

Abstracts

Introductory lecture

GREEN BIO-ECONOMY AND NANO-BIOTECHNOLOGY FOR A MORE SUSTAINABLE ENVIRONMENT

P. Morganti

Professor of skin pharmacology, Dermatology Institute, 2nd University of Naples, Italy;
Visiting professor China Medical University, Shenyang;
R&D director of Nanoscience Centre MAVI, Italy
Morganti@iscd.it

There is a growing recognition that transitioning to a *green bio-economy* could generate a more sustainable growth addressing some of the systemic problems of the current economic system, such as the decline/loss of ecosystem services vulnerability to climate-related risks/disasters and the scarcity of natural resources. Concurrently, the global financial and economic crisis, rising food, fuel prices, and environmental degradation are leading to significant economic, social, and environmental costs with an increase of people inequality and poverty. Thus, according to the UNEP vision, the *green bio-economy* "shows great potential for delivering a *triple bottom line* of job-creating economic growth coupled with environmental protection and social inclusion". This new economical approach, based on the use of raw materials obtained from industrial wastes by the utilization of innovative bio-nanotechnologies and renewable energy could delivery low-carbon and climate-resilient development by more healthy ecosystems. Following these guard lines our research group has developed innovative cosmetic products, food packaging and advanced medications mimicking the biological cross linking processes that occur in nature. In particular, these new structures were made bonding chitin nano fibrils (CN) and lingo-cellulosic polymers by the use of advanced nano-biotechnologies to obtain skin-friendly block copolymeric nano particles and nano composites 100% biodegradable.

In any way all the polymers used were renewable compounds obtained from the fishery's waste and plant biomass respectively. By the use of different methodologies such as gelation casting and electrospinning technologies we made innovative nano particles and composites, entrapping different active ingredients. It is interesting to underline that the obtained chitin-ligno-cellulosic nano compounds have shown interesting defensive and reparative properties when applied on burned or wounded skin, under any kind of form, such as gel/emulsions, non-woven-tissues or nano composite films. Moreover, they have been further *characterized* by the entrapment of different active ingredients to specialize the final product, focusing the research work on the areas of nano biotechnology for producing new nano-structured cosmetic emulsions with an anti-aging activity and innovative and functional nano fibers useful for medical purpose or to produce more degradable plastic compounds. The development of innovative medical devices, made by 100% biodegradable, natural and safe fibers, will probably open new future opportunities, being an important economic driver as the merger of pharmaceutical, cosmetic, biotech and medical device companies. Thus on one hand, medicine and novel technologies based on the use of industrial natural by-products will play a more prominent role in the future providing safe new products with added value for consumers. On the other hand nano composites, also usable to make different containers made by the natural chitin-ligno-cellulosic polymers, could have a chance of becoming a game-changer for the \$ 374-billion-a-year plastic industry, remembering that lignocellulose and chitin are the most abundantly available raw material on earth. Both these polymers in fact, offer good possibilities to create an added value in the field of material development caused by the use of new biotechnologies and the low price.

The area of *green social solution* is a key way to achieve both poverty reduction and a *green bio-economy*, supported by the growing global demand for innovation and interdisciplinary solutions. For these reasons biotechnology, expected to help meet the most urgent global challenges, will be an important pillar of Europe's economy by 2030, indispensable to sustainable economic growth, employment, energy supply and to maintaining the biodiversity of species and a better quality of life. Our technologies are going in

this direction by the results obtained by three EU research projects named, BioMimetic (www.biomimetic.eu), n-Chitopack (www.n-Chitopack.EU), Chitofarma (www.Mavicosmetics.it). Some results and products, usable in the Medical field of a sustainable and advanced Cosmetic Dermatology, will be reported and discussed.

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SUSTAINABILITY OF BIOPOLYESTER COMPOSITES CONTAINING NANO-CHITIN FROM SEA FOOD WASTE

Patrizia Cinelli, Maria Beatrice Coltelli, Sara Salvadori, Irene Anguillesi, Andrea Lazzeri

INSTM- National Interuniversity Consortium of Materials Science and Technology c/o University of Pisa,
Department of Civil and Industrial Engineering, Largo Lucio Lazzarino 1, 56122, Pisa, Italy,
Patrizia.cinelli@diccism.unipi.it

Introduction

A significant source of potential renewable feedstock for polymers is represented by waste material from the fishing industry, exceeding 250 billion tons/years, and considered hazardous due to its high perishability and polluting effect, both on land and sea. To improve the employment of this marine-waste the EU project n-CHITOPACK “Sustainable technologies for the production of biodegradable materials based on natural chitin-nanofibrils derived by waste of fish industry to produce food grade packaging” started to use chitin, a polysaccharide, to produce Chitin Nanofibrils (CN), with needle-like shape and nanostructured average size¹. Intensive exploration and research in the past few decades on polysaccharide nanocrystals, have led to the emergence of more diverse potential applications exploiting the functionality of these nanomaterials². The objective of the project is the production of functional bacteriostatic films and rigid packaging to be used in the food industry which results bio-degradable and sustainable. Poly(lactic acid) (PLA) is widely investigated for its potential applications in both rigid and flexible packaging, and was selected as polymeric matrix for the preparation of the nano-composites. The biodegradability and sustainability, evaluated by Life Cycle Assessment (LCA) studies, of the nano-composites produced through preliminary nano-chitin suspension treatment and successive extrusion was studied in the framework of the project.

Experimental

Degradability of the selected samples was evaluated by ISO 20020-2004 “Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test”, and sustainability of the process was estimated by LCA analysis cradle to grave with SimaPro7, with Ecoinvent database, following guidance of the International reference life cycle data system handbook.

Results and discussion

Samples selected for degradation tests were based on PLA2003D-plasticizer and a commercial PLA based masterbatch (BioComp) as polymeric matrix for the production of nano composites with 2% by weight, on dry basis, of chitin nanofibrils (Table 1).

All the samples presented significant degradation, and the presence of the CN is not hindering the degradation of the nano-composites based on PLA. Thus the nanocomposites are potentially compostable in terms of disintegration of the samples.

Table 1. Samples tested in compost degradation tests

Sample	PLA/Plasticizer (%)	BioComp (%)	Chitin Nanofibrils (%)
1	100	-	-
2	98	-	2
3	-	98	2

The production of chitin nano fibrils was analysed for its environmental impact considering the consumption of resources (water, etc) and energy consumption (Figure 1).

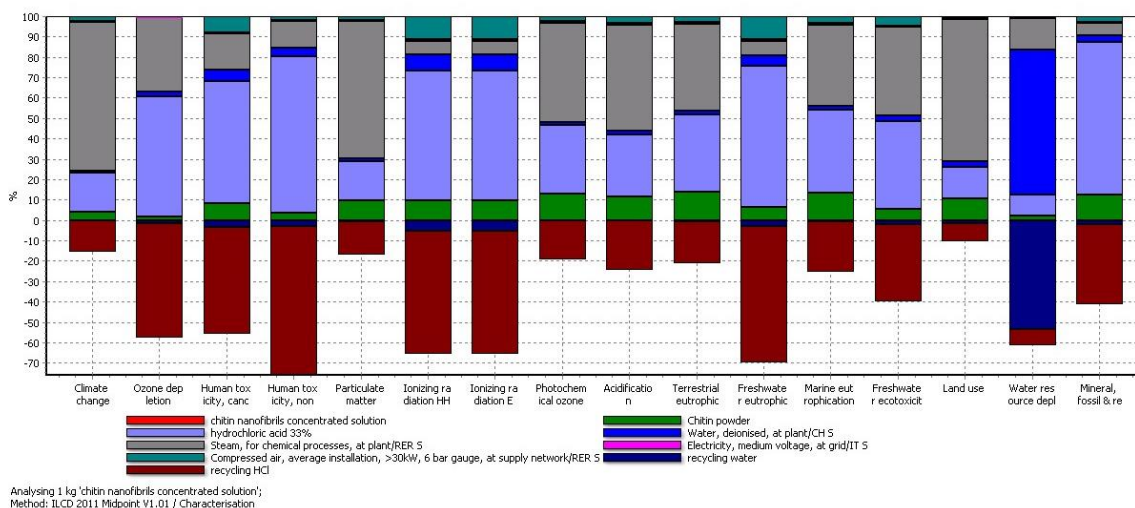


Figure 1. Impact production of nano chitin fibrils considering recovery and re use of chemicals

The end life impact of final products will consider also the results of biodegradation tests, and different possible end life scenarios: landfill and composting.

Conclusions

The presence of 2% of CN in the nano-composites is not hindering the disintegration of the samples in compost, complying with the current Normative.

In the LCA study the most relevant contributes are derived from energy consumption required for the removal of water to achieve dry CN. In the planned industrial production water and other solvents will be collected and recycled, in order to reduce emissions and consumption of raw materials.

Acknowledgements:

Authors acknowledge the financial support from the European Community's Seventh Framework Programme, SME-2012-1, and Grant agreement n ° 315233, n-Chitopack project.

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STRUCTURE AND PROPERTIES OF EXTRUDED BIO-NANO-COMPOSITES BASE ON BIO-POLYESTERS AND CHITIN NANOFIBRILS

Maria-Beatrice Coltelli^{1,2}, Patrizia Cinelli^{1,2}, Irene Anguillesi^{1,2}, Sara Salvadori^{1,2}, Andrea Lazzeri^{1,2}

¹ Inter University Consortium of Materials Science and Technology (INSTM)- c/o University of Pisa,

²Department of Civil and Industrial Engineering, Largo Lucio Lazzarino 2, 56122, Pisa, Italy
mb.coltelli@ing.unipi.it

A renewable feedstock on a worldwide scale is chitin waste material from the seafood industry, exceeding 250 billion tons/year. Recently, it has become possible to produce pure chitin crystals, named “chitin nanofibrils” (CN) for their needle-like shape and nanostructured average size¹. The CN are thus available on an industrial scale in water suspension.

Biodegradable polyesters, such as poly(lactic acid) (PLA) are widely investigated for their potential applications in many sectors². These composites were melt extruded to achieve a good level of dispersion by employing suitable plasticizers to pre-disperse chitin nano-fibrils (CN). The complete removal of water from the plasticizer/CN pre-nano-composite was essential to avoid chain scission³ in the successive extrusion step. The electron microscopy investigation of materials showed the absence of micrometric agglomerates thanks to the adopted preparation method. The effect of plasticization, crystallinity evolution and reinforcement was kept into account to rationalize the results of tensile and DSC tests in order to select bio-nano-composites suitable for both flexible and rigid packaging applications.

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Acknowledgements: Authors acknowledge the financial support of EC Seventh Framework Programme, SME-2012-1, and grant agreement n ° 315233, n-Chitopack project.

CHITOSAN FILMS FILLED BY CHITIN NANOFIBRILS

Jindřich Hašek^{1,2}, Galina Tishchenko¹, Miloš Steinhart¹, Radomír Kužel³, Jana Kovářová¹, Jana Mikešová¹, Francesco Carrezi⁴, Pierfrancesco Morganti⁴, Jan Dohnálek^{1,2}

¹Institute of Macromolecular Chemistry AS CR, Heyrovského nám 2, Praha 6,

²Biotechnological Institute AS CR, v.v.i., Vídeňská 1083, 142 20 Praha 4,

³MFF, Charles University, Ke Karlovu 5, Praha 2, Czech Republic,

⁴Mavi Sud Srl, via le Industria 1, 04011 Aprilia, Italy

Chitosan dissolved in acidified water (pH of about 4.3-4.5) gains the properties of thixotropic gel after addition of aqueous dispersion of chitin nanofibrils (CN). The viscous chitosan/CN mixtures (prior achieving their gel point) can be used for preparation of both films and fibers.

The X-ray diffraction (SAXS and WAX patterns) was applied for inspection of changes of molecular structure of chitosan and CN in the dry state, an aqueous chitosan solution and CN dispersion, and the final dry films with different compositions. The experiments lead us to the following explanation of the observed properties:

– Excellent solubility of chitosan in acidified water, its compatibility with aqueous dispersion of chitin nanofibrils resulting in uniform distribution of CN in chitosan composite films are ensured by electrostatic interactions between the protonated (NH₃⁺) glucosamine groups of chitosan and acetate anions. The latter present even in the dried films having high affinity to water molecules;

- Effect of CN on formation of the CN/chitosan thixotropic gels is defined by the nature of CN: their rigidity due to high crystallinity, their big mass and their surface bearing almost deacetylated glucosamine groups;
 - The deacetylated surface of CN organizes thousands surrounding chitosan macromolecules in domains about ~10 nm far from each nanofibril. The effect of domains partly persists even in the solid phase systems. As a result, the prepared materials gain anisotropic properties;
 - The effect of self-assembly of the domains penetrates through the whole volume already at 5 %-content of CN. At concentrations of nanofibrils over 35 %, the domains already interpenetrate introducing, thus, a new disorder into the molecular system;
 - The chitin-nanofibrils remained intact in all prepared mixtures with exception of those containing salts of heavy metals such as copper acetate. Even small amounts of this salt added to chitin nanofibril dispersion destroyed the crystallinity of nanofibrils. The thinner and smaller CN filaments have high degree of acetylation. They participate in intensive physical crosslinking of nanochitin with chitosan molecules, i.e. system gradually turns to different rheological mechanism;
 - The plasticizers such as glycerol or poly(ethylene glycol) did not changed primarily the structure (space arrangement of molecules in the system). Their effect was due to the changes in dielectric properties and viscosity of the slurry. The molecules of plasticizers present everywhere between chitosan molecules and chitin nanofibrils – even in the dried hygroscopic films.
- Correct understanding of the reasons of the behavior of the studied macromolecular system allows us to design more complex systems possessing the desired properties.

Acknowledgment

The authors gratefully acknowledge the financial support of the European Union (Grant 315233).

EFFECT OF LOW-MOLECULAR WEIGHT ADDITIVES ON RHEOLOGICAL PROPERTIES AND AGING OF CHITOSAN/CHITIN NANOFIBRILS SLURRIES

Jana Mikešová^a, Jindřich Hašek^{a,b}, Galina Tishchenko^a, Pierfrancesco Morganti^c

^aInstitute of Macromolecular Chemistry AS CR, v. v. i., Prague 6, 162 06, Czech Republic

^bInstitute of Biotechnology AS CR, v. v. i., Prague 4, 142 20, Czech Republic

^cMavi Sud Srl, Aprilia, 04011, Italy

mikesova@imc.cas.cz

Introduction

Biomaterials based on chitosan/chitin nanofibrils (CN) nanocomposites are already being successfully used in medicine, e.g. in wound healing. Their ability to suppress microbial growth as well as their biodegradability is highly promising for applications in food packaging [1]. In preparation of chitosan/CN films by solution casting, flow properties get a special importance. The rheological characteristics give necessary recommendations for forming a uniform and stable layer on a bearing support.

In our previous work, a self-assembly process in chitosan/CN slurries [2] was investigated and chitin nanofibrils were recognized as a strong “gelling agent” of chitosan acetic solutions. The incorporation of a small amount of nanofibrils to the chitosan solutions changed their flow properties dramatically and resulted in a solid-like behavior with a yield stress limit. The phenomenon was explained by a chitosan-like surface of chitin nanofibrils and by the interactions inducing orientational cooperativity of thousands of chitosan molecules dissolved in the close neighborhood of the high anisotropic chitin nanoparticle. Addition of glycerol or poly(ethylene glycol), improving mechanical properties of the films, delayed the beginning of gelation and decreased the yield stress of slurries. The effect is caused by an increase in viscosity of the slurries and by their more chaotropic character.

This study brings some new information about the influence of Ca^{2+} , Mg^{2+} and Ba^{2+} ions on gelation of chitosan/CN slurries together with the effects of long-time storage on rheological characteristics of the slurry containing glycerol.

Experimental

The commercial chitosan Giusto Faravelli S.p.A., molecular weight $M_w = 1425$ kDa, degree of acetylation(DA) 20 % and the aqueous dispersion of chitin nanofibrils produced by Mavi Sud S.r.l., (Italy) with DA 95%, the plasticizer glycerol and the hydroxides $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ (Aldrich, Germany) were used. The compositions of the slurries containing metal ions are summarized in Table 1. The amount of glycerol in the aged slurry was 25 wt. % of total content of chitosan and CN. The chitosan/CN/glycerol slurry was long-time stored in the fridge.

The rheological experiments were performed at room temperature, using a rheometer Physica MCR 501 (Anton Paar GmbH, Austria), equipped with an anti-slipping parallel-plate geometry. Viscoelastic properties in oscillatory shear flow were measured in the linear viscoelasticity region. The time-dependent experiments were started after 3 s pre-shearing at the shear rate 0.03s^{-1} , to ensure the same shear history for the measured samples.

Table 1. Composition [wt. %] of chitosan slurries with and without metal ions

<i>Components</i>	<i>CS/CN</i>	<i>CS/CN/Mg²⁺</i>	<i>CS/CN/Ca²⁺</i>	<i>CS/CN/Ba²⁺</i>	<i>CS/Ba²⁺</i>
chitosan (CS)	1.5	1.6	1.7	1.3	1.8
Q water	96	96.9	96.7	97.1	97.3
acetic acid	1.6	0.8	0.8	0.6	0.9
chitin nanofibrils (CN)	0.8	0.7	0.8	0.6	-
$\text{Mg}(\text{OH})_2$	-	0.03	-	-	-
$\text{Ca}(\text{OH})_2$	-	-	0.03	-	-
$\text{Ba}(\text{OH})_2$	-	-	-	0.36	0.05

Results and Discussion

The influence of metal ions on a reversible gelation process in chitosan/CN slurries was examined using time-dependent experiments in the oscillatory flow. To avoid a destruction of the internal structure of slurries, the measurements were carried out at very small deformation. The results of the tests are summarized in Fig. 1 where the time dependences of the storage (G') and loss (G'') moduli are plotted. The moduli of chitosan/CN slurry and the slurries containing Ca^{2+} or Mg^{2+} ions intersect in a crossover point (gel point) where the state of slurries is changed from a viscoelastic fluid to a viscoelastic solid phase. The gel point indicates the formation of a physical network between chitosan macromolecules and chitin nanofibrils due to the self-assembly. The metal ions added to the chitosan/CN slurry influence the kinetics of self-assembly process as well as the strength of the formed physical network. The Mg^{2+} ions delay significantly the gel point of the slurry. In the case of chitosan/CN/ Ba^{2+} slurry, the storage modulus overwhelms the loss one already at the start of the experiment. The data indicate that a strong network (not disturbed by the used pre-shearing conditions) was formed in the slurry during the preparation and storage. In the slurry chitosan/ Ba^{2+} , the slow increase in both moduli with time reflects slight networking of chitosan macromolecules. Nevertheless, in the absence of large rigid nanofibrils, the structure has not achieved the gel point even after 2.5 h.

The effects of long-time storage (aging) of chitosan/CN/glycerol slurry were quantified by changes of viscoelastic characteristics after 1 day and 2, 6, 13, 15, 19 weeks storage in the fridge. The results reveal not only a decrease in viscosity and elasticity during the storage but also a modified viscoelastic behavior of the slurry. The freshly prepared slurry shows a solid-like behavior ($G' > G''$). This phenomenon is connected with a reversible physical network induced by intermolecular interactions between chitosan chains and chitin nanofibrils. The elasticity of the slurry dropped significantly after 19 weeks and the

solid-like region disappeared. The phenomenon demonstrates a decimation of self-assembly gelation in the slurry after long-time storage, caused by a scission (degradation) of chitosan chains.

Summary

The self-assembly process in chitosan/CN slurries, modified by Mg^{2+} , Ca^{2+} and Ba^{2+} ions was elucidated by time-dependent measurements of dynamic moduli after pre-shearing and the gel points were evaluated. It was found that Mg^{2+} ions prolonged and Ba^{2+} ions propagated the gelation of chitosan/CN slurry. The effect of Ca^{2+} ions was not significant.

The aging of CN-filled chitosan slurry modified by glycerol revealed that the elasticity of the slurry decreased and the characteristic solid-like behavior disappeared. The self-assembly gelation in the slurry was decimated due to a scission of chitosan chains after the long-time storage.

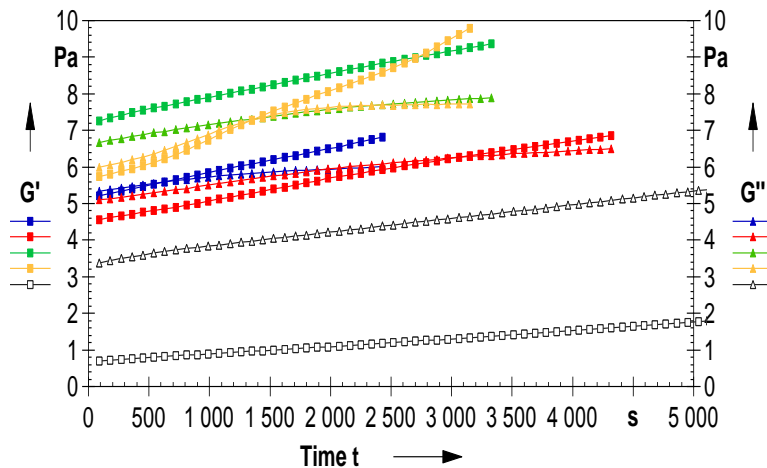


Figure 1. Effects of the metal ions on gelation of chitosan/CN slurries: Time dependences of the storage modulus G' and loss modulus G'' : Chitosan/CN - (■),(▲); chitosan/CN/ Ca^{2+} - (■),(▲); chitosan/CN/ Mg^{2+} - (■),(▲); chitosan/CN/ Ba^{2+} - (■),(▲) and chitosan/ Ba^{2+} (□),(△).

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Acknowledgment

The authors gratefully acknowledge the financial support of the European Union (Grant 315233).

CHITOSAN/CHITIN NANOWHISKERS COMPOSITES: EFFECT OF PLASTICISERS ON THE MECHANICAL BEHAVIOUR

Ivan Kelnar¹, Jana Kovářová¹, Galina Tishchenko¹, Ludmila Kaprálková¹,
Francesco Carezzi², Pierfrancesco Morganti²

¹Institute of Macromolecular Chemistry AS CR, v.v.i., Prague 6, 162 06, Czech Republic

²MAVI SUD s.r.l., via del' Industria 1, Aprilia, 04011, Italy

Ivan Kelnar *kelnar@imc.cas.cz*

Introduction

Chitin and its partly deacetylated derivative, chitosan (CS) represent natural polymers with many valuable parameters including biodegradability and antibacterial activity, which enable an extraordinarily broad range of applications [1]. Currently, the range of applications is limited by the relative rigid polysaccharide chains with significant interactions and also by their significant hydrophilic character. These shortcomings can be eliminated by the addition of a natural polymer-based reinforcement, e.g., chitin [2] nanowhiskers (CNW). At the same time, for most applications in the food packaging area, ductile, compliant films are necessary. For CS and polysaccharide-based films, this issue can be successfully solved by the application of various plasticisers, mostly miscible low molecular weight compounds.

The present study addresses the potential of different miscible compounds to modify the CS matrix/chitin nanowhiskers system. The goal is to improve the balance of mechanical parameters of this rigid polymer-polymer composite by plasticising to prepare elastic compliant films.

Experimental

Due to solubility of CS in water-acetic acid (1%wt) mixture, advantageous water-solution processing technique was applied. Because the goal of this study was a comparison of the efficiency of the different plasticisers in the CS/CNW composite, evaluation of the mechanical properties was performed with relatively “fresh” samples stored 7-10 days in a sealed box with a 43% RH environment. The water content revealed in the test samples by means of thermogravimetric analysis was 10 - 12 % wt.

Results and Discussion

A study of the effect of plasticiser content in the CS/CNW 85/15 system was performed with glycerol, di-, tri- and tetraglycerol. Figures 1a-c show the marked effect of the type and content of plasticiser on the basic mechanical parameters of the composite film performance. The steep decrease of modulus is accompanied with a significant gain in elongation as a consequence of the plasticising effect consisting of an increase of free volume, which is expected to disturb the intermolecular interactions and thus enhance the chain movement. At the same time, the increase in stretchability is lower in comparison with, e.g., plasticised PVC most likely due to the overall higher rigidity of polysaccharide chains. This higher rigidity in turn leads to a still satisfactory level of tensile strength (~20 MPa). Moreover, in spite of the apparent good solubility of CS in water/acetic acid mixture, we observed some minor content of undissolved CS domains, which are only swollen with water. We consider that these domains (most likely originated from less deacetylated CS particles) are forming a physical network beneficial in particular for dimensional stability at elevated temperatures (analogously to plasticised PVC). From Figs. 1 a-c, the best effectiveness is from di- and tri-glycerol, whereas glycerol leads to a significant reduction in strength. The altering of mechanical behaviour with triglyceride content is further demonstrated by corresponding stress-strain curves in Figure 1 d.

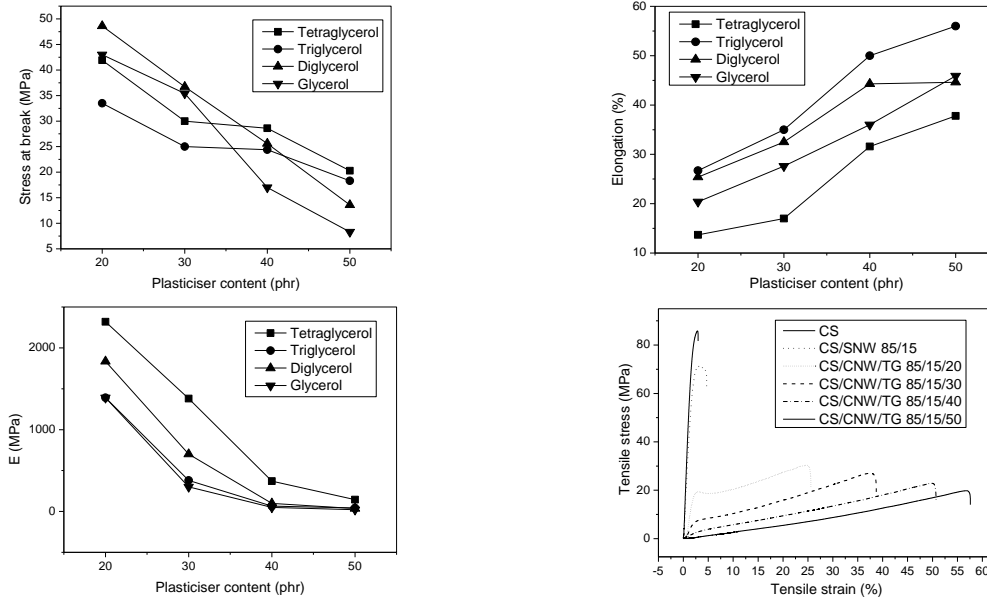


Figure 1. Effect of plasticiser type and content on the mechanical behaviour of the CS/CNW (85/15) composite a) Stress at break b) Elongation c) Young's modulus d) stress-strain curves of unplastitized and triglycerol (TG) plasticized CS/CNW system

Conclusions

The results obtained indicate that the plasticising effect of both selected low-molecular weight and polymeric plasticisers, such as glycerol, di-, tri-, tetraglycerol can influence the mechanical behaviour of the CS/CNW composite significantly. The reason for this pronounced influence can obviously be ascribed to the ability of the plasticisers to support the chain mobility of both components. A suitable combination of chitin nanowhiskers and glycerol-oligomers-based plasticisers represents a tool to prepare a single-polymer composite film with well-balanced mechanical properties and with a fair potential for many applications.

Acknowledgements

The authors gratefully acknowledge the European Union (Grant 315233) and Czech Science Foundation (Grant No 13-15255S) for the financial support.

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CHITOSAN/CHITIN NANOFIBRILS COMPOSITE FILMS: CHARACTERIZATION AND PROPERTIES

Galina Tishchenko¹, Ivan Kelnar¹, Jana Mikesova¹, Jana Kovarova¹, Jindrich Hasek², Libuse Brozova¹, Ewa Pavlova¹, Ludmila Kapralkova¹, Michal Pekarek¹, Libor Kobera¹, Eliška Chanová¹, Adam Strachota¹, Milena Špírková¹, Francesco Carezzi³, Pierfrancesco Morganti³

¹Institute of Macromolecular Chemistry AS CR, v.v.i., Prague 6, 162 06, Czech Republic,

²Institute of Biotechnology AS CR, v. v. i., Prague 4, 142 20, Czech Republic,

³MAVI SUD s.r.l., via del' Industria 1, Aprilia, 04011, Italy

tiscenko@imc.cas.cz

Introduction

Nature is the most skillful Designer of myriad nanocomposites. Crustacean's exoskeletons (the polysaccharide-protein-mineral nanocomposites) are one of them. They contain "chitin" – the linear water-insoluble homopolymer of $\beta(1\rightarrow4)$ -linked *N*-acetyl-D-glucosamine. In exoskeletons, chitin nanofibrils participate in reinforcement of exoskeletons ensuring their structural stability. The deacetylated chitin ("chitosan") becomes soluble at pH 4-4.5 in acidified water. Its viscous solutions, being dried, form flexible films, which remain water-soluble even if they do not crosslinked.

The idea consisted in preparation of highly homogeneous and mechanically stable films by reinforcing the chitosan matrix with chitin nanofibrils. It was based on excellent compatibility of nanochitin and chitosan having high chemical and structural similarity but differing greatly in water-solubility.

These films can be considered as promising candidates for food packaging because of their complete biodegradability, biocompatibility and bactericide effect on pathogenic microbes including *Escherichia coli* and *Staphylococcus aureus*.

Experimental

Commercial samples of Chitin (CS) and CN produced by Italian companies Giusto Faravelli X.p.A, and MAVI SUD S.r.L, respectively, were characterized by FTIR to determine their chemical functionality, by SAXS to estimate their crystallinity, by TGA and DSC to study their thermal degradation at heating up to 800 °C. SEM, TEM and AFM were used for characterization of morphology of CN and the dry and wet state and of composite CS/CN films. The acetylation degree (DA) of both CS and CN was determined by ¹³C CP/MAS solid state NMR analysis. It was equal to 21% and 97% for CS and CN, respectively. Molecular weight (Mw) of CS was determined by GPC (Mw 1425±35 kDa). The pH value of CN was 5.2. Conductivity of the CN dispersion dialyzed against distilled water and concentrated by vacuum evaporation was 0.12 mS/cm. Concentration of CN was 43 mg/g wet dispersion.

Preparation of the CS/CN films was carried out using the designed by us preparation procedure consisting of six steps: 1. Dissolving of CS powder (80-140 μ m) in acidified distilled water to prepare the CS solution. 2. Mixing the CS solution with the estimated amounts of CN and plasticizer during an hour to prepare the homogeneous slurry. 3. De-airing the slurry by vacuum evaporation. 4. Casting the slurry on a support placed on a MSK AFA L800 coater by using a Doctor Blade. 5. Drying a CS/CN film by heating at 50°C under infrared irradiation. 6. Taking off the dry film from a support.

Results and discussion

Since chitosan and CN exhibited excellent compatibility, highly homogeneous chitosan materials with high content of CN can be obtained. The previous lab-tests have shown that CN affected the rearrangement of packing the chitosan chains in composite films resulting in their higher structural stability and better mechanical properties at the swelling/de-swelling cycle in comparison with a purely chitosan film. To verify the effect of the component proportion in the slurry, the films with various CN

content (15, 25 and 35 wt%) were prepared and their mechanical properties (strength and stretching), hydrophobicity (contact angle of the film surfaces) and behavior in contact with water were tested. It was shown by SEM, TEM and AFM analysis that on the nano-scale, the surfaces of CS/CN films were heterogeneous with the top surface (faced to air) enriched with chitin nanofibrils stacked together with chitosan chains. The distribution of CN within CS phase was very homogeneous (Fig. 1).

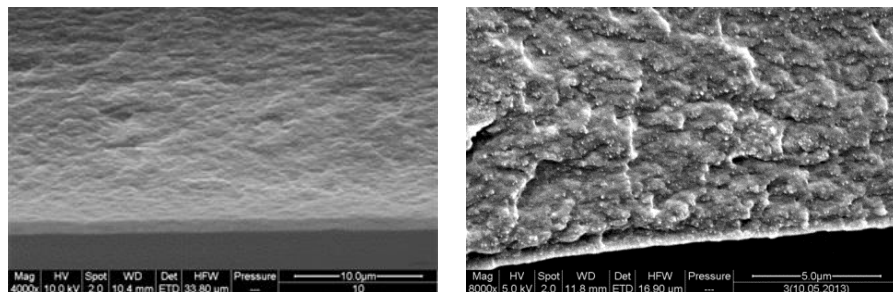


Fig. 1. SEM of the fracture of the CS/NC film

Nano-chitin themselves (i.e. CN) exhibited excellent reinforcing effect on CS phase. The ability of nonplasticized CS/CN film to withstand against the applied tensile forces increased twice with increasing CN content from 15 wt% to 35 wt%. The stretching of the film with 35%-CN content decreased about 60%. However, the elasticity of films prepared from CS and NC only is not sufficient for their using as packaging films. The films were too brittle. For increasing their elasticity, glycerol and polyglycerol-2, -3, or -4 (Solvay, Belgium), which were permitted for application in food industry, were used. If the films with the same CS/CN proportions were plasticized with polyglycerol-3, their rigidity decreased approximately twice in comparison with nonplasticized films, whereas their elongation increased about four times (Table 1).

Table 1. Dependence of mechanical characteristics of CS/CN films on CN and plasticizer content

pG-3, wt% CN, wt%	0	30	Decrease	0	30	Increase
	Maximum stress, MPa			Strain at break, %		
15	44.5	21.9	2.0	6.0	22.6	3.8
25	50.8	28.8	1.8	4.1	14.2	3.5
35	84.8	38.4	2.2	3.8	13.8	3.6

The idea of surface modification of plasticized CS/NC films has arisen after analysis of both the morphology of the films' surfaces of their behavior in contact with water. After dipping a disk of the film with CS/NC proportion (75/25 wt%) plasticized with glycerol (30 wt%) into water, it swam on the surface of water (Fig. 2) but its permeability to water enhanced with time. It should be emphasized that in spite on water permeability, CS films reinforced with nano-chitin and plasticized with polyglycerols did never dissolved during prolonged time.

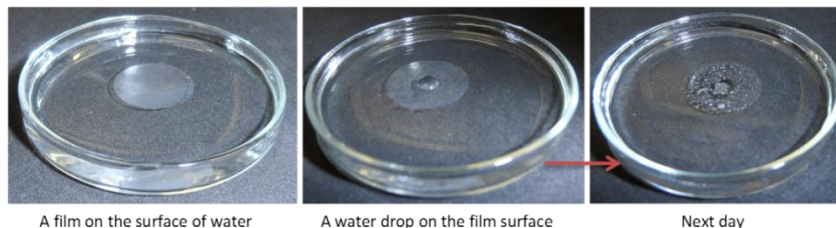


Fig. 2. Behaviour of the film with (CS/NC)/glycerol proportion (75/25)/30 wt% in water

Since the CS/CN films are intended for food packaging, the choice of a suitable modifier for enhancing their water repellence was limited only by those, which have been already permitted for application in food industry. In our study, polylactides (PLA) with Mn 7.7 kDa, 220 kDa and 337 kDa and polyglycerol polyricinoleate (PGPR) known by their hydrophobic properties and biocompatibility were used. After surface modification of CS/CN films, they became as a rule, more rigid and less elastic than the initial ones but their hydrophobicity enhanced considerably.

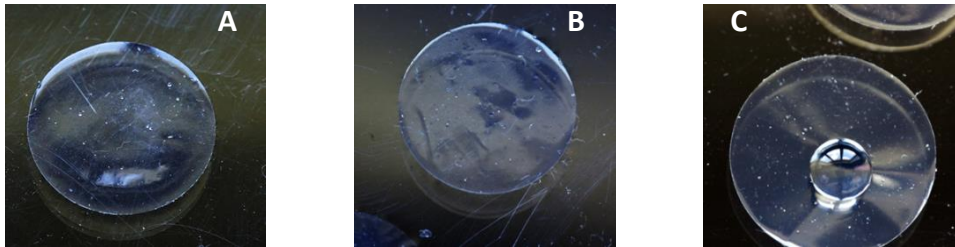


Fig. 3. Swelling in water of PLA-modified CS/CN films in time: A. 5 minutes, B. 10 days, C. a drop of water on the surface of (CS/CN)/polyglycerol-3 film modified with PLA

In contrast to cellulosic KFC paper, which is used for sandwich packaging the the fast food restaurants, the created prototype of CS/CN films had more than three times higher elasticity (about 9-12%) at comparable or somewhat higher mechanical strength, especially after their surface modification with PLA.

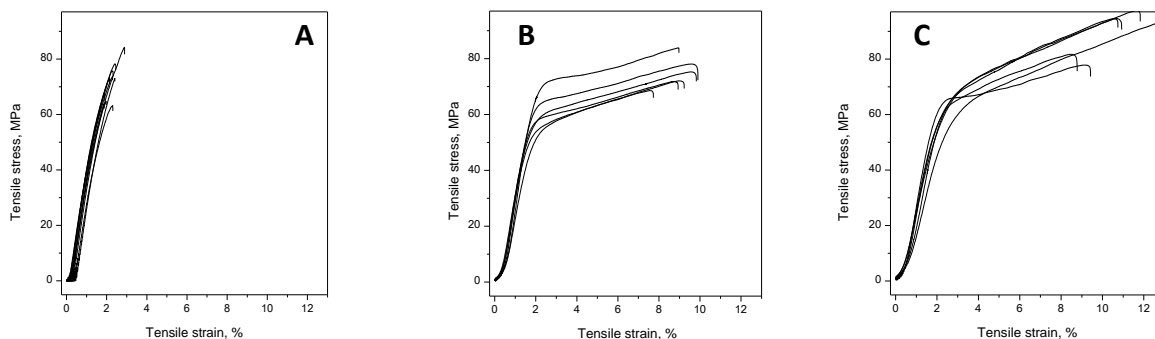


Fig. 4. The stress vs strain dependences of cellulosic KFC paper (A) and the films with (CS/CN)/polyglycerol-3 proportion (70/30)/25 wt% (B); film B modified with PLA (7.7 kDa) (C)

Conclusions

It was shown that the properties of composite completely biodegradable chitosan films reinforced with nano-chitin can be improved by incorporation of some additive such as PLA and PGPR controlling both their mechanical stability and hidrophobicity similarly to those components in crustaceans' exoskeletons, which contribute to formation of the product, excellently stable in water, owing to multiple physical bonds ensuring the perfect spatial adjustment of all components to each other.

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Acknowledgements

The authors gratefully acknowledge the European Union (Grant 315233) for the financial support.

THERMO-ANALYTICAL CHARACTERIZATION OF THE CHITOSAN/CHITIN NANOFIBRILS FILMS PLASTICIZED WITH POLYGLYCEROLS

J.Kovářová¹, G.Tishchenko¹, P.Morganti²

¹Institute of Macromolecular Chemistry AS CR, v.v.i., Prague 6, 162 06, Czech Republic

²MAVI SUD s.r.l., via del' Industria 1, Aprilia, 04011, Italy

Introduction

The aim of the n-CHITOPACK project is the tuning of the casting technique for production of completely biodegradable films from the waste of the sea food industry (chitosan, CS and nano-chitin, NC). These films are intended for using as disposable packaging of food (e.g. sandwiches in the fast food restaurants, cheese and etc.) instead of paper packaging. The replacement of the one-off packaging from cellulose by chitosan/nano-chitin-based ones will decrease the de-forestation and improve the quality of the Air Ocean of the Earth owing to increasing the area of forests being the Lung of our Planet.

One of the parameters, which should be optimized in preparation of the CS/NC films plasticized with polyglycerols, is determination of the temperature allowing carrying out the drying of films effectively without their degradation under heating. Obviously, the knowledge of the decomposition behavior of the films under heating studied by Thermogravimetric Analysis (TGA) will give us very useful information about their composition. Additional information about physical parameters of the studied nanocomposite films (crystallinity, T_g, evaporation and degradation features) can be obtained by means of Differential Scanning Calorimetry (DSC).

Experimental

TGA was performed by using a Perkin Elmer TGA Pyris 1 within the temperature range 30-800 °C under air or N₂ at the gradual temperature rise of 10 °C/min and gas flow 50 ml/min. The weight of a film sample was about 6 mg. The DSC measurements were carried out by using a Perkin Elmer DSC 8500 within the temperature range of -70 – 200 °C under the inert atmosphere of N₂ flow (50 ml/min) at the temperature rise of 10 °C/min. Weight of a film sample was from about 2 to 5 mg.



Fig. 1. A. SEM of chitin nanofibrils, B, C. optical view of the air-dried samples of CN and CN/triglycerol (70/30 wt%) thick films

Results and discussion

In the form of water-insoluble nanofibrils (70-80 nm × 600-700 nm) looked as needle-like particles in SEM pictures (Fig.1A). They formed brittle thick films being dried under air (Figs 1B, C). In TGA experiments, the nontrivial mass loss was observed under heating the samples of CN and CS (5 and 12 wt%, respectively) up to 150 °C due to evaporation of volatiles (mainly water). The decomposition of CN themselves has started at 230 °C achieving the maximum decomposition rate at 360 °C. The film from CS

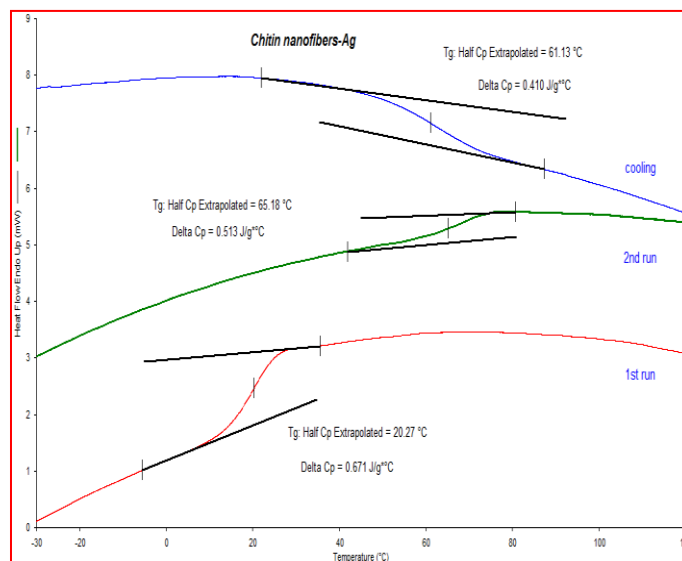
started to decompose at lower temperature than CN at about 160 °C. The temperature of its maximum decomposition rate was also lower (310 °C). For nonplasticized CS/CN films, there are two maxima in the dependences of Δ mass loss, %/ Δt , °C. The first and second maxima are assigned to the decomposition rate of CS and CN, respectively. In comparison with the values of maximum decomposition rates of CS and CN themselves, those in the nanocomposite films are changed as follows: 305 and 364 °C, 309 and 372 °C and 312 and 376 °C, respectively for the films with CS/CN proportion of 85/15; 75/25 and 65/35 wt%. The temperature of the maximum decomposition rate of CN tends to increase with increase in CN content from 15 to 35 wt%. These finding can be explained by changes of the structural order in the films due to interactions between chitin nanofibrils and chitosan chains, which become higher with increase in CN content in CS phase.

If the CS/CN films with CS/CN proportion of 85/15 wt% were plasticized with triglycerol, the temperature of the maximum decomposition rate of CS in the films increased from 304 °C to 308 °C and to 312 °C with increase in glycerol content from 30 wt% to 40 wt% and to 50 wt%, respectively. Obviously, glycerol molecules interact with CS chains and higher temperature is needed for decomposition of these molecular complexes.

At the same content (30 wt%), the effect of polyglycerol-3 and polyglycerol-4 on the decomposition behavior of CS/CN films with the component proportion of (85/15 wt%) under heating were comparable. This can be explained by the comparable composition of these plasticizers containing di-glycerol (26.7 and 1.5 wt%), tri-glycerol (43.3 and 41.2 wt%), tetra-glycerol (19 and 35.2 wt%), penta- higher glycerols (10.1 and 19.1 wt%) for polyglycerol-3 and polyglycerol-4, respectively. Polyglycerol-2 containing 90.3 wt% of di-glycerol and admixture of glycerol (9.2 wt%) affected the decomposition of CS/CN films (85/15 wt%) considerably. There were three maxima in the dependences of Δ mass loss, %/ Δt , °C at: 264 °C, 316°C, and 388 °C. The first and the second maxima are assigned to decomposition of chitosan phase, in which molecules of di-glycerol have at least two different binding sites. DSC experiments gave excellent opportunity to evaluate the effects of *water loss*, *plastification* on T_g values, sample *homogeneity*, *thermal history* and NH_2 and OH binding sites on CS chains.

Sample	Triglycerol wt%	Tg, °C from DSC measurement		Weight loss after 1 st run, %	Temperature °C
		1 st run	2 nd run		
NC (thick film)	0	—	—	6.8	180
NC-Ag	0	+20.3	+65.2		150
NC-Ag	0	—	+107.2		180
NC film	30	-61.2	-60.1	0	50
NC film*	30	-56.4	-41.3		150
NC thick film	30	-60.2	-37.5	5.7	180
CS/NC (85/15)	0	+60.7	+65.9	33.0	200
CS/NC (85/15)	20	-32.9; +0.7	-34.0; +1.0	3.2	50
CS/NC (85/15)	20	+28.5	-18.3	5.1	80
CS/NC (85/15)	30	-31.5	-28.0	0.5	80
CS/NC (85/15)	40	-56.2	-44.9	9.5	80
CS/NC (85/15)	50	-61.5	-49.7	27.0	80
CS/NC (85/15)	30	-19.5	+5.0	17.0	80
CS/NC (85/15)	30	—	—	59.1	80

* repeated experiment



Conclusions

The always present *water* as revealed by TGA experiments affects the properties of the chitosan/chitin nanofibrils films as well as of their plasticized analogs. Free amino and hydroxy groups in chitosan are the most probable binding sites for *H-bonding*. Water acts as a plasticizer lowering the T_g of individual components as well as of their composites. To eliminate the effect of moisture *is not easy*. All polyol plasticizers display interactions with chitosan and CS/CN composites via *H-bonding*. Various values of T_g of chitosan or chitin nanofibrils in the literature, i.e. 203, 195, 103, 140-150, 130-139 °C. Single value of T_g means miscibility of chitosan/CN composition in the amorphous phase. A broad water evaporation peak in the vicinity of 100–130°C covers T_g of water-plasticized chitosan.

Acknowledgements

The authors gratefully acknowledge the European Union (Grant 315233) and Czech Science Foundation (Grant No 13-15255S) for the financial support.

BIODEGRADABLE FOOD PACKAGING FILMS BASED ON CHITIN NANOFIBRILS

PhD. Eng. LAURENTIU MOLDOVAN¹, Senior Researcher Eng. GABRIELA PANTEA¹

¹ SC RODAX IMPEX SRL, Bucharest, Romania, 35 Sadului Street, district 5, 052167

rodax-impex@yahoo.com; gabriela_pantea1985@yahoo.com

Use of waste derived natural chitin nanocrystals (known as *chitin-nanofibrils-CN*) and the identification of the best ways for industrial exploitation of sea food waste at the European scale have been researched in the project N-CHITOPACK (www.n-chitopack.eu).

Development of improved technologies to produce alternative bio-based packaging products it is nowadays aim of the manufacturers for new materials.

The researchers involved in the study of new biodegradable materials based on chitosan and CN, developed packaging films with environmental benefits using biodegradable polymers.

RODAX realized tests for the films prototypes: Chitosan/CN composites, multi-layered material, chitosan/CN, CN-PLA, BioComp BF 7210 with chitin.

Tests of the packaging films include the following tests: sealing properties, cutting, bending, stretching, resistance, leaking, burst, and integrity of the package.

The results of the tests showed the possibility of their use on the market for food and goods packaging.

Acknowledgements

Authors acknowledge the financial support of EC Seventh Framework Programme, SME-2012-1, grant agreement n° 315233, n-Chitopack project.