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 SiO_2 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.

References
[1] Gilman JW. *Appl Clay Sci* 1999;15:31–49.
[2] Zanetti M, Camino G, Mulhaupt R. *Polym Degrad Stab* 2001;74:413–7.
[3] Kashiwagi T, Shields JR, Harris RH, Davis RD. *J Appl Polym Sci* 2003;87:1541–53.
[4] Kashiwagi T, Du F, Douglas JF, Winey KI, Harris RH, Shields JR. *Nature Materials* 2005;4:928-33.

[5] Kashiwagi T, Grulke E, Hilding J, Harris Jr RH, Awad WH, Dougls *J. Macromol Rapid Commun* 2002;23:761–5.
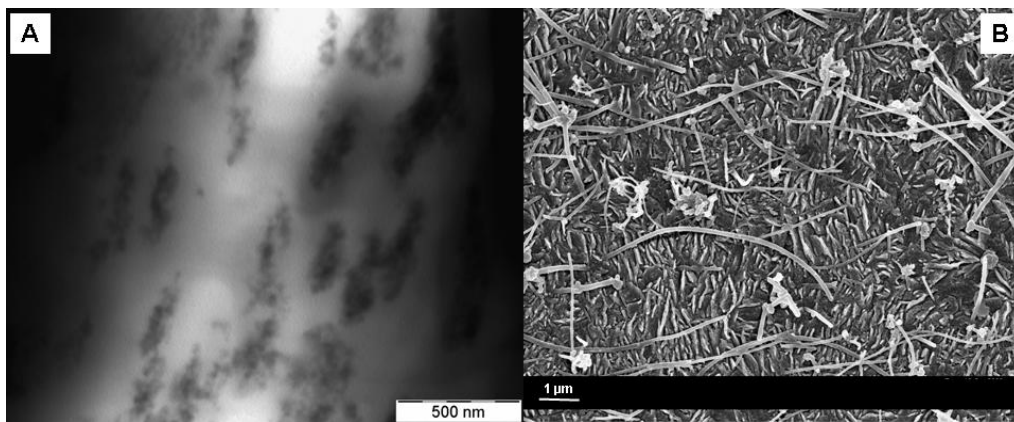[6] Zanetti M, Bracco P, Costa L. *Polymer Degradation and Stability* 2004;85:657-65

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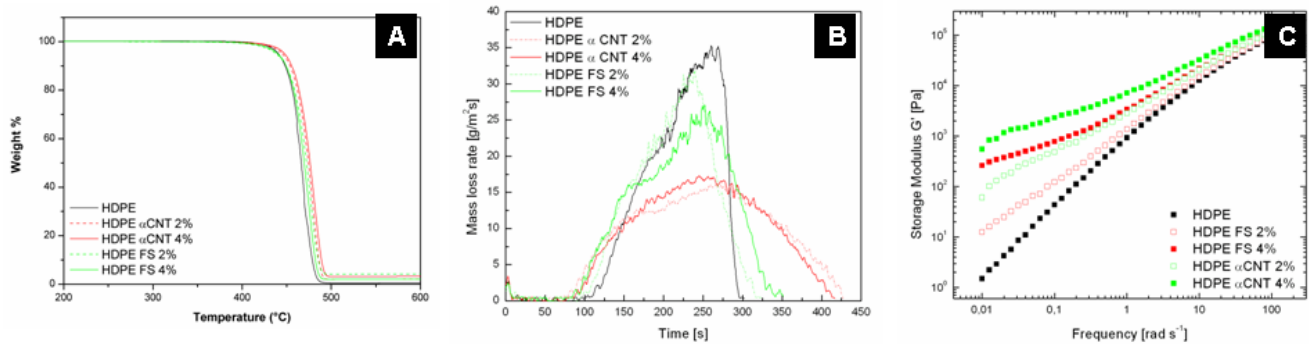

Fig. 2 Nitrogen TGA (A), gasificator (B) and viscoelastic (C) data for CNT and FS nanocomposites