal transition temperatures of the acetabular components (A) and tibial plateau (T)

	Tg SOFT	**1st endotherm**	**2nd endotherm**
B80A	21°C	119°C	160°C
A1	27°C	87°C	166°C
A2	26°C	118°C	166°C
A3	16°C	93°C	165°C
T1	24°C	89°C	160°C
T2	23°C	96°C	166°C

Thermal behavior of thermoplastic polyurethanes (TPU)

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Introduction. TPU's are melt-processable elastomers with outstanding toughness, durability and processing ease. They also exhibit good blood and tissue compatibility rendering them suitable materials for medical device [1]. TPU are linear segmented block copolymers consisting of three basic building blocks: the polyol (polyether or polyester or polycarbonate) that forms the soft segments, the diisocyanate and the chain extender that form the hard segments. The immiscibility of these segments causes the phase separation giving a morphology based on hard segment domains dispersed in a soft phase matrix, or vice versa, depending on the reciprocal amount. The soft phase gives the flexibility, whereas the rigid phase provides the elastic recovery by acting as a physical crosslink. In this work two thermoplastic polycarbonate urethane containing different amount of urethane rigid blocks has been studied in DSC and TGA in order to establish the effect of temperature on micro phase morphology and thermal degradation. The effect of temperature on hydrogen bonds was monitored with in-situ FT-IR.

EXPERIMENTAL

The study were performed on Bionate® 80A and 90A (B80A and B90A), polycarbonate urethane (DSM PTG, Berkley, CA) in form of pellet. These polyurethanes are based on 4,4'-diphenylmethane-diisocyanate (MDI), 1,4-butanediol (BD) chain extender and poly(1,6-hexyl 1,2-ethyl carbonate) diol (PHECD) soft segment.

Thermal stability and degradation were measured in a thermo gravimetric analyzer (TGA Q500 balance, TA Inc.), with alumina pan in a 60 cm^3/min nitrogen or air flow and with a 20°C/min heating ramp from 50°C up to 800°C. A differential scan calorimeter (DSC Q200, TA Inc.), provided with a cooling system RCS90, was used to detect the thermal transitions. The DSC measurements were performed with closed aluminium pan under nitrogen atmosphere (50 cm^3/min) and with a 20°C/min heating rate, from -75°C up to 230°C cyclically. The measurements were carried out on a single pellet (each sample weigh 10-15 mg).

FT-IR spectra at different temperature were collected with a Micro–FTIR (Perkin-Elmer, Spectrum spotlight 300, 16 scans per spectrum and a resolution of 4 cm^{-1}) on TPU films contained in a heating cell (Linkam TMS 94) with a 3°C/min heating rate from 30°C up to 230°C and then cooled at the same rate.

Results and Discussion. TGA of B80A and B90A in nitrogen flow exhibit a quite simple decomposition path: the materials start to decompose at about 230°C producing a stable residue (2 wt.%). The same path is showed by 90A in air until the char formed during the first step of weight loss is decomposed by O_2. However B80A seems to be more stable in air than in nitrogen atmosphere showing a stabilizing effect of oxygen on the first step of degradation. Above 550°C the char formed is completely volatilized by the oxidative action of oxygen.

The DSC thermograms show three characteristic steps. In the case of B80A is observed a glass transition temperature (Tg) at -21 °C, followed by two endothermic peaks at 119 ° C and 162 ° C respectively. In the case of B90A these three signals were at -15°C, 121°C and 175°C.

The Tg is attributed to the soft phase. As the observed value is higher than the Tg of the corresponding aliphatic polycarbonate, it will depend on a number of polyurethane segments distributed in the soft phase. The first endotherm observed in the thermogram is believed to arise from the melting of a fringed micelle microstructure [2]. The second endotherm is due to the heat absorbed from the system to form and homogeneous phase with complete mixing of the hard and soft segments [3].

In order to consider the effect of thermal history on the phase morphology samples were annealed at different temperature and then observed in DSC. The DSC thermograms of annealed B80A are reported in Fig. 1a: increasing the annealing temperature the Tg increases, indicating an increase in the amount of the polyurethane hard segments mixed with polycarbonate blocks in the soft phase. Even the melting peak increases indicating and increasing of the short order length in the fringed micelle microstructure. The value raised by this peak is about 30°C higher than the annealing peak.

The mixing endotherm peak remains substantially unchanged. Where the annealing was conducted at temperatures above the mixing temperature, the appearance of a exothermic peak at about 60°C is observed, and is associated to the microphase demixing.

The microphase morphology induced by the annealing treatment resulted to be unstable respect time. In figure 1b are reported the DSC curves of samples annealed over the mixing temperature and then aged at room temperature for different time. The Tg shifts from 3°C to -21°C after 60 days, indicating a progressive removal of polyurethane from the soft phase. After 16 hours it become evident the appearing of the micelles melting peak at about 55°C, indicating the ability of the hard polyurethane blocks to organize themselves in a short length order. The temperature of this peak, and then the extension of the ordered phase, depends from the temperature at which the samples were aged. Increasing the aging time corresponds to an increase of ordered phase, observed as an increase of peak area. The micro-IR spectra collected during the cooling of the material detected the restoring of the H-bond.

Conclusions. Thermoplastic polycarbonate urethane containing different amount of urethane rigid blocks has been studied in DSC and TGA. Thermal stability resulted to be unaffected by the presence of oxygen in the case of 90A or slightly increased in the case of 80A. In the other hand, the temperature at which the thermal degradation takes place is very close to the processing temperature. The microphase morphology resulted to be highly dependent from the thermal history. Both these findings suggest that in certain applications, such as orthopedic device, these aspects must be taken into special account.

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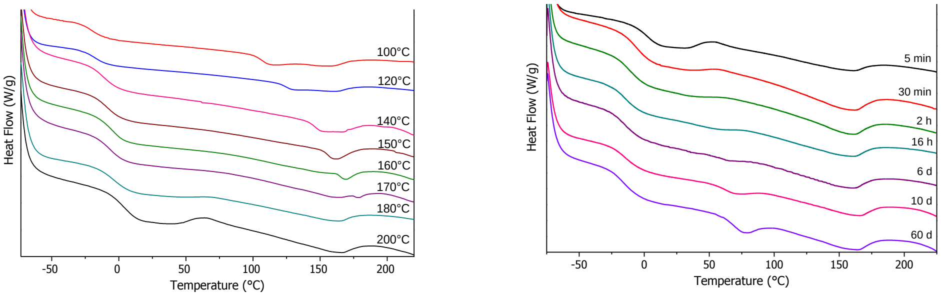

Fig.1 a) DSC curves of B80A annealed at different temperatures; b) DSC curves of annealed B80A at different storage time.

TOWARDS FUNCTIONAL NANOTUBES THROUGH GRAFTING OF ANTIOXIDANT MOLECULES ONTO THE SURFACE OF MW-CNTs: AN INNOVATIVE APPROACH IN THE CHARACTERIZATION

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In the last years several studies on the functionalization of nanofiller surface have been made. Moreover, numerous approaches in CNTs functionalization and/or modification are available in literature; they can be summarized as defect functionalization, covalent and non-covalent functionalization, and functionalization through click chemistry[1-2].

In this work, a commercial anti-oxidant molecule was grafted onto the outer surface of commercial grade OH- and COOH-functionalized MW/CNTs using two different approaches, in particular, the functionalization of MW/CNTs-OH to AO(O)-MW/CNTs and the functionalization of the MW/CNTs-COOH to MW/CNTs-aminoalcohol and in a second step to AO(CO)-MW/CNTs.

Furthermore, the modified nanotubes were characterized using traditional structural investigation methods, and an innovative approach based on MALDI-TOF mass spectrometry was adopted as well. FTIR, ATR FT-IR, TGA and SEM analyses suggest that both the adopted chemical protocols leaded to covalent functionalization of nanotubes with the anti-oxidant molecule. The presence of by-products, however, makes the aforementioned techniques unable to give unambiguous evidences about the actual grafting of the anti-oxidant. A clear proof of the successful functionalization was instead given by MALDI-TOF analyses, which has also revealed to be able to discriminate between physical immobilization and covalent linkage of the anti-oxidant molecule, see Figure 1. Moreover, by-products and organic contaminants have been also detected.

Differently from traditional structural techniques such as FT-IR, ATR FT-IR and TGA, MALDI-TOF analysis thus reveals to be a powerful tool for the characterization of functionalized CNTs, allowing for a discrimination between physical immobilization and covalent linkage of low-molecular weight anti-oxidant molecules.

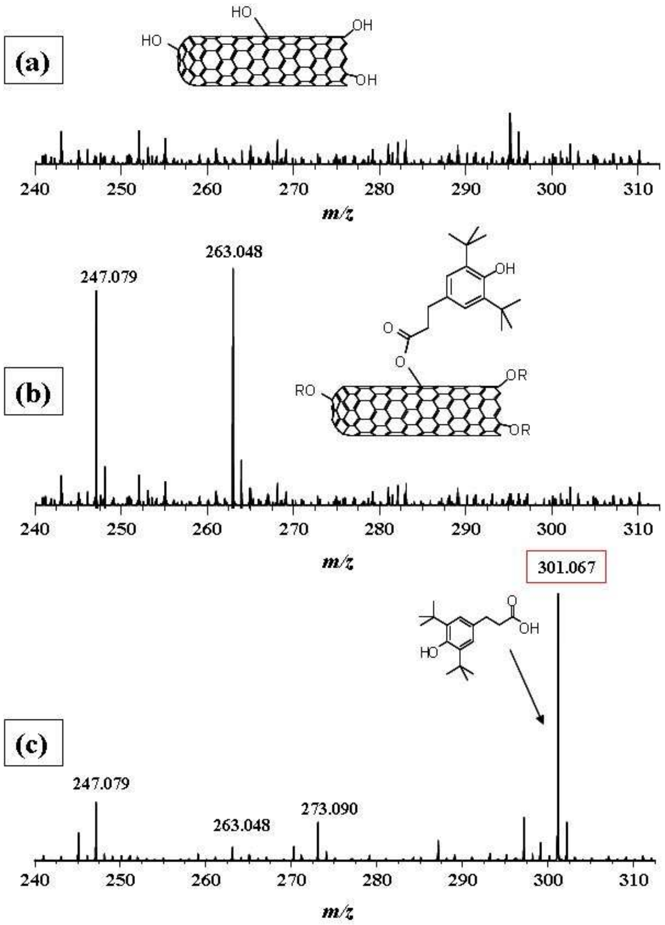

Figure 1. MALDI-TOF mass spectra of (a) MW/CNTs-OH, (b) AO(O)-MW/CNTs and (c) hydrolyzed AO(O)-MW/CNTs

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POLYMER BASED NANOCOMPOSITES FOR NOVEL GENERATION GREENER MATERIALS

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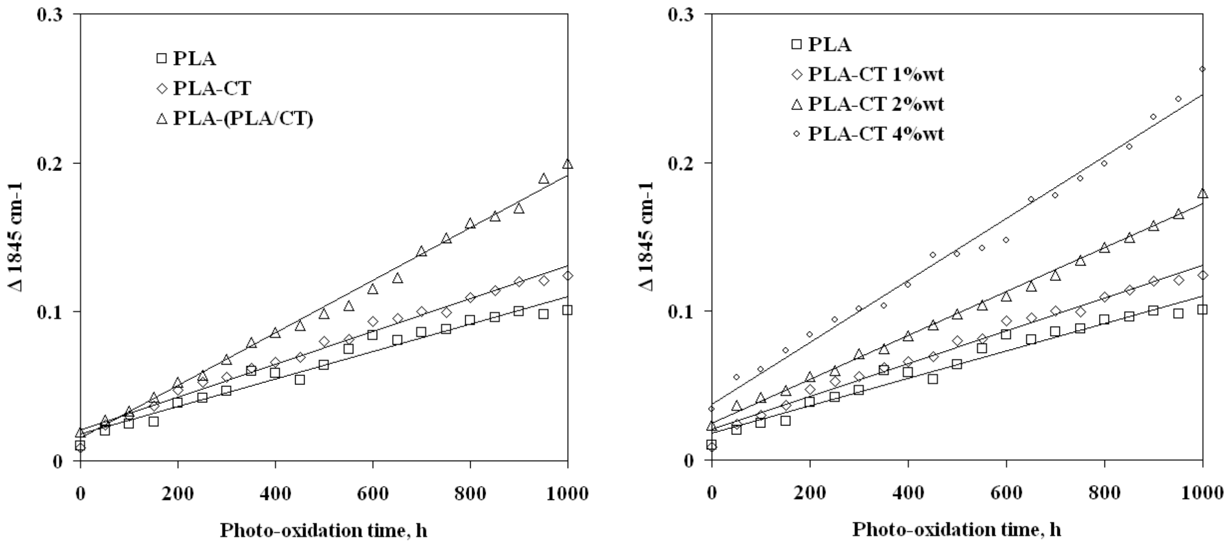
In the last years the replacement of the traditional polymeric materials with green materials has gained great interest for both academic and industrial words. A very interesting challenge is the formulation of novel generation greener materials with controlled durability. The incorporation of specific additives and/or molecules into micro/nanospheres prior to compounding can be considered a powerful and versatile approach to control system durability and/or to confer stimuli-responsiveness to the bio-polymers.

In this work, polysaccharide-based nanospheres (i.e. chitosan nanospheres) were compounded into a bio-polyester (i.e. PLA) following two different protocols. In the first protocol, the cross-linked chitosan nanospheres (obtained by ionotropic gelation) were introduced into PLA by hot-melt extrusion (PLA/CT). According to the second protocol, the aqueous dispersion of chitosan nanospheres were mixed with a PLA dioxane solution to induce simultaneous precipitation of PLA and nanospheres from the water/dioxane solution. The so formulated PLA/chitosan nanospheres were then compounded with neat PLA in different proportions, in order to prepare the blend with controlled chitosan loading (PLA-(PLA/CT)). The formulated PLA/chitosan thin films were subjected to accelerated artificial weathering using UV-B lamps.

The control of particle size distribution of crosslinked chitosan prior to compounding was performed by dynamic light scattering, while nanocomposites thermal and morphological properties were investigated by TGA and DSC, and SEM analyses, respectively. Morphological analysis suggests that a better dispersion of chitosan nanospheres is achieved for PLA-(PLA/CT) and in all cases the presence of chitosan affects the crystallization behavior of PLA. System durability, i.e. photo-oxidation behavior, of the PLA/chitosan thin films was followed by mainly by FT-IR and UV-visible spectrometry. In Figure 1 (a-b), the evaluation of the band at 1845 cm-1, due to the formation of the anhydride species in PLA upon UV-B exposure[1-2], as a function of the photo-oxidation time for PLA/chitosan compounds obtained by the two different protocols and PLA/chitosan compounds at different chitosan loading contents are reported. The rate of photo-degradation for PLA-(PLA/CT) is higher that for PLA/CT film, possibly due to the increased contact areas between the two polymeric phases.

Furthermore, the rate of photo-oxidation increases by increasing the cross-linked chitosan content, see Figure 1 (b). The last effect could be explained by considering a preferential formation of macroradicals in the chitosan phase and their propagation to PLA.



(a) **(b)**

Figure 1. Evaluation of band at 1845 cm^{-1} as a function of the photo-oxidation time of PLA and PLA/CT compounds

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POLYMER ELECTROLYTES BASED ON PAN AND MIXED SALTS FOR PHOTOELECTROCHEMICAL APPILCATIONS: FORMULATION AND CHARACTERIZATION

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Polymeric gel electrolytes have acquired great interest in the last years because of their use in ionic devices like photo-electrochemical solar cells. These materials are obtained by the immobilization of liquid solutions (ethylene carbonate (EC). propylene carbonate (PC) and some organic and/or inorganic salts) in a polymeric matrix of polyacrilonitrile (PAN), polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVdF)[1-2].
In this work, the rheological behavior of PAN-based gel containing tetrahexylammonium (Hex_4NI) and magnesium iodide (MgI_2), plasticized by EC and PC, has been studied at given temperatures and frequencies. In Figure 1, the complex viscosity as function of the temperature at the frequency 1 s^{-1} of the four investigated systems is reported. The PAN-EC-PC system shows a slight decrease of the complex viscosity between 20 and 60 °C and a sudden decay above 60 °C. The $Hex_4N^+I^-$ loading into PAN-EC-PC leads to a significant increase of the complex viscosity values. Some retention in the viscosity decay at higher temperatures can be noticed because the $Hex_4N^+I^-$ presence hinders the relaxation motions of the polymeric macromolecules. It is very interesting to highlight that the progressive substitution of Hex_4NI with an inorganic salt, i.e. MgI_2, implies a different rheological response of the system. In particular, the rise of the plateau in the low temperature range is clearly noticeable and, especially at highest amount of MgI_2, the complex viscosity does not change until 85 °C, after that the observed decay is gradual. Moreover, the rise of this plateau is only slightly dependent on the MgI_2 salt content. This result is very important from a processing point of view because the system can be processed at temperature higher than room temperature without excessive

fluidization. Beyond, the presence of MgI_2 modifies the dielectric and calorimetrical response and improves the performance of the photoelectrochemical cell where this is used, based on previous investigation[3-4].

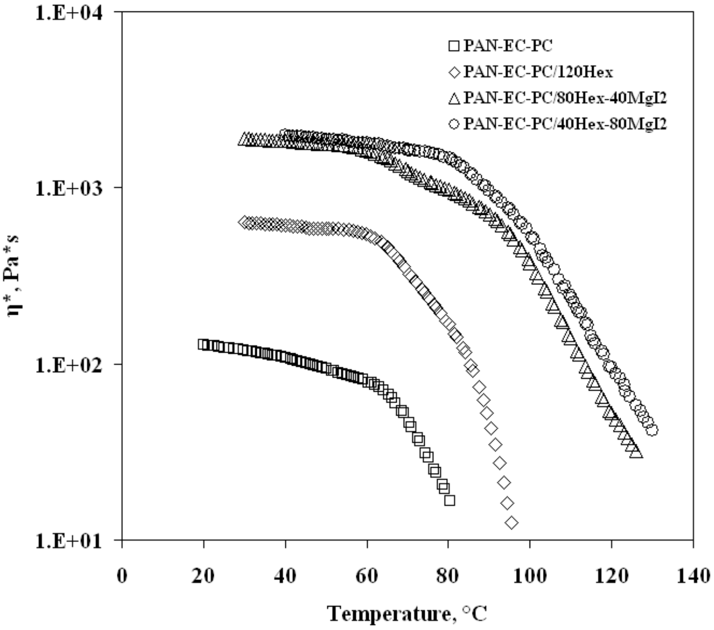

Figure 1. Complex viscosity of all investigated samples as a function of the temperature

Moreover, the cross over point between the G' and G'' (curves not reported) for PAN-EC-PC is about 75 °C, while, $Hex_4N^+I^-$ loading into PAN-EC-PC system shifts this point at about 95 °C. It is very important to highlight that the cross over point for both MgI_2 additivated systems is above 120 °C. In particular, the cross over between G' and G'' for $80Hex_4N^+I^-/40MgI_2$ and $40Hex_4N^+I^-/80MgI_2$ are 124 and 129 °C, respectively.

The obtained rheological results suggest that the progressive substitution of Hex_4NI with MgI_2 leads to a significant improvement in the rheological behavior of the PAN-based electrolytic gel due to the decrease of the mobility of the macromolecules and probably to an increase of the interaction between the inorganic ions and the macromolecules.

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KINETICS OF THE FORMATION OF ISOPHORONE DIISOCYANATE (IPDI) BASED POLYURETHANE FOAMS: IN SITU FTIR STUDY

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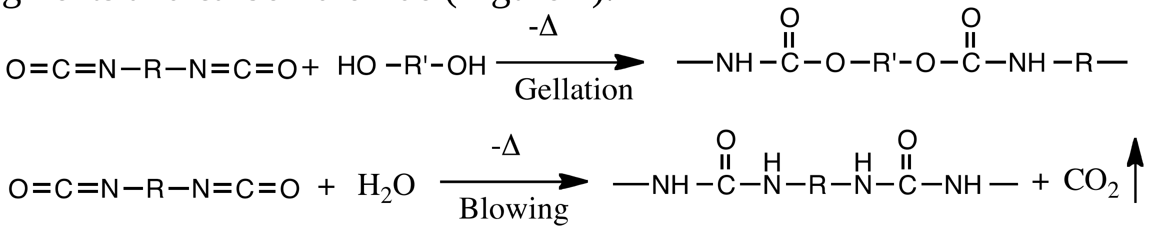
Introduction: The polyurethane foam chemistry is based on the reactions of isocyanates with polyfunctional hydroxyl compounds and water[1]. The reaction of isocyanate with polyol, called gelling reaction forms urethane linkages and increases the molecular weight while the reaction of isocyanate with water, known as blowing reaction, forms urea hard segments and carbon dioxide (Figure 1).



$$O{=}C{=}N{-}R{-}N{=}C{=}O + HO{-}R'{-}OH \xrightarrow[\text{Gellation}]{-\Delta} {-}NH{-}\overset{\overset{O}{\parallel}}{C}{-}O{-}R'{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}NH{-}R{-}$$

$$O{=}C{=}N{-}R{-}N{=}C{=}O + H_2O \xrightarrow[\text{Blowing}]{-\Delta} {-}NH{-}\overset{\overset{O}{\parallel}}{C}{-}\overset{H}{N}{-}R{-}\overset{H}{N}{-}\overset{\overset{O}{\parallel}}{C}{-}NH{-} + CO_2\uparrow$$

Figure 1: Reactions taking place during the PU foam formation.

The vast majority of water blown polyurethane foams are obtained at room temperature, and therefore the more reactive aromatic isocyanates are used. Polyurethane foams obtained from less toxic aliphatic isocyanates, as the one described in this work, are much less studied systems because the lower reactivity of the aliphatic isocyanate groups implies the use of higher foaming temperatures.

Materials and methods: The foams were prepared from isophorone diisocyanate (Vestanat IPDI, Evonik Industries) and a polyether polyol (Desmophen 4042 BT Bayer), using dibutyl tin diacetate, stannous octoate and 1,4-Diazabicyclo[2.2.2]octane (Aldrich) as catalysts and a silicon surfactant (Tegostab B8110 Evonik Industries). Water was used as blowing agent. The reaction mixture was introduced in a 70 ºC thermostatized Attenuated Total Reflectance (ATR) accessory (Fast-IR Harrick) provided with a ZnS crystal and infrared spectra were obtained as a function of the reaction time using a Nicolet Magna 560 spectrometer.

Results and discussion:

The infrared spectra (Figure 2, left) obtained during the foaming process showed the gradual weakening of the isocyanate stretching band at 2270 cm^{-1} (a) and the increase of the amide I and II bands at 1700-1500 cm^{-1} (b) assigned to the formation of urethane and urea groups.

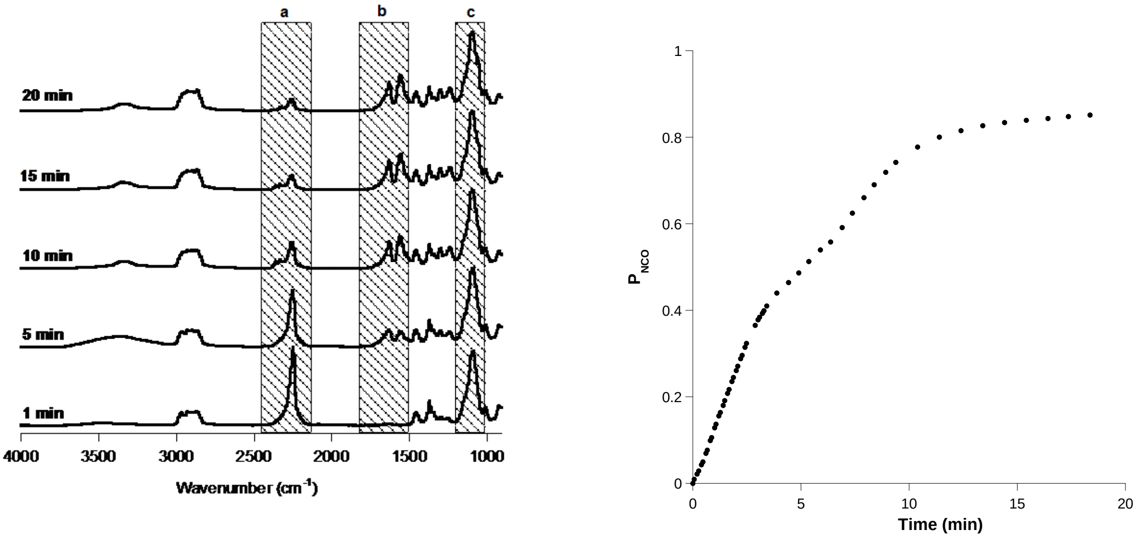


Figure 2: Infrared spectra obtained during the foaming process (left) and isocyanate conversion (right) as a function of time.

The isocyanate conversion (Figure 2, right) was determined from the absorbance of the isocyanate measured at different times and using the ether stretching vibration band at 1100 cm^{-1} (c) as an internal reference. High conversions were obtained at reaction times similar to those reported for aromatic isocyanate based polyurethane foams[2].

Conclusion: The kinetics of aliphatic isocyanate based polyurethane foams was successfully studied by ATR-FTIR spectroscopy.

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INFLUENCE OF ACCELERATED AGING AND FOOD SIMULANTS ON THE ADHESION OF A-C:H FILMS IN CLARIFIED POLYPROPYLENE

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In this work, the influence of time, temperature and contact with liquid food simulants on the adhesion of amorphous hydrogenated carbon films (a-C:H) was studied. The Diamond Like Carbon (DLC) and Polymer Like Carbon (PLC) films obtained by Plasma Enhanced Chemical Vapor Deposition (PECVD) were deposited on clarified polypropylene (cPP). The cPP samples coated with the a-C:H type PLC and DLC were submitted by accelerated aging test (45°C for 1000 h and 55°C for 480 h) [1] and were exposed to contact with food simulants, 3% acetic acid and 10% ethanol, as specified by the FDA [2]. The adhesion between a-C:H and polymeric substrate was analyzed using scanning electron microscopy (SEM) and tape test.

The SEM micrographs before the accelerated aging test indicated that the PLC film (Figure 1-b) has a structure with less surface tension, and therefore regions with detachment points less evident in relation to the DLC film (Figure 1-a).

After the contact of the samples with 3% acetic acid at 45°C for 1000 h it was observed that the PLC film has lower detachment (Fig. 1-d) when compared with DLC films (Fig. 1-c). The same behavior was observed for samples subjected to contact with 10% ethanol for 450 h at 55°C. After the accelerated aging test, the DLC films (Fig. 1-e) showed more crack points when compared to PLC films (Fig. 1-f).

The results obtained with the tape test are in agreement to those of SEM. The a-C:H film coating on cPP substrates was easily removed from all samples for all conditions. The adhesion results were contrary to previous observations that used a polar polymer (PET) as the substrate [1,3]. At those studies, pre-treating the recycled PET substrate for 2.5

minutes with oxygen plasma provided good adhesion between the substrate and the a-C:H coating layer, before and after the accelerated aging test. The good adhesion observed for PET samples can be attributed to two factors: the polarity of PET and its Tg (around 70°C [4,5]), which is higher or close to those of the aging test temperatures.

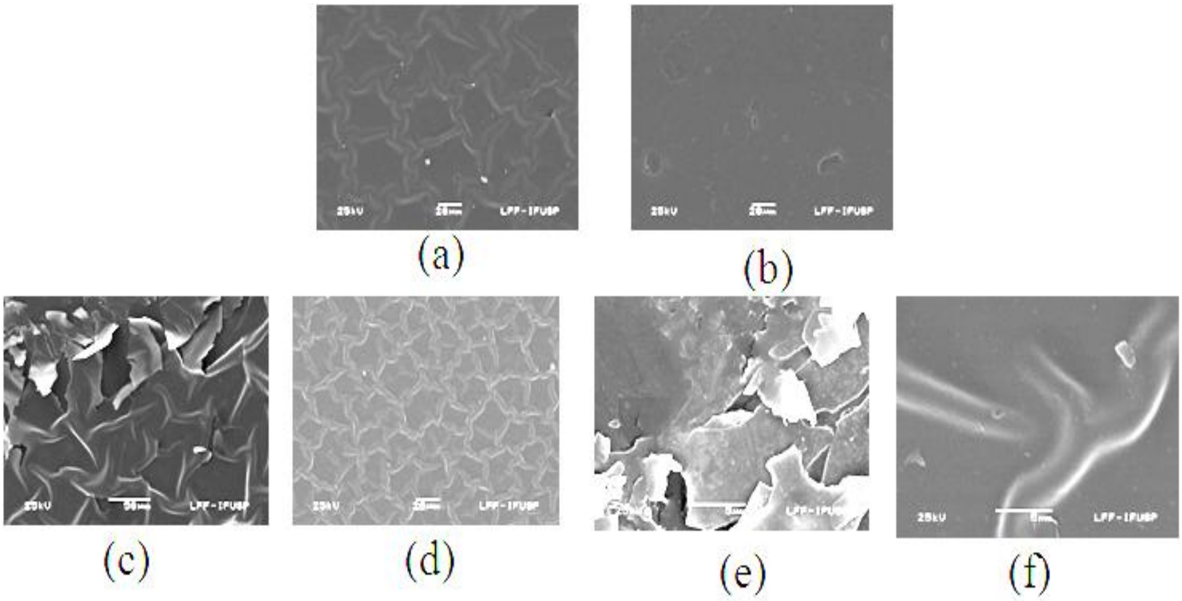

Figure 1: SEM micrograph of a-C:H films before the accelerated aging test: (a) DLC film and (b) PLC film. The a-C:H films after the accelerated aging test submitted to the contact with: (c) and (d) acetic acid at 45°C for 1000 hours and(e) and (f) subjected to ethanol at 55°C for 450 hours. Images: (c) and (e) DLC film and (d) and (f) PLC films.

Finally, the accelerated aging test proved to be important to predict whether the adhesion of a-C:H films remain effective during the shelf-life of a food packaging.

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SYNTHESIS AND MODIFICATION OF POLY(2-ISOPROPENYL-2-OXAZOLINE) WITH DIFFERENT FLUORESCENT PROBES

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Functional polymers represent powerful tools in the construction of bioconjugates with various bioactive species (e.g.proteins, saccharides, drugs, etc.). Radical polymerization can be used for the preparation of homopolymers and copolymers on the basis of unsaturated 2-oxazolines[1]. Resulting polymers contain free 2-oxazoline ring able to provide addition reactions with carboxylic acids, phenols or thiols[2]. Addition and polyaddition reactions of 2-oxazolines are widely used in polymer chemistry in polymerization processes, for the chain extension and crosslinking[3]. Furthermore, polymers prepared from 2-oxazolines belong to biocompatible materials and represent perspective materials for different bioapplication[4-6].

In this contribution, free radical polymerization of 2-isopropenyl-2-oxazoline is described. Poly(2-isopropenyl-2-oxazoline) was prepared from2-isopropenyl-2-oxazoline using azobisisobutyronitrile (AIBN) as initiator at 60 °C for 8 hours (Fig. 1).

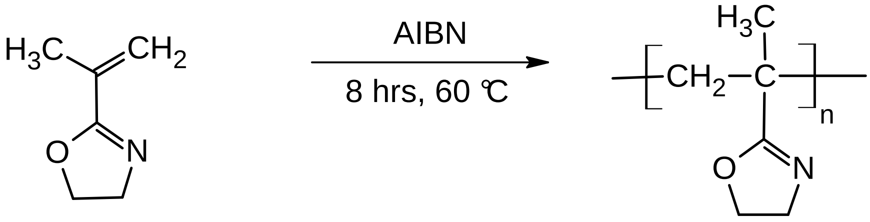

Fig. 1. Free-radical polymerization of 2-isopropenyl-2-oxazoline.

The structure of the prepared poly(2-isopropenyl-2-oxazoline) was confirmed by NMR and FTIR. The presence of 2-oxazoline ring gives us the possibility to attach different molecules to the main chain of the polymer. Therefore, the model reaction of the prepared polymer with different different fluorescent probes (namely pyrene-1-carboxylic acid, coumarine-3-carboxylic acid) was studied (Fig.2).

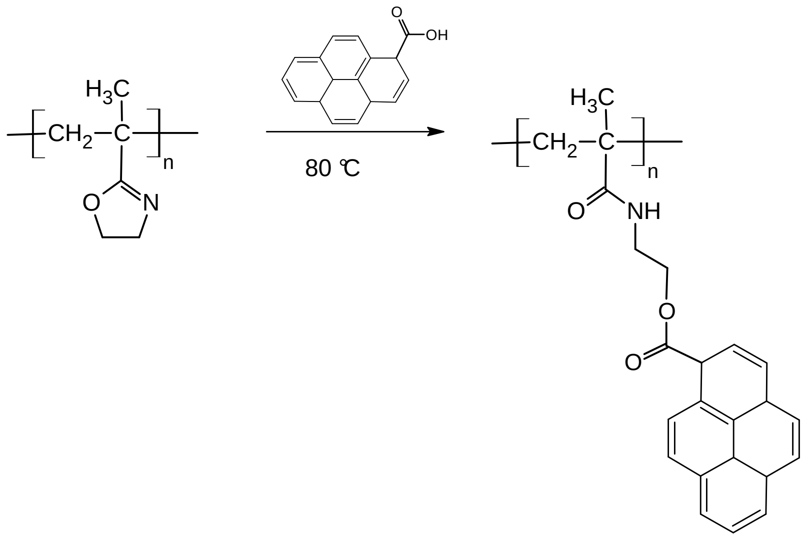

Fig.2. The model reaction of poly(2-isopropenyl-2-oxazoline) with pyrene-1-carboxylic acid.

The reaction was monitored with NMR and FTIR and the optimization of reaction conditions was performed, too. Reaction between poly(2-isopropenyl-2-oxazoline) and fluorescent probe should represent the reaction analoguous to known „*click*“ reactions.

Acknowledgement: Authors are thankful for the financial support of Slovak Grant Agency VEGA in the project No. 2/0151/12.

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PERMEATION OF WATER VAPOR IN AMORPHOUS HYDROGENATED CARBON FILMS DEPOSITED BY PLASMA ON POST CONSUMER PET RECYCLED

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Amorphous hydrogenated carbon (a-C:H) thin films has been widely studied as protective coating in the variety material in a lot applications such as food packaging made of recycled polymer [1-4]. In the literature, films with a high percentage of sp^3 hybridization are known as diamond like carbon (DLC) and films with hybridization sp^2/sp^1 are called polymer-like carbon (PLC)[5-7]. The a-C:H films can be synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD) that usually employed high frequency, pressure, hydrocarbon precursor gas and others parameters [8,9].Thus, depending on process parameters, film structure range from PLC and DLC phases[10]. In this work, a-C:H film with PLC and DLC structures was deposited by PECVD on the surface of the post consumer poly(ethylene terephthalate) recycled (PET-PCR) and evaluated the water vapor barrier properties for each structure.

To synthesize a-C:H films on the surface PET-PCR, a PECVD system was employed conform reported by Oliveira *et al* [11]. To evaluate the water vapor barrier properties of each structure was performed permeation of water vapor. In order to examine the surface topography of the a-C:H films were employed optical microscope analysis before and after permeation of water vapor.

The Table 1 shows the results of permeation of water vapor.

Table 1 Permeability of the a-C:H structures

a-C:H structure	Permeability (g/Pa.s.m)±DS	Reduction (%)
DLC	$6.17.10^{-10}$ ±0,05	2.10
PLC	$5.26.10^{-10}$±0,27	16.50
PET-PCR	$6,30.10^{-10}$	0

The PLC coating presents a reduction on the permeability almost 16% while DLC films 2%. Optical micrographs (Figure 1) show scratches along the surface of the DLC before water permeability while the surface PLC film was uniform. These results showed that internal stress inside the DLC structures higher than PLC films, as show in previous work [10]. This behavior can be explain to presence of higher amount of hydrogen atoms (C-H sp^2/sp^3) in the structure PLC that make it less rigid when compared DLC films (C-C sp^3).

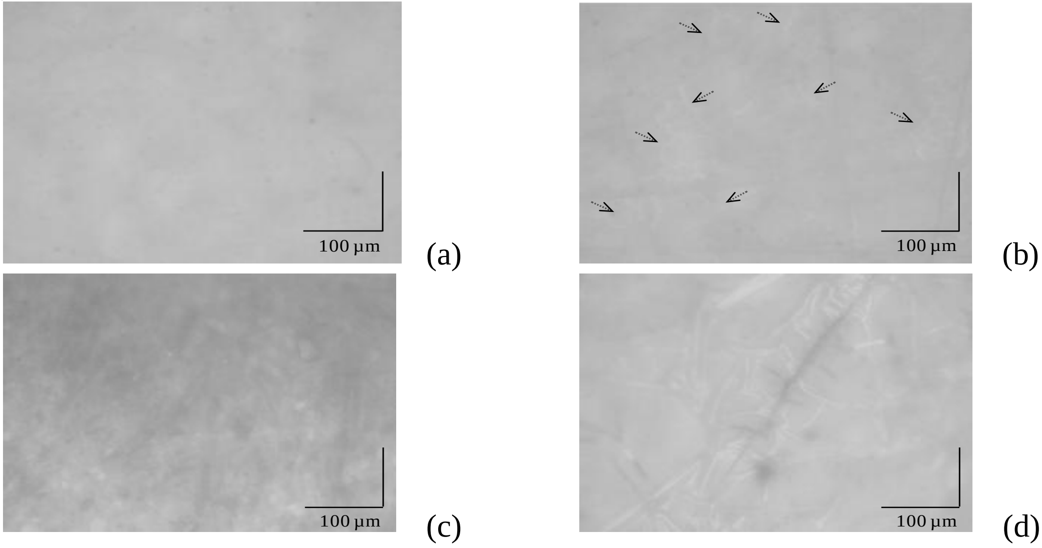

Figure 1:Optical micrography of PLC (a, c) and DLC (b, d) films before (a, b) and after (c, d) analysis permeation.

After permeation of water vapor (Fugure 1 c) the surface PLC films was similar before the same analysis. On the other hand the buckling and cracks in DLC films increased (Figure 1 d) that can explain the poor permeability water vapor conform observed Table 1.

Thus,was observed that PLC structures presents better barrier properties to water vapor due to mechanically stable films when compared with DLC films.

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PREPARATION AND CHARACTERIZATION OF 3D PLA POROUS SCAFFOLDS

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The design of adequate scaffolds for tissue regeneration and the choice of the material to be used are strictly connected with the specific cell/tissue culture and the architecture of pores play a central role. Due to their known biocompatibility and their modular kinetics of degradation, polylactides (PLA) are currently studied for their potential as three-dimensional structure in tissue engineering. In order to enhance flexibility, to tune the degradation rate and to promote the surface hydrophilicity of the PLA-based scaffold, several studies have been carried out on the possible modification of PLA bulk and surface by adding polyethylene glycol (PEG).

One of the most common techniques to prepare porous scaffolds is the particulate leaching method, which involves the selective leaching of a mineral or organic compound as porogen agents. The main advantage of particulate leaching methods is the effective control of porosity and pore size by variation of the amount and size of leachable particles. On the other hand the drawback of this technique is the lack of interconnectivity between the pores.

In this work, 3D porous scaffolds were prepared by using a partially miscible polymer system, PLA/PEG, melt blended with NaCl, in which the salt and PEG role as porogen agents. Moreover, the effect of the molecular weight of the PEG used in the blend was evaluated.

The superficial content of PEG was controlled by adopting appropriate optimized conditions of water leaching.

The morphological results were correlated with in vitro viability, adhesion and proliferation tests critical for the further migration/ differentiation phase in 3D structures on human SK-Hep1 liver adenocarcinoma cells, used as model system.

The morphological analysis (figure 1) revealed that when the PEGs are added, almost all the salt was leached and interconnected porous structures with a good assortment of large and small pores are formed. The mechanism of pores formation involves a sequential solubilization of PEG and NaCl that co-operate to bring the water deep in the scaffold core during the leaching operation.

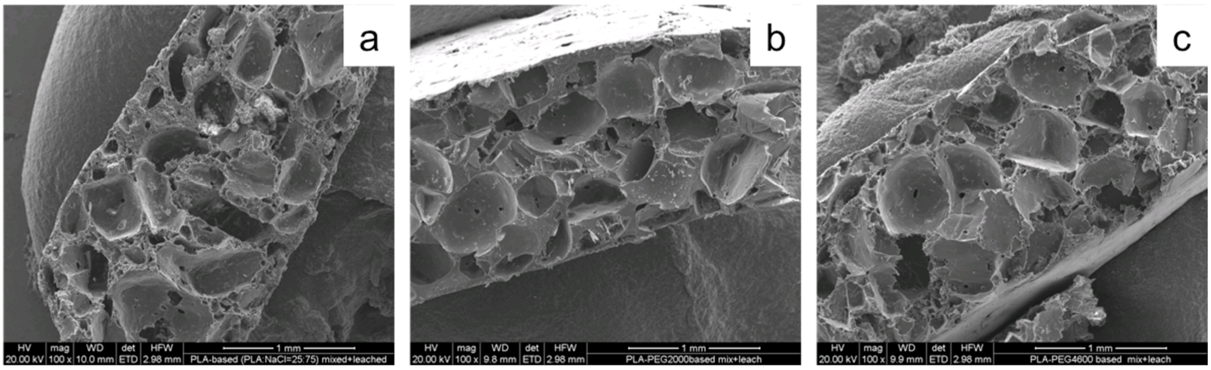

Figure 1 SEM micrographs of a) PLA-based, b) PLA/PEG2000-based c), PLA/PEG5000 based scaffolds, leached in distilled water for 168 h at room temperature.

The results demonstrated that the higher the molecular weight of PEG added, the smaller the pores size is, likely due to an increased melt viscosity (i.e. higher stresses) that reduces PEG droplets size and fractionate NaCl crystals during processing. Moreover, the PEG amount on the surface of polylactide-based 3D scaffolds is optimized by means of processing.

Cells cultured in the presence of PLAbased or in PLA-PEGs-based scaffolds did not show significant differences if compared to the 2D control on plate, showing therefore that the analyzed scaffolds do not induce cytotoxicity.

All the scaffolds showed adhesive capabilities, comparable to those obtained when they are treated with ECM components as type-I collagen. Moreover, SK-Hep1 cells well adhered to the scaffold and diffusely grew inside it. The results eventually demonstrated the potentiality of the use of these scaffolds in a study of human adenocarcinoma processes in a realistic 3D substrate and or as structures for tissue engineering.

INVESTIGATION INTO THE EFFECT OF LAUNDERING ON THE SURFACE CHARACTERISTICS OF FLUOROPOLYMER TREATED COTTON FABRIC

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The performance of two different fluorocarbons (cationic and nonionic fluorocarbon) in combination with 1,2,3, 4 -butanetetracarboxylic acid (BTCA) crease resist finish on cotton fabric was examined in relation to laundering and abrasion. The effect of laundering in a commercial detergent and abrasion is to reduce the water/oil repellency. The loss of repellency was partially reversed by a heat treatment/ironing probably due to re-orientation of the fluoropolymer chain. In general, the cationic fluorocarbon offered better repellency performance in terms of laundering and abrasion than the nonionic fluorocarbon on the cotton fabric. The nature of reduction in repellency performance due to laundering was probe by Secondary Ion Mass Spectrometry(SIMS), X-ray Photoelectron Spectroscopy which revealed a loss of surface fluorine at the fibre surface and a concomitant build up of surfactants on the fibre surface.

NANOMECHANICAL PROPERTIES OF PLASMA-TREATED POLYLACTIC ACID FOR PACKAGING APPLICATIONS

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Recently, a number of techniques have been utilized for modifying the barrier properties of polymers including coating polymers with films [1-2], addition of inorganic/organic compounds [3-4], and co-extrusion [5]. However, these techniques present some disadvantages such as adhesion failure of coating films upon mechanical deformation, deteriorated mechanical properties of polymers and changing of color of polymers. The process of co-extrusion and addition of compounds may increase the production cost associating with the processing facility. The use of plasma treatment appears to be suitable for industrial application as solvents are eliminated and the treatment time is short to achieve significant change in the properties governed by surface characteristics.

Plasma treatment is one of the new technologies to achieve the modification of surface characteristics of polymeric materials. The interactions between the plasma and the surface molecules of polymers lead to the surface phenomena such as etching, cross-linking and activation [6-7].

In this work, a radiofrequency (RF) discharged plasma generated in air atmosphere by pressure 100 Pa has been used to modify PLA surface. PLA pressed samples were prepared from PLA granules in 190°C. Before plasma treatment, the samples were subjected to vacuum for 48 hours, by temperature of 50°C. The RF plasma discharge was applied for 30, 60, 90, 120 and 180 seconds. The nanoindentation analysis in this work has been performed using a Hysitron TriboLab® Nanomechanical Test Instrument (equipped with a Scanning Probe Microscope (SPM) and a Berkovich probe). In all depth-sensing tests a total of 10 indents are averaged to determine the mean H & E values for statistical purposes, with a spacing of 50 μm (~45% RH, 23°C) [8].

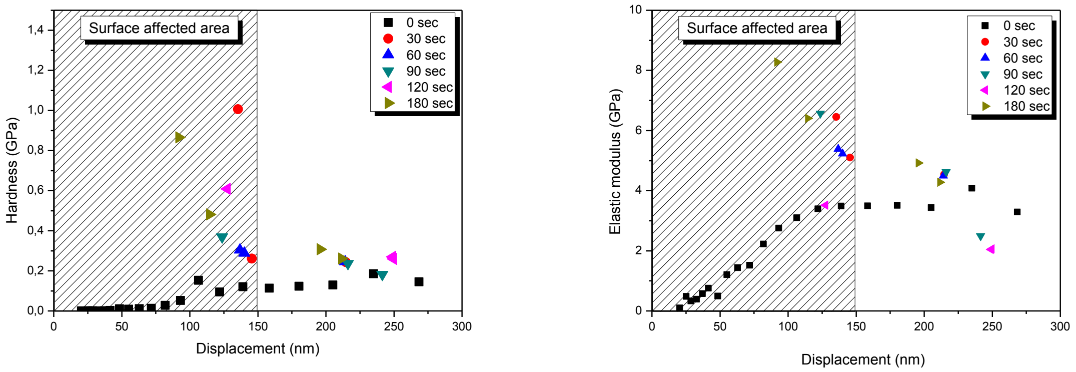

Figure 1 Nanomechanical properties (H, E) of PLA samples.

In Fig. 1, the nanomechanical properties (H, E) of PLA samples are presented, where surface affected hatched area is noted; all PLA samples exhibit an almost hard-like surface area where H and E are enhanced. As the tip penetrates further, both H and E tend to reach pristine PLA's values. The plasma treatment created topographical change which is due to the interactions of plasma species and thermal effect [8]. However, the bulk structure of the film remains unchanged as is suggested by thermal analysis and measurements of water vapor permeability measurements [8]. Further investigation on the bulk property of PLA will be carried out.

Acknowledgement

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MODIFICATION OF POLYPROPYLENE BY ADDING LONG BRANCHES TROUGH MELT RADICAL REACTION

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Introduction: Polypropylene (PP) has become one of the most widely used commercial polyolefins. It has many excellent properties, such as low density, high melting temperature and good chemical resistance. However commercial PP is a highly linear polymer. This limits its use in applications such as thermoforming, foaming and blow molding because it lacks of melt strength and good extensional properties. One of the most effective strategies to improve elongational properties is to modify the structure of the linear polymer molecules by incorporating long branches. In this work long chain branched PP was prepared by reaction in the molten state in the presence different concentrations of glycerol. The modified PPs exhibit improved rheological properties and higher melt strength.

Experimental: A commercial PP with grafting degree of 1.0 % weight maleic anhydride (Polybond 3200) of Uniroyal Chemical Co was the departure material (Pg). Bidistilled glycerol (99.5% purity) in concentrations ranging from 0.1 to 5 % w/w was employed as crosslinker to induce the formation of branches. The preparation of samples took place in a Brabender Plastograph® mixer at 190°C and 40 rpm for 15 min. The modified PPs are identified as PgG# where # is the weight percentage of glycerol (see Table 1). The degree of modification of the materials was evaluated by FTIR spectroscopy. The rheological tests on small amplitude oscillatory shear (SAOS) were performed in a AR-G2 rheometer (TA Instruments. The weight average molecular weight (Mw), polydispersity (Mn/Mw) and branching frequency were determined by size exclusion chromatography (SEC) at high temperature (135°C) with triple detection.

Results and discussion: The recognition of ester groups by FTIR allowed quantifying the weight percentage of grafted glycerol. The SEC analysis of the original Pg and their modifications was employed to determine parameters such as molecular weight and molecular structure (branch frequency), confirming the topological modification of the linear Pg chains through the incorporation of branches.

Table 1: Molecular characteristic and rheological parameters of the initial Pg and the modified samples

	Pg	PgG01	PgG03	PgG05	PgG10	PgG50
Mw	117000	147100	351100	590000	625000	669100
Mw / Mn	2.7	3.1	6.6	6.2	3.1	2.8
% weight Glycerol grafted	0	0.10	0.26	0.37	0.43	0.34
Branch Frequency	0	0.01	0.08	0.30	0.40	0.62
η° (Pa.s)	83	92	251	1396	-	-

The presence of long chain branches changes the value of zero shear viscosity (η_o) whose values are quite sensitive to the density and the length of these branches. Figure 1 shows the curves of dynamic viscosity (η′) for all samples at 180°C. The evolution η′ in the low frequency region increases as the dose of glycerol was increased. This behavior is attributed to the existence of larger relaxations times associated with the presence of LCB in the structure of PP. Further work with elongational viscosity measurements is in progress.

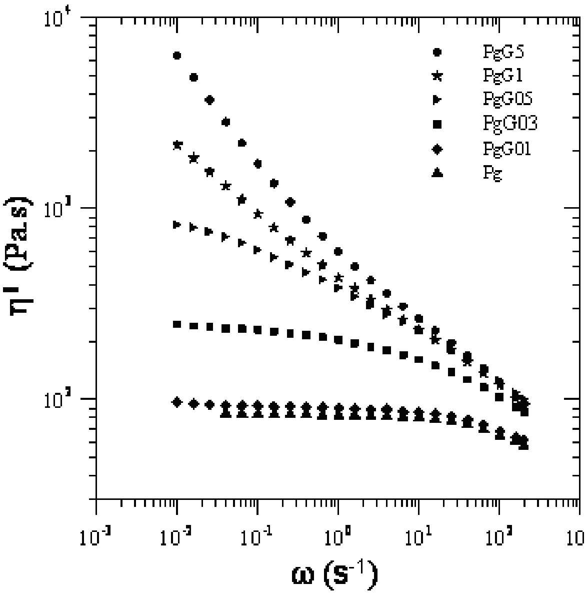

Fig. 1 Evolution of η′ with frequency for the modified PP

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CROSS-LINKING MODIFICATION OF HYALURONAN-ITACONIC ACID FILMS TO PREPARE PLATFORMS WITH POTENTIAL APPLICATION TO DRUG DELIVERY SYSTEMS

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Introduction: Traditional dosage forms (solutions, suspensions and ointments) are limited in solving a lot of eye diseases mainly due to the rapid and extensive loss of the formulation of precorneal area under drainage, blinking and tear replacement. The hyaluronic acid sodium salt, also known as hyaluronan (HA), is a naturally occurring, high molecular mass linear biopolymer. It is a promising biomaterial to design modified drug delivery systems (DDS) in ophthalmic applications. Due to HA low stability in living tissues, some chemical modifications are necessary to obtain stable films that are appropriate to be used as DDS in ophthalmic applications. In this work we explore crosslinking formulations for HA using polyethylene glycol diglycidyl ether (PEGDE) in the presence of itaconic acid (IT) to obtain hidrogels appropriate to prepare films with good bioadhesive and mechanical properties as potential DDS.

Experimental: HA systems were synthesized from HA/IT/PEGDE (PEGDE-film) solutions. The amount of each reactive was adjusted to achieve (1:1:2) HA/IT/PEGDE molar ratios solutions. Swelling behavior, mechanical properties, in vitro biocompatibility on a human corneal epithelial cell line[1] and in vivo adhesion and irritation tests were tested on the obtained hydrogels.

Results and discussion: All films showed a homogeneous and smooth surface by SEM with low swelling ratios. The human corneal epithelial (HCE) cell line was used to determine whether films were biocompatible after 24 h exposure in terms of: i) Cell viability, ii) Cell proliferation, and iii) Cell inflammation. As shown in Fig. 1, corneal cells exposed to sterilized PEGDE-film for 24 h exhibited viability superior to 90% and good proliferation rate. Controls included cells alone and cells exposed to 0,001 % benzalkonium chloride (BKC). Cell viability was calculated as a percentage with regard to control cells.

To measure cell proliferation rate alterations, the Alamar Blue (resazurin) test was used. Control cells without film exposure were included.

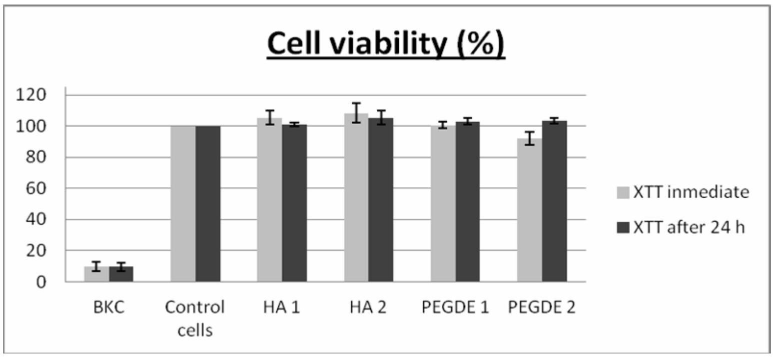

Fig. 1 Cell viability studied by XTT kit.

Cell proliferation was calculated as a percentage with regard to control cells. As shown in Fig. 2, after 24 hs of cell exposure to the films, the rate growth measured for 72 hours shows no significant differences with the control cells. No inflammatory processes were observed on cells exposed to PEGDE-films. Also, the film composed with PEGDE- films, caused minimal in vivo conjunctival and corneal irritation. No intraocular irritation was observed during 72 hours of study. The results obtained are encouraging towards the design of a novel DDS for corneal applications.

Acknowledgements: The authors wish to thank the support of CONICET, ANPCyT, UNS and EADIC II programs.

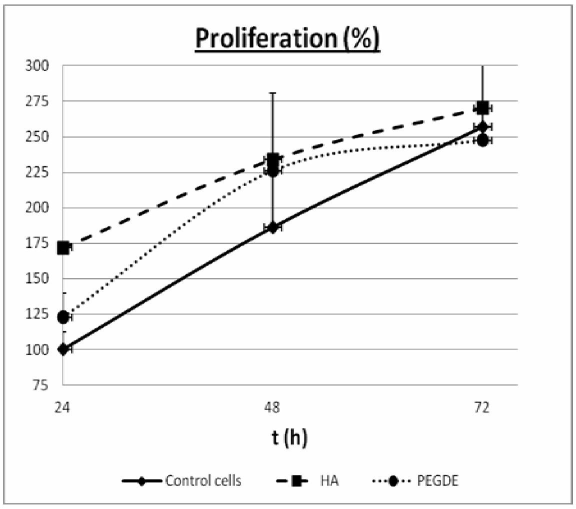

Fig. 2 Cell proliferation rate studied by Alamar Blue test.

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ELECTROSPINNING OF S-PEEK-WC NANOFIBERS

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Proton exchange membrane fuel cells have attracted growing attention as an alternative technology for power production in both automotive and stationary applications due to their ability to convert the chemical energy of a fuel (hydrogen) directly into electrical energy with relatively high efficiency, for their adaptable size and low operating temperature. Current state-of-the-art PEM materials are perfluorinated polymers, such as Nafion® or Flemion® which have their good physical and chemical stability together with high proton conductivity under a wide range of relative humidity conditions at moderate operation temperatures [1-5]. However, they suffer from such disadvantages as limited operation temperature (0–80 °C), high cost, insufficient durability and high methanol permeability. To overcome these obstacles, the scientific community has been involved in development of alternative acid-functionalized aromatic hydrocarbon-based polymers such as: sulfonated poly (ether-ether-ketone) [6-8], sulfonated polysulfone [9-11], sulfonated polybenzimidazole [7] and [12], sulfonated poly-phenoxybenzoyl-phenylene [8], sulfonated polyphosphazene [13], sulfonated polyethersulfone with cardo [14]. Nevertheless, there are still unresolved practical application issues of these membranes due to low proton conductivity under low-humidity conditions, although they show high proton conductivity under high humidity conditions.

Literature on PEM generally agrees that scaling down the conductive polymer to the nanometer size scale my impact positively its properties and subsequently its performance in devices. In particular, long-length nanofibers are able to form porous networks with high surface-area-to-volume ratios, and decrease diffusion lengths. While there are numerous techniques to create nanostructures, electrospinning is the only technique that allows fabrication of nanofibers at long-length scales [15, 16]. In a typical electrospinning apparatus an electric field is used to create a charged jet of polymer solution. As this jet travels in air, the solvent evaporates leaving behind charged fibers that can be electrically deflected or collected on a metal collector.

Sulfonated polyether-ether-ketone with cardo group (S-PEEK-WC) polymer (figure 1) was studied as a new material for alternative membranes potentially applicable in PEMFC [17]. In this work, in order to obtain an high surface area nonwoven fabric, DMF solutions of S-PEEK-WC with sulfonation degree of 83% have been electrospun. The electrospinning experiments were performed at room temperature. The polymer solution was placed into a 10mLsyringe connected to an (KDS 100) infusion pump. ATeflon tube connects the syringe to a metal tip, and the tip is electrically charged by a high voltage. An aluminum plate was used as the collector and the collector was connected to the ground. The applied voltage and the tip-to-collector distance were fixedat 30 kVand 200 mm, respectively. The electrospray product S-PEEK-WC solution showed a great dependence on the solution concentration. In figure 2 are reported the SEM pictures of the result of the electrospinning of solutions of 30%wt and 40% wt. of concentration respectively. As can be seen in fig 2 A at a concentration of 30%wt. the beads were deposited on the collector. At this concentration the viscosity is too low to contrast the surface tension and drops will form instead of fibers. However, looking at the figure it is possible to observe the presence, as well as beads, of some of the fibers. Increasing the polymer concentration to 40% wt. (fig. 2 B) the electrospinning produced an uniform nonwoven fabric composed of fibers of S-PEKK-WC. Size of fibers is centered about 150nm. Size and distribution of the fibers was evaluated by means of graphics elaboration software (Image-J) on several images and the results are reported in fig 3.

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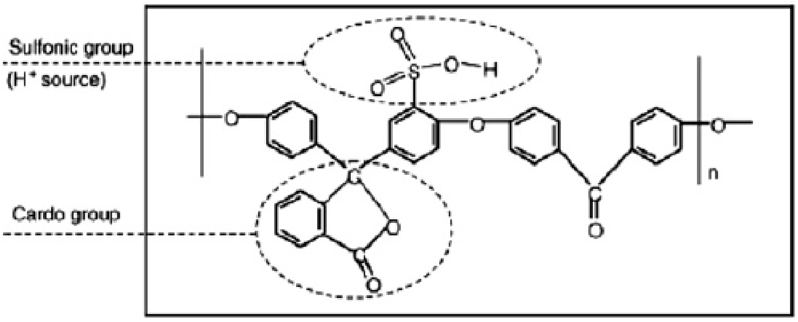

Figure 1. Scheme of the sulfonated PEEK-WC

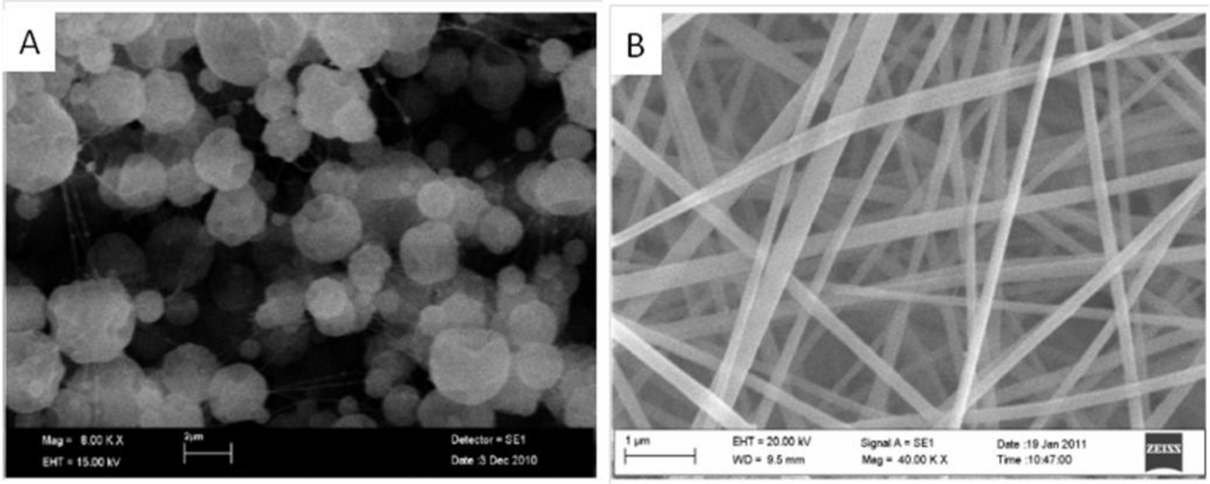

Fig 2. SEM images of products obtained by electrospinning solutions of S-PEKK-WC in DMF at diffetent concentrtion (30%wt. A and 40%wt B).

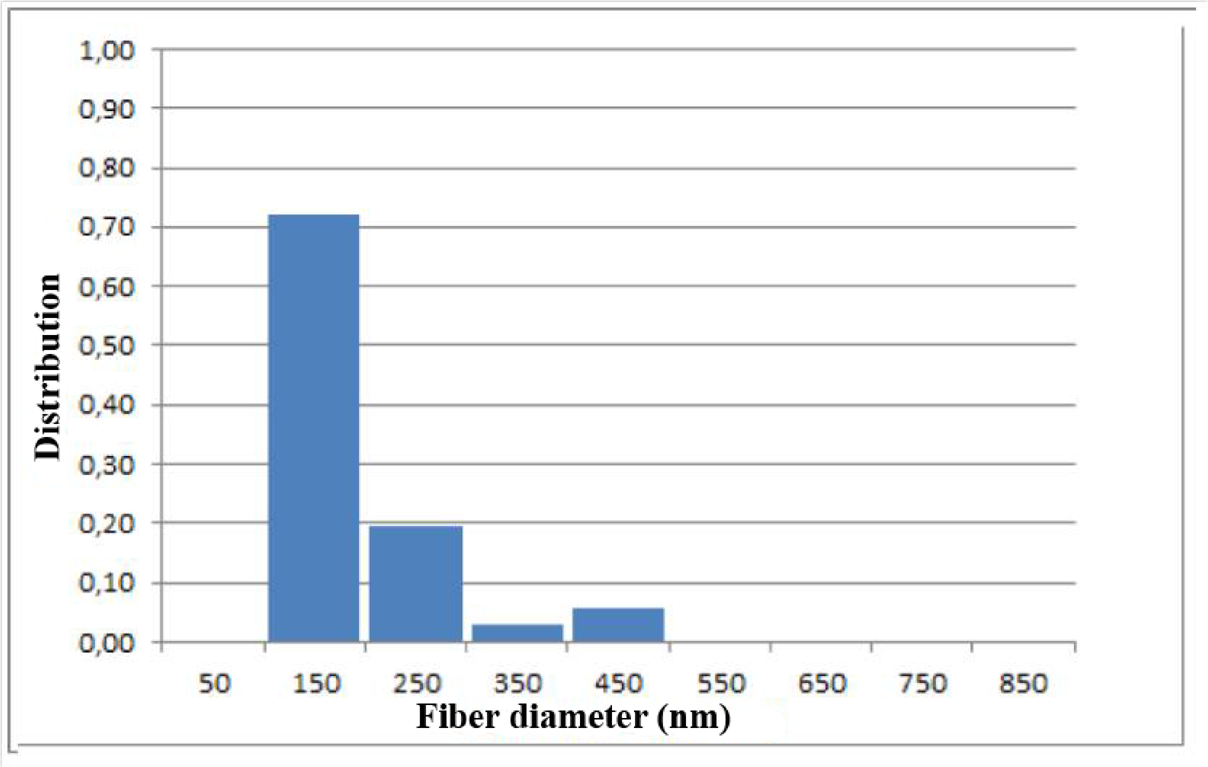

Fig 3Diameter and distribution of fiber obtained from electrospinning of DMF solution at 40% wt. of S-PEEK-WC.

INFLUENCES OF EXFOLIATED GRAPHITE ON BARRIER PROPERTIES OF THERMOPLASTIC POLYURETHANE

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Introduction. The air containment issue is a fundamental aspect for manned modules due to the need to limit as much as possible the daily air leakage rate which has to be closer to the one of current metallic modules for the International Space Station.

Commercial polymeric films for food packaging industry have very good air tightness capability, but they are formed by the co-extrusion of 3 different materials, one of which is usually Polyethylene (PE) as external layer. The PE drawback is the bonding difficulty to metallic flanges, the studies on existing bladder materials are therefore focused on the improvement of the air-tightness performances of thermoplastic Polyurethane (TPU), increasing at the same time the sealing properties. An effective strategy for enhancing the barrier properties of a polymer is through the addition of a small amount of nanofiller, which reduces oxygen permeability while still maintaining the ease of processing of the polymer. Polymer–clay nanocomposites (PCNs), containing exfoliated clay nanosheets, have been studied for well over a decade due to promising improvements in their barrier properties. The barrier properties of PU/organoclay nanocomposites have been previously evaluated in our project. Results shown that the permeability exceeded the maximum permitted for this application. This negative result can be attributed either to poor dispersion of clay nanosheets and the hydrophilicity of the clay surface. Recent advances in the field of graphene opened to the possibility to obtain polymer nanocomposites containing layered nanosheets of non hydrophilic nature. Moreover, using graphenic materials is possible to have nanosheets with an aspect ratio greater than that of clays. Nanocomposites containing different graphenic nanofillers have been prepared either by melt mixing and solvent mixing. The air permeability of the composites has been evaluated.

Result and Discussion. Considering the application the TPU used was Elastollan® 1185A produced by BASF. As nano-fillers two different grade of exfoliated graphene nano-platelet (xGnP – produced by XG Siences) have been chosen. xGnP are constituted of short stacks of graphene sheets made through a proprietary manufacturing process. The standard particle thickness is about 7 nanometers. Platelets are available in various grades with average particle diameters of 5, 15 or 25 microns. Samples of both 5 and 25 microns have been used.

With the aim to improve the compatibility among nano-graphene and PU, and then to improve the dispersion, the samples of xGnP have been oxidized to obtain graphene oxide (GO). Formerly called graphite oxide, graphitic oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. Graphite oxide is then a layered material consisting of oxygenated graphene sheets bearing oxygen functional groups on their basal planes and edges. As fourth filler a fraction of the GO has been thermally expanded at 400°C in an oven under nitrogen flow in order to obtain the thermally expanded graphene oxide (TEGO). From the X-ray diffraction profile (Fig 1.A) is possible to determine the typical staking of graphite (3,41 Å) in xGnP samples. On the other hand after oxidation treatment the interlayer distance augmented to 9,24 Å in GO (Fig 1.B). The absence of diffraction peak in TEGO (Fig 1.C) indicated the complete exfoliation subsequent the expansion process.

Several concentrations of nano-graphene were introduced in the PU matrix by melt-mixing using a micro-extruder operated at 190°C with a rotor speed of 200 rpm for 15 min. The composite is then pressed at 175°C to obtain a film for subsequent permeability measurements. For comparison, nano-composites with the same composition were prepared via solution casting. Samples are prepared by combining a solution of polymer dissolved in dimethylformamide (DMF) and a dispersion of graphene in the same solvent. The suspension is then precipitated, separated from the solution; the resulting composite is then dried and hot-pressed into films.

In Figure 1 the XRD of the obtained composite is compared with those of the polymer and of the fillers. Using the xGnP the resultant composite still show the peak of the filler indicating the formation of a microcomposite in view of the fact that neither intercalation nor exfoliation has been obtained. In the other hand the exfoliation was achieved using both GO and TEGO. In the case of GO the exfoliation take place during the mixing (melt or solvent) favored by the polar groups on the graphene layers. In the case of TEGO the graphene layers was already exfoliated and the disordered structure was maintained during the mixing (melt or solvent), namely there weren’t collapse phenomena, even if the TEGO, being thermally reduced, posses les polar group able to increase the compatibility with the polymer.

The permeability tests have been performed using compressed dry-air at 23° C. The values of transmission rate were obtained directly from the instrument while the permeability was calculated considering the material thickness, using the conversion factors present in the ASTM D1434 standard. The air permeability achieved with graphene based composites are often compared with that of TPU and summarized in Table 1.
As can be seen the addition of xGnP reduces the permeability of the material but this reduction is not substantial since the efficiency of the charges is lowered by the fact that the filler did not reach a nano-dispersion. In the case of GO the nano-dispersion leads to a further reduction in permeability gaining a value of 31, 0 ml mm /m^2 day atm. However, the best result is obtained in the case of TEGO. This result could belong from a better degree of dispersion than in the case of GO.

Conclusions. Graphene based composites and nanocomposites of TPU suitable of bonding and sealing to metallic flanges have been prepared via blend mixing and solvent mixing. The degree of dispersion resulted comparable among the two mixing method. Effective reduction of the air permeability was achieved in nanocomposites.

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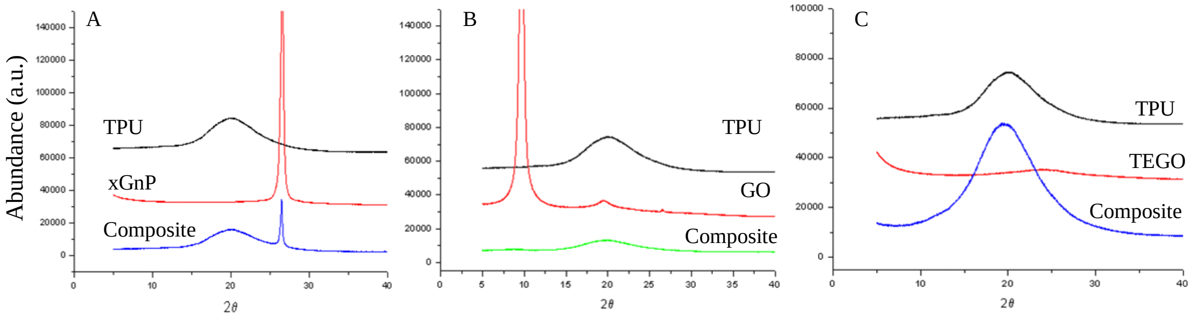

Fig 1 X-ray diffraction patterns comparison of TPU, nanofiller and relative composites.

Tab 1. Air permeability of polyurethane (elastollan) and relative composites.

Sample	**Permeability (ml mm /m^2 day atm)**
TPU	50,1
TPU, 5% nG5	43,4
TPU, 5% GO	31,0
TPU, 5% TEGO	18,6

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