FIRE RETARDANT BEHAVIOUR OF POLYLACTIC ACID NANOCOMPOSITES

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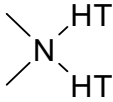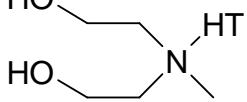
Introduction: The physical and mechanical properties of PLA make it a good candidate as replacement for petrochemical thermoplastics in several application areas. The properties profile of commercial PLA is in some aspects similar to synthetic thermoplastics (mechanical strength, elastic recovery and heat sealability), while it shares other properties with bio-based polymers (biodegradability, dye-ability, barrier characteristics). According to two major companies producing PLA, namely Nature Works and PURAC, about the substitution potential for PLA, they agree on the potential for PLA or PLA components to partially replace low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyamide (PA) and polyethylene terephtalate (PET), as well as seeing possibilities for PLA to substitute for polymethylmethacrylate (PMMA). Even if PLA is primarily used in packaging and the textile sector today, its expected market should be rapidly extended to transportation and electrical and electronic equipment (E&E) sectors. Thus it can be clearly seen that flame retarding PLA is (or will be) becoming an issue for this polymer.

Of particular interest is the developed nanocomposite technology consisting of a polymer and nanoparticles because they often exhibit remarkably improved mechanical and various other properties as compared with those of virgin polymer at loading as low as 3–5 wt%. In PLA nanocomposites it was reported that this family of composites exhibits improved properties including a high storage modulus both in the solid and melt states, an increased flexural properties, a decrease in gas permeability, an increased heat distortion temperature, an increase in the rate of biodegradability of pure PLA, etc. Adding a small amount of clay has been shown to reduce PHRR for numerous polymer nanocomposites. The suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a potential barrier to both mass and energy transport.

The aim of this paper is to characterise the degree of nanodispersion in PLA/clay nanocomposite using and to evaluate the reaction to fire of this nanocomposite.

Experimental: Poly(L-lactic acid) "NatureWorks® PLA Polymer 3051D", was obtained from Natureworks. Organic modified montmorillonites, CLOISITE® 20A (Cl20A) and CLOISITE® 30B (CL30B) were purchased from Southern Clay (U.S.A.). The characteristics of the nanoparticles used in this work are listed in Table 1. Flamestab NOR 116 (F1), an oligomeric N-alkoxy hindered amine which acts as a flame retardant and flame retardant synergist in polyolefin applications was supplied by Ciba Specialty Chemicals. The amount and the type of the different nanofillers were indicated in Table 2.

Table 1. Characteristics of nanoparticles used

Type of nanoparticles	Commercial name	Modifier structure	Code
Montmorillonite	CLOISITE 20°		Cl20A
Montmorillonite	CLOISITE 30B		Cl30B

HT = hydrogenated linear alkyl chains: $C_{8\sim18}$

Results and Discussion:

The morphology of the samples was determined using wide-angle X-ray scattering (XRD), scanning electron microscopy (SEM) and, in the case of nanocomposites, transmission electron microscopy (TEM). As a result of PLA melt blending with 2.5 and 5.0 wt% of (organo-modified) montmorillonite intercalated nanocomposites were prepared by using Cl20A or Cl30B.

PLA based nanocomposites were further analysed by means of TEM. The incorporation of Cl20A in the PLA matrix shows certain level of intercalation as well as the occurrence of exfoliated silicate layers. When correlating these observations with XRD results, we can conclude that the Cl20A forms partially exfoliated nanocomposites. Cl30B based nanocomposites show a certain level of intercalation but the number of silicate layers for stack are lower respect to Cl20A and a higher number of small stacks of swollen clay layers and single dispersed layers can be observed in the TEM micrograph. Thus from XRD and TEM results, it is clear that the dispersion and interaction of the Cl30B in PLA is better than that obtained with Cl20A. This can be attributed to the stronger interactions between the polymers and Cl30B, originated from the hydrogen bonding between the carbonyl group of PLA and hydroxyl groups.

Table 2. Composition of the different samples

Samples Name	PLA %wt	Cloisite %wt(Type)	Fl %wt
PLA	100.0	-	-
PLA1Fl	99.0	-	1.0
PLA25Cl20A	97.5	2.5 (Cl20A)	-
PLA50Cl20A	95.0	5.0 (Cl20A)	-
PLA25Cl30B	97.5	2.5 (Cl30B)	-
PLA50Cl30B	95.0	5.0 (Cl30B)	-
PLA50Cl30B1Fl	94.0	5.0 (Cl30B)	1.0

The cone calorimeter is being used extensively for flammability testing nowadays as the test supplies useful data for interpreting the combustion behaviour of materials in real fires. Under 35kW/m^2 heat flux in the cone calorimeter it is found that the two organoclays used have very different effect on fire behaviour of PLA e.g. in terms of peak of HRRs and of average HRRs at 3min.

The HRR plots obtained from the Cl30B nanocomposites are typical of thermally thick charring materials: an initial increase is seen of the HRR which goes through a maximum due to the formation of a surface char layer which protects the underlying material from the flame. The PHRR value of PLA5Cl30B is reduced by 29%, as compared to pristine PLA while the avg HRR decreases by 23%. Addition of the fire retardant Fl to the PLA nanocomposite did not lead to further reduction of avg HRR or of PHRR. The results obtained by CL20A show a less effective behaviour of this nanoparticles in agreement with the data obtained by morphology analyses. PLA25Cl20A is quite similar to pristine PLA while there is an behaviour similar to nanocomposites containing Cl30B for PLA50Cl20A.

For a more detailed evaluation of fire behaviour limiting oxygen index test were performed. In order to better characterize the fire behaviour not only the limiting oxygen index number (LOI) is reported but also the burning time as a function of oxygen concentration (OC) were studied. The plots of PLA and PLA1Fl can be separated into two successive regions, in the first the burning time is directly proportional to oxygen concentration, in the second the flame is stable and arrives to the end of the specimen. In this case PLA1Fl shows an higher LOI demonstrating an effect of the fire retardant.

PLA nanocomposites show a behaviour different from pristine PLA, practically once ignited it usually tends to burn completely and the LOI depends mainly by the OC at which the nanocomposites ignites. From previous studies[1] it was suggested that in nanocomposites ignition could be controlled by nanoparticle-catalyzed oxidation of the gases generated at the surface of the condensed phase by volatilization of the polymer and thus conditions for ignition are created as soon as the polymer decomposition temperature is reached. In contrast for pristine polymer enough volatiles from bulk polymer pyrolysis have to be produced to mix with air above the specimen to reach the lower flammability limit.

1 A. Fina, G. Camino Polym. Adv. Technol. 2011, 22, 1