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Fire retardancy behavior of PLA based nanocomposites

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ABSTRACT

To understand and improve the fire retardancy behavior of polylactic acid, we have incorporated two structurally different additives, sepiolite and organically modified montmorillonite. A novel approach (combination of electrospinning and extrusion/injection molding) is employed to address critical issues like char enhancement as well as the homogeneity/uniformity of the inorganic barrier during combustion of polymer nanocomposites. Fundamental knowledge is gained on the mechanisms of fire retardancy, particularly with samples of different thicknesses (thermally thin *versus* thermally intermediate/thick). Volumetric imaging of the residues provided a deeper understanding of the formation or the evolution of the inorganic barrier. Considerable insight on the dependency of biodegradation on the environment (primarily) and on the compromising effect of high aspect ratio nanoparticles is also obtained. This knowledge has a broader scientific impact and is critical to design the new generation of eco-benign flame retardant and biodegradable polymer nanocomposites.

1. Introduction

'Fire' is an important topic, not just from a scientific viewpoint, but also from a day-to-day living perspective. As polymers form the core of the modern world, understanding this science to fine-tune the materials for achieving highest fire safety standards is extremely important. But considering eco-friendliness [1–4], ultimate mechanical/physical properties, and processing difficulties, unsatisfactory fire performance of polymers and their composites is a major obstacle [5]. The incorporation of nanoscale fillers (like clays, nanotubes, POSS, etc) in polymers, though, showed a positive potential toward flame retardancy (reductions in heat release/mass loss rates and delayed burning), they are unable to meet the existing fire standard requirements [6–11]. This has led to the continued usage of conventional agents (halogen/phosphorous based compounds or metal hydroxides).

Besides, to accommodate the insufficient infrastructure and envelop the production-disposal rates of various kinds of *mixed* polymer waste, recently, emphasis is on biodegradability of polymers. This issue is important for applications like packaging and electronics whose life span is very short [12–14]. But the relatively poor performance/functionality of the current commercially available biodegradable polymers is a major concern. For e.g., polylactic acid (PLA), a widely used biodegradable polymer suffers from low thermal deformation tolerance and inferior mechanical performance. Apart from this, its biodegradability is dependent on several external factors (temperature, environment, pH, etc.) and often, its degradation rate is slow compared to the rate of (waste) accumulation.

Here we focus on one of the important facets of PLA, fire response *via* cone calorimeter, in the presence of two structurally different additives, sepiolite and organically modified montmorillonite. In the process, novel methodology will be utilized to address issues at various sensitive stages of the combustion process related to homogeneity/uniformity of the barrier and char enhancement. These are a couple of issues that have been identified in our previous investigations on the combustion behavior of polymer nanocomposites as critical along with thermal stability of the materials, migration of nanoparticles to the burning surface, etc [5,7,15,16]. It is also important to note that cone calorimeter, though is considered as a bench-scale testing methodology to assess and obtain insights on a developing fire behavior of a material, it has its limitations. In particular, the one dimensional burning (the flame

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front penetrates only the depth of the sample) and the influence of thickness of the sample. Despite the fact that for most of the applications like electronics (circuit boards) and coatings, generally, 'thermally thin' samples are required, there are very few examples in the literature dealing with thermally thin polymer nanocomposites. So, an additional objective of the study is to understand the effect of sample thickness on cone calorimetry data by considering thermally thin (1 mm) and intermediate thick (3 mm) samples and at various incident heat fluxes.

2. Experimental work

2.1. Raw materials

Transparent PLA (trade name: 'PLA Polymer 2002D') was purchased in the form of pellets from NatureWorks LLC, UK with a melt index of 5–7 g/10 min (at 210 °C/2.16 kg). This grade is derived from annually renewable resources and has a D-content of 4% (96% L-lactide content). Montmorillonite (MMT) used in this work is organically modified (OMMT) and supplied by Southern Clay Products Inc., USA with a trade name of Cloisite® 30B. It has a cation exchange capacity of 90 mequiv/100 g. The organic modifier is an alkyl ammonium surfactant, methyl, tallow, bis-2-hydroxyethyl quaternary ammonium chloride. The loss on ignition of the OMMT was about 30 wt%. Refined, unmodified sepiolite was kindly provided by Tolsa S.A, Spain. Polyvinyl alcohol (PVA, trade name Mowiol® 56-98) and zinc borate (ZB) were purchased from Sigma–Aldrich, Spain. PVA is a fully hydrolyzed grade with an average molecular weight of ~195,000 g/mol and melting point ~220 °C; while hydrated ZB ($2ZnO.\ 3B_2O_3.\ 3.5H_2O$) has ~45% of ZnO content and ~36% B_2O_3.

2.2. Processing of nanocomposites

PLA pellets and the desired proportions of the additives (~1.5–2 kg) were dry-mixed and oven-dried at 60 °C, overnight. Then, they were melt-compounded in a Leistritz twin-screw extruder within the temperature range of 175–190 °C and a screw speed of 300 rpm. Subsequently, a portion of the extruded pellets were oven-dried and molded into 100 × 100 × 1 mm^3 square plates using a Nestal 100 tons injection molding machine with the barrel and mold temperatures maintained at 200 °C and 60 °C, respectively. Remaining pellets were compression molded into 100 × 100 × 3 mm^3 plates using a hot-plate press (LabPro 400) at 190 °C with a pressure of 4 MPa for 10 min. The compositions and designations of the samples are listed in Table 1.

2.3. X-ray diffraction

A Philips X'Pert-MPD (EQ 31-02) X-ray diffractometer with CuKα radiation ($\lambda = 1.54$ Å) at a generator voltage of 45 kV and a current of 40 mA was used to study the diffraction behavior of clay(s), as processed P0 to P3 samples and the surfaces of the residues of all samples after burning in order to analyze their structural changes. All the experiments were conducted in the reflection mode at ambient temperature with 2θ varying between 2° and 30°. The scanning rate was 0.040°/min.

2.4. Morphology observations

To investigate the morphology and dispersion of fillers in the materials, firstly, a 2 × 1 cm^2 rectangular block was cut from the cross-section of the core of injection molded plates perpendicular to the mold filling direction. This was carefully trimmed down on one of the faces, to an appropriate size of about 0.5 × 0.5 mm^2 for cryomicrotoming. Ultra-thin sections of ~70–90 nm in thickness were cryogenically sliced off at 0.2 mm/s from the trimmed surface with a diamond knife in liquid N_2 environment at −80 °C using a Leica EM UC6 microtome. They were picked up using a droplet of 2.3 mol sucrose and placed on formvar/carbon coated 400-mesh copper grids. After thorough rinsing with distilled water for at least 0.5 h to wash away the sucrose, the collected sections were subsequently observed using a JEOL JEM-1010 transmission electron microscope (TEM) at an accelerating voltage of 100 kV, which is capable of obtaining digital images.

Table 1
Compositions and designations of the processed materials.

Material	PLA	Sepiolite	OMMT	ZB	PVA
P0	100	–	–	–	–
P1	95	5	–	–	–
P2	95	–	5	–	–
P3	90	5	5	–	–
P4[a]	85	5	5	4	1

[a] The processing of P4 is different to others. Here, instead of adding PVA along with other additives during the dry-mixing step, a novel approach was used. PVA was electrospun onto PLA pellets uniformly and subsequently, the coated pellets were used to prepare the nanocomposite, following the same procedure as the rest of the samples. The basic idea is to disperse PVA in the matrix at a submicron to nanoscale. A NANON-01A electrospinning unit (Mechanics Electronic Computer Corporation, MECC Co. Ltd. Japan) was used for the purpose. 5% PVA solution is prepared by dissolving the desired amount of PVA in deionized water while heating at 90 °C with continuous magnetic stirring for 24 h. The clear solution was then cooled to room temperature, which was subsequently used for electrospinning using the following parameters: voltage ~21 kV; feed rate ~1.5 ml/h; and the distance between the tip of the needle and collector ~15 cm. The diameters of the fibers are in the range of 200–300 nm.

2.5. Nanoindentation

To analyze the mechanical properties like elastic modulus and hardness, nanoindentation was carried on the injection molded samples using a depth sensing MTS Nanoindenter XP after drying them in an oven at 60 °C overnight. Experiments were performed using a Berkovich three-sided pyramidal diamond indenter with a nominal angle (defined by the tip axis and faces) of 65.3° and at a load of 20 mN. A minimum number of five tests were carried out for each condition and all the tests were performed at ambient condition (22 ± 1 °C). Additionally, a holding period of 10 s is maintained at the peak load to allow for dissipation of creep displacement and not affect the unloading curves. The unloading data is fitted to a power law function, as proposed by Oliver and Pharr [17], to determine the hardness and modulus.

2.6. Biodegradability tests

Samples of dimension 10 × 10 × 1 mm^3 were cut from the injection molded plates for the biodegradability tests. Before subjecting to the test conditions, all samples were washed in ethanol, later in distilled water and subsequently, dried in an oven at 60 °C overnight. To study the biodegradability of the materials at room temperature and at 60 °C: two types of composts (sludges S1 and S2) and distilled water (hydrolysis test) were used as mediums. Both sludges are the waste of paper industry and kindly supplied by Holmen Paper Madrid, S.L. They contain about 29–33% of organic content, minor quantities of potassium, zinc, cadmium, copper, chromium, nickel, lead and carbonates. The C/N ratio was 34.9 and 67.7 for S1 and S2, respectively. Notable points are the similar relative humidity (30–40%) and variations in basicity (7.2 for S1 and 7.6 for S2). For each testing condition, 5-6 samples of each material were used; they were buried completely in the sludges (in sealed bottles) or in distilled water and at the defined times (for