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Effects of nanoparticles on thermal degradation of polylactide/aluminium diethylphosphinate composites

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ABSTRACT

We investigated the thermal degradation characteristics of polylactide (PLA) aluminium diethylphosphinate (AlPi) composites involving SiO_2, halloysite (HNT) and organically modified montmorillonite (OMMT) via direct pyrolysis mass spectrometry. Presence of nanoparticles, SiO_2, HNT and OMMT affected both thermal stability and relative yields of thermal degradation products of PLA/AlPi. The trans-esterification reactions and interactions between PLA and AlPi were depressed in the presence of SiO_2 and HNT. The increase in thermal stability detected in the presence of OMMT was associated with generation of cross-linked structure as a consequence of reactions between the organic modifier of montmorillonite, the carbonyl groups of PLA and phosphinates.

1. Introduction

Polylactide, (PLA) is biodegradable aliphatic thermoplastic polyester that can be produced from renewable sources is a promising alternative to petroleum based polymers. Although it has good properties when compared to other biodegradable polymers, its wide range of industrial applications is still limited due to poor thermal and mechanical resistances. Morphological, thermal and mechanical properties of biodegradable polymer nanocomposites of PLA and several organically modified montmorillonites (nanoclays), were investigated by several scientists [1–13]. Influence of the organic modifier of the clay (Cloisite 30B, Cloisite 15A and Dellite 43B) and its amount (3 and 5%) on thermal behavior of PLA based nanocomposites was studied by Arajuo et al. [5]. Incorporating Cloisite 30B (C30B) in PLA matrix was investigated as functions of the content and of the hydration state of nanoclays [6]. Zaidi et al. showed that significant layered nanofillers dispersion into PLA can be successfully accomplished by melt intercalation technique and concluded that the production of a nanocomposite based on PLA associated to organically modified montmorillonite, Cloisite 30B (C30B) can be an efficient route to extend the application of the polymer as a biodegradable material, with the possibility to finely tune properties by adjustment of the nanofiller content [7].

The effects of nanosize and microsize clays on the kinetics of the thermal degradation of polylactides were also studied [10]. Roy et al. determined that the addition of organically modified clays into the PLA matrix improves the mechanical, and barrier characteristics and biodegradability, yet, promotes the degradation rates [12]. This effect was determined to be much more pronounced for the samples containing high levels of clay, and product patterns of polylactide were shifted towards shorter lactic acid oligomers as compared to the product patterns of plain polylactide and halloysite modified polylactide hydrolyzed under the same conditions.

Besides nanoclays, studies on the effects of nanofillers such as SiO_2 and halloysite on thermal behavior of PLA also appeared in the literature [14–17]. Zhang et al. determined increase in thermal stability of PLA in the presence of silica [14]. It has further been determined that the increase in thermal stability in the presence of SiO_2 depends on the amount of SiO_2 added into the PLA matrix [15]. Effect of temperature and nanoparticle type on hydrolytic degradation of poly(lactic acid) nanocomposites were investigated [17]. Aluminium diethylphosphinate (AlPi) is a halogen free fire retardant acting in the gaseous phase by generating phosphorous containing compounds such as PO, PO_2, HOPO, $HOPO_2$ and in the condensed phase developing intumescent effects and inorganic glass formation [18–25]. It has been shown that aluminium diethyl phosphinate combined with chemically modified montmorillonite clay provides an alternative to brominated flame retardants in glass fiber reinforced PBT composites [18,19]. In a recent study, Isitman et al. investigated the influence of nanoparticles, spherical SiO_2, rod-like halloysite, (HNT)

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and plate-like montmorillonite, (OMMT) on fire behavior and mechanical properties of PLA containing aluminium diethylphosphinate (PLA/AlPi) processing improved fire behavior compared to neat PLA and the observed trends were correlated with the geometry of nanoparticles [24]. It has been determined that, among these nanoparticles, only OMMT enabled reduction in fire risks suppressing both heat release and mass loss rates compared to PLA/AlPi.

In this study, thermal degradation characteristics of PLA/AlPi involving SiO_2, HNT and OMMT were studied via direct pyrolysis mass spectrometry in order to investigate the effects of nanoparticles on the thermal degradation mechanism of PLA in the presence of AlPi.

2. Experimental

2.1. Materials

Polylactide, PLA, with Mn ~ 19,0000, was provided by Cargill Dow. Aluminium diethylphosphinate, (AlPi) was purchased from Clariant (Germany). Dimethyldichlorosilane treated fumed silica (Aerosil R 974), nanosilica was obtained from Evonik Degussa (Germany). The clay mineral predominantly in the form of nanotubes, halloysite, (HNT) was purchased from Aldrich. Cloisite-30B, OMMT, modified with methyl tallow bis-2-hydroxyethyl ammonium was provided by Southern Clay Products Inc. (USA). The preparation of PLA, melt-compounded with 20 wt% fillers composed of 85 wt% AlPi and 15% nanoparticles, was described in a recent publication in details [24].

2.2. Morphological analyses

The XRD data were collected using a Rigaku X-ray diffractometer (Model, Miniflex) with CuKα (30 kV, 15 mA, λ = 1.54051 Å). The 2θ diffraction diagrams were recorded at 25 °C in the 1–10° range. Transmission electron microscopy (TEM) analyses were carried out using a FEI Tecnai G2 Spirit BioTwin CTEM on the specimens cut from the middle portion of injection molded samples.

2.3. Thermal analyses

Thermogravimetry analyses (TGA) were performed on a PerkinElmer Instrument STA6000 under nitrogen atmosphere at a flow rate of 20 mL/min and a heating rate of 10 °C/min.

Direct pyrolysis mass spectrometry (DP-MS) analyses were performed on a 5973HP quadrupole mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. 70 eV EI mass spectra, at a rate of 2 scan/s, were recorded. 0.01 mg samples in the flared glass sample vials were heated to 450 °C at a rate of 10 °C/min. Experiments were repeated at least twice to ensure reproducibility. The variations in temperature and in relative intensities are always less than 5%.

3. Results and discussions

We have recently determined that incorporation of AlPi reduced the fire risks by lowering peak heat release rate (PHRR) from 578 to 443 kW/m^2 and peak mass lost rate (PMLR) from 24.4 to 17.2 g/(m^{2}s) and by increasing limiting oxygen index (LOI) from 23 to 27.5% [18]. Addition of nanofillers had no remarkable effect on LOI values but caused some variations in fire retardancy parameters such as PHRR, PMLR and fire growth index, FGI. Upon incorporation of SiO_2, no remarkable improvements in these fire retardancy parameters compared to PLA/AlPi, was detected. In the presence of HNT, the PHRR and PMLR values were increased indicating a negative effect on fire retardancy of PLA/AlPi. On the other hand, OMNT enabled reduction in fire risks, suppressing both peak heat release and mass loss rates remarkably, to 283 kW/m^2 and 5.7 g/(m^{2}s) respectively.

Table 1
TGA data for PLA, PLA/AlPi, PLA/AlPi/SiO_2, PLA/AlPi/HNT, PLA/OMMT and PLA/AlPi/OMMT.

Sample	$T_{10\%}$ (°C)	T_{max} (°C)		Residue %
		Step 1	Step 2	
PLA	332	355		
PLA/AlPi	324	359	495	1.3
PLA/AlPi/SiO_2	335	364	481	5.0
PLA/AlPi/HNT	318	353	495	3.5
PLA/OMMT	338	380		1.0
PLA/AlPi/OMMT	333	369	496	4.3

3.1. Morphology of the composites

The influence of morphology of nanoparticles, spherical SiO_2, rod-like halloysite and plate-like montmorillonite on fire behavior and mechanical properties of PLA containing aluminium diethylphosphinate (AlPi) was reported recently [24]. TEM images and XRD patterns of PLA/AlPi composites involving nanoparticles were analyzed to determine the dispersion of the nanoparticles in the PLA matrix. Nanosilica was homogenously dispersed in the matrix with some agglomeration forming local clusters in the sub-micron scale (Fig. 1a). On the other hand, TEM images of PLA/AlPi/HNT showed aggregates of halloysite particles and almost no change was observed in the interlayer space of 0.7 nm of HNT in the PLA/AlPi matrix indicating that the interlayer was inaccessible to PLA chains (Fig. 1b). Cloisite 30B has a distinct maximum at around 2λ = 5.6° (Fig. 1c). This peak was almost totally disappeared in the XRD of PLA/OMMT composite. The nanocomposite revealed only very small bulge around 2θ = 3.5° indicating a good dispersion of the organoclay, and exfoliation of the nano platelets in the PLA matrix. In the case of PLA/AlPi/OMMT, the XRD pattern demonstrated partially intercalated/exfoliated clay nanocomposite morphology in accordance to TEM images. Regions of montmorillonite aggregates in addition to regions of exfoliation were detected indicating that presence of AlPi affected dispersion of OMMT (Fig. 1d).

3.2. Thermal degradation of PLA/AlPi composites involving nanoparticles

The TGA data for neat PLA, PLA/AlPi, PLA/AlPi/SiO_2, PLA/AlPi/HNT, PLA/OMMT and PLA/AlPi/OMMT are summarized in Table 1. PLA has a significantly low maximum decomposition temperature compared to AlPi, therefore, PLA/AlPi compound showed a two-step degradation behavior, the first being due to decomposition of PLA the second due to decomposition of AlPi [24]. On the other hand, thermal decomposition of PLA was started at lower temperatures in the presence of AlPi indicating that AlPi interfered with the decomposition of PLA. A slight increase in thermal stability of PLA was observed upon incorporation of SiO_2, whereas, it was decreased in the presence of HNT. The incorporation of OMMT into PLA and PLA/AlPi matrices improved thermal stability of PLA chains.

In a recent study, we applied DP-MS, and collision induced dissociation, CID, MS/MS/MS techniques to investigate thermal degradation mechanism and thermal degradation products of neat PLA and PLA involving aluminium diethyl phosphinate, AlPi, as the flame retardant [25]. The results indicated two dominating decomposition pathways for neat PLA under the experimental conditions; chain homolysis and trans-esterification reactions yielding