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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.

Keywords: fire retardancy; biodegradability; PLA; clay; polymer nanocomposites.

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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 towards 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 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/10min (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 (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 ~218°C; while hydrated ZB (2ZnO. 3B₂O₃. 3.5H₂O) has ~45% of ZnO content and ~36% B₂O₃.

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 mm x 100 mm x 1 mm 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 mm x 100 mm x 3 mm 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 CuK α radiation (λ = 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 speed was 0.040°/min.

2.4. Morphology observations: To investigate the morphology and dispersion of fillers in the

materials, firstly, a 2 cm x 1cm long 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 mm by 0.5 mm 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 N₂ 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.

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 (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 x 10 x 1 mm³ 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 room temperature tests - 2 weeks, 4 weeks, 8 weeks and 15 weeks; for 60°C tests – 6.5 weeks), samples of each material were removed, washed with water and dried at room temperature for 24 h. For each test, based on the sample mass before and after degradation, the average percentage of mass loss was calculated. Also, for selected conditions, weight-

average (Mw) molecular weights of PLA nanocomposites were determined by means of gel permeation chromatography (GPC; Waters GPCV2000), using 1,2,4 trichlorobenzene as the carrier solvent with a flow rate of 1.0 ml/min. To reduce the complications and have a better understanding of the effect of nanoparticles, biodegradability analysis was only carried on P0 to P3 samples.

2.7. Thermal/fire tests and characterization of residues: Thermogravimetric analysis (TGA) was conducted to determine the changes in weight with temperature on a TA Instruments TGA Q50 from room temperature ($\sim 25^{\circ}\text{C}$) to 700°C at a rate of $20^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. The combustion experiments were performed in a dual cone calorimeter (from Fire Testing Technology, UK) on injection and compression molded plates at different incident heat fluxes ranging from 25 to $50 \text{ kW}/\text{m}^2$. The samples were oven-dried overnight at 60°C prior to testing. The instrument was capable of recording ignition times, heat release and mass loss rates, specific extinction area (SEA), CO and CO_2 yields. All sides of the samples were wrapped in aluminum foil except for the upper face, which was exposed to the heat flux. Oxygen index tests were also carried out using a Fire Testing Technology, UK instrument on bars of $100 \times 6.5 \times 3 \text{ mm}^3$. The paramagnetic oxygen analyzer has an accuracy of $\pm 0.1\%$ oxygen. Digital photographs of the leftover residues were taken immediately after the test. Non-destructive analysis of the residues was also carried out using X-ray tomography (Phoenix Nanotom) at a voltage of 80 kV. Simply put, the process involves the acquisition of radiographs or a set of projections all around the sample, which will be reconstructed to obtain a 3D view of the whole volume. A total of 1800 images were collected here for reconstruction.

3. Results and discussion

3.1. Structure and morphology: In the x-ray patterns of P0 and selected nanocomposites, P1 to P3 shown in Fig. 1, a broad peak from $2\theta \sim 10^{\circ}$ to 23° with a maximum at $2\theta \sim 16^{\circ}$ is evident pointing to the predominant amorphous nature of the PLA matrix. In P1, only the characteristic peak of sepiolite at $2\theta \sim 7.42^{\circ}$ (110) is revealed due to its non-swelling nature. But in P2, two close peaks at $2\theta \sim 3.5^{\circ}$ and 5.1° corresponding to interlayer distances of $\sim 2.52 \text{ nm}$ and 1.73 nm , respectively, indicate the presence of OMMT layers with predominately two different extents of intercalation; and an obvious (further) enlargement of the interlayer distance(s) of OMMT¹ due to the diffusion of polymer chains during melt compounding. TEM micrographs of the binary nanocomposites shown in Fig. 2a and 2b reveal that

¹ OMMT powder showed a diffraction peak at $2\theta \sim 5.2^{\circ}$ corresponding to a basal spacing of 1.7 nm , much higher than 1.1 nm of the pristine sodium clay.

sepiolite needles and organoclay layers are distributed homogeneously and the degree of defibrillation (for sepiolite) / and intercalation (for OMMT) is high resulting in many individual particles. The average size of sepiolite needles ranged from 9 to 20 nm (up to 30 nm in some cases). It is important to note that shear stress alone could not achieve defibrillation/exfoliation when the matrix polymer does not have good compatibility with clay(s) [18]. For example, Bilotti *et al.* [19] reported that even when 2.5 wt% of sepiolite is added to polypropylene *via* a two-step blending process, dispersion was poor with micrometer-size clusters of sepiolite. In the present case, strong interaction of PLA matrix is possible with unmodified sepiolite and modified MMT, which originates from the hydrogen bonding between C=O groups of the polymer and hydroxyl groups of sepiolite/Cloisite-30B organic modifier. This compatibility leads to good dispersion of clay(s) in the PLA matrix.

In the ternary hybrid, P3, there is only one distinct peak of OMMT at $2\theta \sim 5.9^\circ$ (beyond the characteristic 5.2° of OMMT used in the study) corresponding to a d-spacing of ~ 1.49 nm (Fig. 1). This collapse clearly indicates the degradation of some of the surfactant during processing in the additional presence of sepiolite. Generally, at higher inorganic filler loadings, greater shear forces are generated in the extruder (which contributes to friction among the particles), ultimately resulting in the degradation of the low molecular weight long chain alkyl ammonium surfactant. Following the XRD pattern, TEM micrograph of P3 shows that the degree of exfoliation of OMMT layers is relatively poor compared to P2 and most of them are intercalated stacks; however, the distribution of these intercalates is good (Fig. 2c). Similarly, the presence of OMMT affected the defibrillation of sepiolite. Individual needles are rarely seen and most of them are present as bundles/clusters ranging from 32 to 60 nm in width. The differences in geometry of sepiolite (fibrillar) and OMMT (platelet) make it easier for their identification in the TEM micrograph of ternary hybrid (Fig. 2c). Besides, owing to their aspect ratio, during injection-molding, only the translation motion of OMMT platelets is possible and rotational motion is generally negligible. This generally results in a clear evidence of layers (and not as planar discs) or stacked layers in TEM micrographs (that are taken from sections microtomed normal to the flow direction). Sepiolite, on the contrary, is also easily identified based on its size (thickness).

In P4, where 1 wt% of PVA was electrospun onto PLA pellets before compounding, PVA particles are uniformly dispersed in PLA matrix and the image (Fig. 2d) looks as if it was a polymer blend (with at least 10-20% of one of the components) reinforced with clay(s). PVA has a melting point ~ 220 - 230°C , which is beyond the processing temperature of PLA nanocomposites and therefore retained the fiber/elongated particle shape. But due to the higher shear forces, the fibers broke apart yielding mostly elongated particles. PVA can be easily identified in the micrograph based on the fibrous structure and

due to the electron density contrast with PLA and inorganic particles. However, the dispersion quality of OMMT and sepiolite is relatively poor with frequent stacks/clusters. ZB is a microscale particle and therefore, not visible in this field-of-view. Although the distribution quality of PVA clearly suggests the success of the adopted electrospinning approach; but on the negative side, affects the dispersion quality of clay(s).

Hardness and modulus values of all samples are shown in Table 2, which clearly indicate the importance of nanoscale dispersion (evident from P1 vs P2), loading (P1, P2 vs P3), and the presence of well-dispersed soft additive even at a low loading (P3 vs P4). We have also conducted crystallization studies of these materials, which confirmed the amorphous nature of PLA matrix. Also, as glass transition T_g and melting point T_m temperatures of all materials remained relatively constant (at $\sim 63.3^\circ\text{C}$ and 149°C , respectively) within the experimental error of $\pm 1-2^\circ$, the curves are not shown here.

3.2. Compromising effect of modification/aspect ratio of nanoparticles on biodegradability and thermal stability:

It is well-known that (compost) degradation of bio-based polyesters like PLA occurs *via* a two-stage process including a critical step of hydrolytic degradation of ester bonds into lower molecular weight polymers and oligomers followed by biological degradation by microorganisms (like proteinase K and *Amycolatopsis* sp.) to carbon dioxide, water and humus [20, 21]. Ray *et al.* [22] have pointed to the importance of terminal hydroxylated edge groups of the silicate layers towards the biodegradation process of PLA, particularly during the first step. That is, they allow an easier permeability of moisture into the material enhancing the heterogeneous hydrolysis of the matrix. In the present study, despite the presence of large numbers of hydroxyl groups on sepiolite and organoclay, when the tests were carried out at room temperature ($\sim 23^\circ\text{C}$), irrespective of the environment (sludge or water) and time periods (2, 4, 8 and 15 weeks), the %mass losses (normalized) for P0 to P3 are very low and within the experimental error (the highest being 0.76%). Nonetheless, GPC analysis revealed some evidence of degradation, in the form of lower weight average molecular weight (Mw), particularly in the case of sludge S2 and for P0 and P1 (after 15 weeks of exposure, Fig. 3a). Apart from the importance of basicity in biodegradation (the pH of the three environments investigated, water, S1 and S2 were 7.0, 7.2 and 7.6, respectively), these results clarify the dual effect of high aspect ratio nanoparticles; that is, the barrier effect of silicates can significantly increase the time to initiate the first step of the biodegradation process. When the biodegradability experiments were conducted at 60°C (which is in fact the glass transition temperature of PLA), all samples exhibited a considerable surface deformation and whitening, clear signs of the hydrolytic degradation process that changes the refraction index of the sample, after only 45 days (6.5 weeks) of degradation. Irrespective of the presence or absence of clay

particles, degradation occurred and resulted in considerable mass losses (30-40% in water and S1 whereas 90-100% in S2 (Fig. 3b). But the molecular weights reduced by almost 96% in all cases (P0 to P3 and in water, S1 or S2) compared to their respective original samples. These results clearly point to the primary importance of mobility of matrix chains (further influenced by pH) in the biodegradation process of PLA than the presence of hydroxyl groups and the aspect ratio of nanoparticles. But when the chains are not mobile and under slightly neutral pH values, even the presence of large numbers of hydroxyl groups can be compromised due to the barrier effect of nanoparticles.

Analogous to biodegradation results, thermal stability of PLA/clay nanocomposites is also a compromise between the barrier effect of nanoparticles and their modification process. This is also directly evident by comparing the TGA results of OMMT and unmodified sepiolite powders. By 400°C where a complete decomposition of neat PLA is generally expected, OMMT loses ~19% of its weight compared to 4% with sepiolite pointing to the advantage of the latter. Fig. 4 shows the TGA curves of neat PLA and its nanocomposites in nitrogen. In the binary nanocomposites, the thermal stability of the PLA matrix is improved by the presence of sepiolite (see Table 2 for the onset (5% weight loss) and maximum (50% weight loss) decomposition temperatures of all samples). Defibrillated and unmodified sepiolite leads to a barrier effect towards polymer decomposition products, thus increasing both onset and maximum weight loss temperatures. The barrier effect is supposedly strong with MMT layers due to higher aspect ratios. This positive effect obviously is compromised by the presence of low molecular weight organic surfactants in P2. A combination of processes that happened in P1 and P2 are reflected in P3. The amounts of the final residues were proportional to the clay contents of the samples. In the hybrid material containing PVA (decomposing (first step) between 300-400°C) and ZB (lost up to 9% weight by 400°C), the thermal stability is severely affected. Considering the loadings of these fillers, the observed decreases cannot be directly attributed to their presence; but indirectly, to the drastically reduced molecular weight of the material. As indicated by GPC, weight average molecular weight of PLA in this material reduced close to 40% after processing due to the alkaline nature of PVA.

3.3. Combustion behavior:

3.3.1. Ignition and HRR/MLR curves: For thermally thin samples (1 mm thickness), HRR curves for all samples are shown in Fig. 5a and 5b at irradiance fluxes of 25 and 35 kW/m², respectively. The curves of the nanocomposites (particularly with OMMT) shift towards the left of the neat PLA curve indicating that these materials start to burn early. Table 3, where the times-to-ignition (T_{ig}) are listed for all samples also confirms the expected reductions in T_{ig} at higher heat flux of 35 kW/m² compared to 25

kW/m^2 for corresponding materials. In a recent study [23], it was concluded that for the process of ignition, several millimeters of sample thickness contribution to fuel production is required, and is not a surface-dependent-only process. Specifically, the rapid T_{ig} with nanocomposites was attributed to the (a) nanoparticle-catalyzed oxidation of the gases generated at the surface of the condensed phase by volatilization of the polymer and (b) reduced thickness of the material contributing to fuel production. Besides, after the thermal decomposition of organic surfactants through the Hoffman degradation reaction, the acidic clay site formed on the layered clay surface will have a direct interface with the remaining polymer. Layered silicates in acid form are generally known to cause hydrocarbon cracking, which will further degrade the polymer. Therefore, a combination of different parameters can be attributed to the early T_{ig} of nanocomposites, particularly for layered silicates.

Before discussing further, it is important to note that in most of the non-charring polymer-based nanocomposites irrespective of the radical trapping effect and catalytic activity of clay layers (unless the nanoparticles are specifically functionalized to promote dehydrogenation or oxidative dehydrogenation catalysis), structural collapse during combustion and formation of a multilayered carbonaceous-silicate barrier at the polymer surface is the major mechanism of fire retardancy in terms of reductions in HRRs/MLRs. Also, in the present work, considering the same loadings of fillers in thin and thick samples, barrier formation will be a determining mechanism. With thermally thin samples, peak HRR values are slightly higher for nanocomposites compared to neat polymer. In thermally thin samples, due to the limited volume, the whole sample is pyrolyzed at the same time and there cannot be any dependency on the conductivity of the material to control the heat transport into the material (and therefore no or little viscosity gradients as well). Similar to the results presented here, Kashiwagi *et al.* [24] noted that the fire retardancy mechanism of layered silicates completely disappears in thermally thin polyamide 6 and polypropylene samples and no noticeable reductions occur in peak HRR as well as decreasing the time to ignition.

For 3 mm thick samples, the HRR curves are as expected for nanocomposites with layered silicates; that is, considerable reduction in peak HRR and a delayed burning in P2 and P3 (see the curves at a selected and representative irradiance flux of 35 kW/m^2 , Fig. 5c). Mass loss rate curves follow the same pattern as HRR curves and therefore are not shown. These results point to crucial mechanistic changes during combustion of thermally thin and intermediate thick PLA nanocomposites. For thermally thick samples, the surface temperature is dictated by the thermal gradient within the sample and so the thermal conductivity and viscosity gradients are important. This in turn indicates that the fire performance (or HRRs) of thermally thin and thick materials can be related to the competition between the formation of a

surface carbonaceous-silicate shield and the volatilization to fuel (polymer). Obviously in thicker materials, the competition seems to favor barrier formation, while for the other case, volatilization dominates. These statements can be further validated by comparing the HRR data of 3 mm samples at two different heat fluxes. For this purpose, only representative HRR curves of neat PLA and P3 are shown at incident heat fluxes of 35 and 50 kW/m² (Fig. 5d). Dramatic %reductions in HRR are noticed for nanocomposite compared to neat material. Compared to the 25% reduction in peak HRR at 35 kW/m², almost 60% reductions are achieved at 50 kW/m².

The above observations and discussions are also in line with flame-out times; that is, the limited volumes in thermally thin samples compared to intermediate or thick samples combined with promotion of catalytic oxidation and hydrocarbon cracking with nanoparticles contribute to the extremely low flame-out times. For instance, at an incident heat flux of 25 kW/m², the flame-out time for neat PLA is 300 s; while it is in the range of 150-185 s for P2 to P4. This dramatic drop in flame-out periods is also reflected in the total heat released (an important parameter signifying the fire size and its potential hazard). That is, despite slightly higher peak HRR values of nanocomposites, the total heat released is lower than neat polymer (see Table 3). Additionally, similar to TGA results, the fire performance of P4 is not satisfactory compared to P1 to P3 despite a good dispersion of char enhancing agent and the presence of sepiolite and MMT.

3.3.2. Performance of P3 versus other samples: The performance of P3 is the best and points to a possible synergism of polymer/montmorillonite nanocomposite in the additional presence of sepiolite. However, as shown above, the fire response of P1 (with just 5 wt% sepiolite) is poor compared to neat PLA. Indeed, at all investigated irradiance fluxes and thicknesses, though the residue of P1 looked uniform due to homogeneous dispersion of sepiolite, it was only a thin layer of coating that was left behind. Marosfoi *et al.* [25] revealed similar observations with sepiolite in polypropylene matrix; that is, the %reductions in HRR with just sepiolite (irrespective of the modification) alone are not highly promising. Hapuarachchi and Peijs [26] also found that 5 wt% of sepiolite has a similar effect on heat release capacities (measured using pyrolysis combustion flow calorimeter) compared to 2 wt% of multi-walled carbon nanotubes in PLA. This poor fire performance of sepiolite was explained by considering their inter-channel networks that could hold accumulated heat and use it as a heat source to accelerate the decomposition process in conjunction with the heat flow supplied by the outside heat source.

The residues of samples with layered silicates were relatively thick and rigid despite the presence of cracks clearly underlining the importance of layered ‘nanoscale’ fillers. Representative images of the

residue of P2 to P4 are shown in Fig. 6 (incident flux: 35 kW/m^2 and 3 mm sample). In P4, as evident, PVA/ZB changed the structure of the char and enhanced the char formation to some extent. Nevertheless, among all samples, P3 has the most uniform, continuous, homogeneous, and physically strong char; only a few minor cracks are observed at this scale (in P2 cracks are deep). This suggests a possible synergism and less prevalence of the above-mentioned mechanism of accumulation of heat in sepiolite inter-channel networks. Even during the burning process, intumescent type of behavior was observed (swelling of the char occurred up to 12 mm above the surface of the sample). This is understandable by following the structural collapse of sepiolite particles with temperature and is one of the reasons why sepiolite was used as an FR in combination with organoclay. During combustion, all three types of water molecules (zeolitic, bound and structural) are released from sepiolite making it an intumescent FR (though the magnitude of swelling is limited) as it may influence the char structure owing to its bubble-nucleating effect. So, theoretically, higher migration rates of montmorillonite layers to the burning surface are expected (at least in the case of thermally thick samples). Additionally, upon the removal of sorbed water molecules from sepiolite, folding/collapse of its channels occur (at about 550°C) and might hold the neighboring silicate layers or the network structure. This concept has been used in the past to functionalize/embed Ag or Cu or TiO_2 nanoparticles on the sepiolite surface [27].

To get more physical insights into the combustion processes, volume imaging approach was adopted to visualize the 3D structure of the residue leftover after burning. Selected tomograms of P3 (incident flux of 35 kW/m^2 and thicknesses 1 and 3 mm) are shown in Fig. 7. The preferential organization of clay particles, particularly montmorillonite platelets around the trapped bubbles (voids) clearly follows the Gibbs adsorption isotherm. That is, any differential in the surface energy of a multi-component system could result in a relative enrichment at the air interface of the lower-surface-energy material [28, 29]. This also points to the mechanism of how the rising bubbles take the clay layers along with them and help in the formation of an insulating barrier at the burning surface.

From Fig. 7a (thermally thin samples), it is evident that as the entire volume of the material is pyrolyzed at the same time, there is little time available for the migration of clay layers. In the absence of strict temperature or concentration gradients, and as the structural collapse and formation of numerous bubbles occur simultaneously, this results in the arresting of the bubbles (Fig. 7b) and random compaction of the char at different places. Some of these zones are pointed with arrows in Fig. 7a. In the case of 3 mm thick samples, as expected from our previous TEM investigations [5, 7], full migration of clay platelets to the top burning surface is a problem. However, the structural collapse and the formation of uniform but intermittent (and thick) inorganic barriers at different thicknesses of the sample are evident (Fig. 7c

and 7d). It is also important to note the resolution of the tomography system adopted here for the investigated volume of materials, which is $\sim 2.4 \mu\text{m}$. Despite this, the clear evidence of collapsed structures points to the thickness of these intermittent layers. On the contrary, for sepiolite particles, considering their size, no distinctive migration to the burning surface or regrouping is seen in the tomogram (Fig. 7e). This is a clear confirmation of why the performance of P1 is poor compared to P2; and why the char, and ultimately the performance, of P3 is better than P2 (due to the mechanical reinforcement of the char).

3.3.3. XRD analysis: Wide-angle XRD analysis was also carried out on the collected residues to understand the clay particle and carbonaceous structures therein. As expected and in line with the previous studies, with layered silicates, a peak appeared at $2\theta \sim 7.05^\circ$ (d-spacing 1.3 nm) suggesting the collapse of delaminated nanostructures of layered silicates present prior to burning. Considering the completely dehydrated individual clay layer thickness as 0.7 nm, then the rest 0.6 nm can be attributed to the carbonaceous matter intercalated into silicate layers. Obviously, the intensity of this peak decreased in the additional presence of sepiolite, where the characteristic peak of sepiolite at $2\theta \sim 7.42^\circ$ dominated. Apart from these, no other distinctive features are noted in the curves and so, the XRD curves are not shown.

On a closing note, the importance of understanding the fire performance with cone calorimeter can be illustrated by looking at the limiting oxygen index values (Table 3). Though the LOI value of neat PLA is 20%, it even melts and flows down very easily on exposure to flame even at 18%. Similar behavior (but slightly improved) is observed for P1. But in P2 and P3, despite their slightly higher and similar LOI values, there is no such dripping behavior pointing to the increased viscosity of the material due to the presence of layered silicates. This clearly suggests that LOI numbers does not indicate the real performance of the material. Nonetheless, in LOI, the sample is burned in the least challenging configuration (candle-like) and so, even a material with higher LOI number than 22 may burn in ambient if ignited at the bottom edge.

4. Conclusions

- The fine dispersion of OMMT and sepiolite in binary nanocomposites was significantly affected by the additional incorporation of PVA and ZB. But uniform dispersion of PVA particles in the matrix was achieved when electrospinning approach was adopted.

- Biodegradability results pointed to the importance of environment (primarily) and on the compromising effect of high aspect ratio nanoparticles and alkaline particles.
- Thickness of samples was deduced as a critical parameter while evaluating the fire response of a material (specifically, nanocomposites) *via* cone calorimetry. Crucial mechanistic changes were attributed for this phenomenon. In thermally thin samples, the whole sample is pyrolyzed at the same time without any considerable temperature/viscosity gradients; while in thicker samples, the surface temperature is dictated by the thermal gradient within the sample.
- The drastic reduction in molecular weight of hybrid material had a negative influence on its thermal stability and fire performance.
- Tomograms of the residues of thermally thin and thick ternary nanocomposite further provided an insight on the preferential organization of clay particles.

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6. References

- [1] Zaikov GE, Lomakin SM. Ecological issue of polymer flame retardancy. *J Appl Polym Sci* 2002;86:2449-62.
- [2] Hale RC, La Guardia MJ, Harvey E, Matt Mainor T. Potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere* 2002;46:729-35.
- [3] Mizukawa K, Takada H, Takeuchi I, Ikemoto T, Omori K, Tsuchiya K. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. *Mar Pollut Bull* 2009;58:1217-24.
- [4] Bertazzi PA, Consonni D, Bachetti S, Rubagotti M, Baccarelli A, Zocchetti C, et al. Health effects of dioxin exposure: A 20-year mortality study. *Am J Epidemiol* 2001;153:1031-44.
- [5] Dasari A, Cai GP, Yu ZZ, Mai Y-W. Flame retardancy of polymer-clay nanocomposites. In: Tjong SC, Mai Y-W, editors. *Physical properties of polymer nanocomposites*. Cambridge: Woodhead Publishing Ltd.; 2010. p. 347.
- [6] Bourbigot S, Duquesne S, Jama C. Polymer nanocomposites: How to reach low flammability? *Macromol Symp* 2006;233:180-90.
- [7] Dasari A, Yu ZZ, Mai YW, Cai G, Song H. Roles of graphite oxide, clay and POSS during the combustion of polyamide 6. *Polymer*. 2009;50:1577-87.
- [8] Kashiwagi T. Flame retardant mechanism of polyamide 6–clay nanocomposites. *Polymer*. 2004;45:881-91.
- [9] Kiliaris P, Papaspyrides CD. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Prog Polym Sci* 2010;35:902-58.

- [10] Laoutid F, Bonnaud L, Alexandre M, Lopezcuesta J, Dubois P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater Sci Engng: R* 2009;63:100-25.
- [11] Schartel B, Potschke P, Knoll U, Abdelgoad M. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. *Europ Polym J* 2005;41:1061-70.
- [12] Gregory MR. Environmental implications of plastic debris in marine settings- entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Phil Trans R Soc B* 2009;364:2013-25.
- [13] Gross RA, Kalra B. Biodegradable polymers for the environment. *Science*. 2002;297:803-7.
- [14] Thompson RC, Moore CJ, Saal FSV, Swan SH. Plastics, the environment and human health: Current consensus and future trends. *Phil Trans R Soc B* 2009;364:2153-66.
- [15] Cai G, Dasari A, Yu Z-Z, Du X, Dai S, Mai Y-W, et al. Fire response of polyamide 6 with layered and fibrillar nanofillers. *Polym Degrad Stab* 2010;95:845-51.
- [16] Dasari A, Yu ZZ, Mai YW, Liu S. Flame retardancy of highly filled polyamide 6/clay nanocomposites. *Nanotechnology*. 2007;18.
- [17] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J Mater Res* 1992;7:1564-83.
- [18] Fornes TD, Yoon PJ, Hunter DL, Keskkula H, Paul DR. Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. *Polymer*. 2002;43:5915-33.
- [19] Bilotti E, Fischer HR, Peijs T. Polymer nanocomposites based on needle-like sepiolite clays: Effect of functionalized polymers on the dispersion of nanofiller, crystallinity, and mechanical properties. *J Appl Polym Sci* 2008;107:1116-23.
- [20] Ray SS, Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Prog Mater Sci* 2005;50:962-1079.
- [21] Fukushima K, Abbate C, Tabuani D, Gennari M, Camino G. Biodegradation of poly(lactic acid) and its nanocomposites. *Polym Degrad Stab* 2009;94:1646-55.
- [22] Ray SS, Yamada K, Okamoto M, Ueda K. Control of Biodegradability of Polylactide via Nanocomposite Technology. *Macromol Mater Engng* 2003;288:203-8.
- [23] Fina A, Camino G. Ignition mechanisms in polymers and polymer nanocomposites. *Polym Adv Technol* 2011;22:1147-55.
- [24] Kashiwagi T, Shields JR, Harris Jr RH, Awad WH. Flame retardant mechanisms of a polymer clay nanocomposite. In: Lewin M, editor. *Recent advances in flame retardancy of polymers*. Norwalk: Business Communications Co.; 2003. p. 14-26.
- [25] Marosfoi BB, Garas S, Bodzay B, Zubonyai F, Marosi G. Flame retardancy study on magnesium hydroxide associated with clays of different morphology in polypropylene matrix. *Polym Adv Technol* 2008;19:693-700.
- [26] Hapuarachchi TD, Peijs T. Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for polylactide and its natural fibre reinforced composites. *Compos A* 2010;41:954-63.
- [27] Pecharromán C, Esteban-Cubillo A, Montero I, Moya JS, Aguilar E, Santarén J, et al. Monodisperse and Corrosion-Resistant Metallic Nanoparticles Embedded into Sepiolite Particles for Optical and Magnetic Applications. *J Am Cer Soc* 2006;89:3043-9.
- [28] Lewin M. Some comments on the modes of action of nanocomposites in the flame retardancy of polymers. *Fire Mater* 2003;27:1-7.
- [29] Defay R, Prigogine I. *Surface tension and adsorption*. New York: John Wiley & Sons; 1966.

Tables and Figure Captions

Table 1. Compositions and designations of the processed materials.

Table 2. Elastic modulus and hardness values of PLA and its composites calculated from nanoindentation curves along with TGA data (onset and maximum decomposition temperatures).

Table 3. Important cone calorimetric data extracted at irradiance fluxes of 25 and 35 kW/m² and limiting oxygen index values for neat PLA and its nanocomposites. Cone calorimeter data was based on 1 mm thick samples whereas LOI values are for 3 mm thick samples.

Fig. 1. X-ray diffraction patterns of neat PLA (P0) and its binary (P1 and P2) and ternary (P3) nanocomposites. Patterns were recorded on the surface of the samples parallel to the mold direction.

Fig. 2. TEM micrographs showing the distribution and dispersion of sepiolite and OMMT in P1 to P4. The white arrows in (c) point to some of the OMMT stacks, whereas black arrows indicate sepiolite clusters; the light grayish regions indicated by arrows in (d) are PVA particles. All the micrographs are taken from the mid cross-section of the core region of injection molded samples normal to the flow direction.

Fig. 3. (Normalized) % reductions in (a) Mw and (b) mass of neat PLA and its nanocomposites subjected to different conditions. (a) Room temperature and after 15 weeks of exposure; and (b) 60°C and after 45 days of exposure.

Fig. 4. (a) Mass loss and (b) DTG curves of neat PLA and its nanocomposites.

Fig. 5. HRR curves of neat PLA and its composites with varying thicknesses tested at different irradiance fluxes: (a) 25 kW/m² and 1 mm samples; (b) 35 kW/m² and 1 mm samples; (c) 35 kW/m² and 3 mm samples; and (d) comparison of the HRR curves of 3 mm thick neat PLA and P3, at irradiance fluxes of 35 and 50 kW/m².

Fig. 6. Digital photographs of the residues left after combustion tests at an incident heat flux of 35 kW/m² for (a) P2; (b) P3; and (c) P4.

Fig. 7. Tomograms, with (a, c, e) and without (b, d) matrix of combustion residues of thermally thin (a, b, e) and intermediate thick (c, d) samples of P3. The drastic differences in the organization of silicate layers and the reasons for the poor performance in terms of HRR of thermally thin samples is clear when a-d are compared. An example showing the even distribution of sepiolite particles even in the burned sample is given in (e). Note the difference in scale bars.

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*	85	5	5	4	1

*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.

Table 2. Elastic modulus and hardness values of PLA and its composites calculated from nanoindentation curves along with TGA data (onset and maximum decomposition temperatures).

Sample	Elastic modulus (GPa)	Hardness (GPa)	TGA	
			T _{5%} (°C)	T _{50%} (°C)
P0	4.76 ± 0.05	0.296 ± 0.005	335.6	373.5
P1	4.98 ± 0.13	0.299 ± 0.004	345.7	376.5
P2	5.05 ± 0.03	0.320 ± 0.002	335.4	381.0
P3	5.69 ± 0.28	0.374 ± 0.016	342.1	378.2
P4	5.23 ± 0.19	0.289 ± 0.018	298.3	330.2

Table 3. Important cone calorimetric data extracted at irradiance fluxes of 25 and 35 kW/m² and limiting oxygen index values for neat PLA and its nanocomposites. Cone calorimeter data was based on 1 mm thick samples whereas LOI values are for 3 mm thick samples.

Sample	Ignition time, s		Peak HRR, kw/m ²		Time to peak HRR, s		Flame-out period, s		Total heat released, MJ/m ²		LOI, %
	25	35	25	35	25	35	25	35	25	35	
P0	66	43	332	394	101	74	300	220	26.88	22.82	20
P1	66	42	332	419	105	79	258	212	28.93	29.28	20.6
P2	63	39	371	467	90	82	162	129	24.34	24.88	20.8
P3	54	36	345	398	90	69	154	133	22.82	23.75	20.8
P4	51	32	376	423	75	62	173	150	24.92	25.12	20.6

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7