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Engineering flame retardant biodegradable polymer nanocomposites and their application in 3D printing

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ABSTRACT

Flame retardant, environmentally sustainable nanocomposites were made by melt blending poly (lactic acid) (PLA) with melamine polyphosphate (MPP) and Cloisite 30B (C-30B). The composition of the nanocomposite was highly specific and guided by interfacial energy minimization principals which balanced enthalpic and mechanical contributions. In this critical range, even small changes in the filler concentration can have a large impact on the performance of the material. We showed that while addition of 17% MPP can increase the flame resistance of PLA, (achieving a UL-94 V2 rating) the mechanical properties were significantly degraded. Addition of only 1% C-30B reversed these effects and yielded a nanocomposite with enhanced mechanical properties and passing the UL-94 V0 flame test. This compound was able to be extruded and fed into a Makerbot Replicator 2X Fused Deposition Modeling (FDM) 3D printer, where the printed samples were indistinguishable mechanically from their molded counterparts and also achieved the UL-94 V0 rating. The enhanced performance occurred only within a very narrow composition window. Cone calorimetry revealed that while a significant decrease in the heat release rate, accompanied by the formation of an intumescent char, was achieved by the addition of 1% C-30B to the MPP/PLA blend, a very poor char, corresponding the increase in the heat release rate, was obtained with addition of 2% C-30B. These results were explained in view of the altered phase morphology observed in Transmission Electron Microscopy (TEM).

1. Introduction

In the last decade, poly (lactic acid) (PLA) has been receiving increased attention for replacing conventional polymers because of its biodegradability. As the first large-scale produced bio-based plastic, PLA has good mechanical properties and primarily degrades through hydrolysis. As a result, it is now used in diverse areas such as traditional packaging, textile fabrication and biomedical implants [1–4]. However, an important factor which limits the broader use of PLA in new areas such as electronics and automotive is its flammability. Numerous studies have been focused on producing flame retardant PLA composites [5–13]. Lin et al. [14] synthesized a novel chemical, poly (1, 2-propanediol 2-carboxyethyl phenyl phosphinate), which not only increased the flame retardancy, but also enhanced the elongation rate of PLA. Liao et al. [15] improved the flame retardancy and crystallinity of PLA using a synthesized phosphorus and nitrogen based flame retardant. Murariu et al. [16,17] found that either calcium sulfate/organoclay or expanded graphite were able to significantly decrease the heat release rate of PLA by 30% and allowed the composites to pass the UL94 HB test. Intumescent PLA flame retardant systems have also been reported [18–24]. Ammonium polyphosphate (APP) based intumescent system has been widely used and proven to be very effective to make PLA flame retardant. However, APP has very high persistence rating in the environment according to U.S. Environmental Protection Agency (EPA)'s assessment [25]. Since the PLA composite will be disposed in landfills, the fillers must be environmentally safe when they are present as the PLA decomposes. Therefore, using APP in PLA system is not consistent with our "environmental sustainable" purpose. In this study, we use melamine polyphosphate (MPP) which has been reported by

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EPA to be less persistent and have no bioaccumulation in the environment [26]. MPP is a halogen-free, nitrogen-containing, phosphorus-based flame retardant agent gaining increased attraction in the flame retardant polymer industry [19]. During combustion, the melamine component of MPP sublimes by absorbing significant amount of heat and releases a nitrogen-rich gas to dilute oxygen of the ambient air, and the polyphosphate component enhances the char formation by catalyzing the dehydration of polymer chains [27–31].

Previous research showed that the addition of organoclays enabled the flame retardant particles to disperse more evenly inside the polymer matrix, thereby further enhancing the flame retardancy [32–36]. In this study, we used Cloisite 30B, which has been shown to be partially exfoliated within the PLA matrix [37], to optimize the dispersion of MPP in PLA. After optimizing the flame retardant system for both thermal and mechanical properties, we then processed the PLA nanocomposites for use in Fused Deposition Modeling (FDM) 3D printing. Flame test and multiple mechanical tests were used to compare the performance of 3D printed nanocomposites, relative to those produced by standard methods. This extension of flame retardant PLA nanocomposites in 3D printing has tremendous manufacturing potential since 3D printing technology has the ability to customize complex products without prototyping mold tools which cause high manufacturing expense and environmental issues [38–41]. In addition, the integrality of the 3D printing process significantly decreases the cost of parts assembly and the cumulative energy consumption of polymer manufacturing [42]. In this case, the application of flame retardant PLA nanocomposites in 3D printing is expected to have very broad prospects in the electrical and automotive industries.

2. Experimental

2.1. Materials

Melamine polyphosphate (MPP) was purchased from BOC Sciences with purity above 98%. Cloisite 30B (C-30B), supplied by Southern Clay Inc., is Na MMT clay modified with bis (2-hydroxyethyl) methyl hydrogenated tallow quaternary ammonium salt. Poly (lactic acid), PLA 4042D, was purchased from the Natureworks LLC with a density of 1.24 g/cm^3 and molecular weight of 120,000 g/mol.

2.2. Nanocomposites preparation

A C.W. Brabender was used to mix PLA pellets with MPP and C-30B powders. The initial chamber temperature was set at 180 °C and the rotor speed was 20 rpm. PLA pellets were first poured into the chamber for melting, the MPP and C-30B were then added and mixed with PLA at 100 rpm for 10 min. The mixtures were ground into small pieces using a Granu-Grinder granulator for sample preparation. Some of the mixture pieces were directly molded by a hot press into different shapes required for flame and mechanical tests. The rest of the pieces were first extruded for the 3D printable filaments using an EX2 Filabot at a temperature of 155 °C and a flow rate of 100 mm/s. These filaments were then fed into a Makerbot Replicator 2X 3D printer which was used to produce the samples with the same dimensions as those produced via hot press molding. Printing was performed at 229 °C with 100% fill and a flow rate of 90 mm/s.

2.3. Characterization methods

2.3.1. Flame testing

UL-94 vertical burning test has been used to determine ability of the samples to the self-extinguish. The tests were conducted according to the ASTM D 3801 standard and the dimensions of the specimens are 127 mm long, 12.7 mm wide, and 3.2 mm thick. The limiting oxygen index (LOI) of each sample was measured according to ASTM D 2863. The dimensions of the specimens are 100 mm long, 6 mm wide, and 3 mm thick. The time to ignition (TTI), average heat release rate (AHRR), peak heat release rate (PHRR), and total heat release (THR) were recorded using a Stanton Redcroft Cone Calorimeter with the heat flux of 50 kW/m^2. The cone specimens are prepared as square plates with 76.2 mm side length and 5.1 mm thick.

2.3.2. Thermogravimetric analysis (TGA)

The TGA was conducted using a Mettler Toledo TGA851 under nitrogen flow. A little piece of sample (about 10 mg) was put into a crucible and heated from 40 to 800 °C at the rate of 20 °C/min. The weight loss curves were recorded by a STARe Thermal Analysis Software.

2.3.3. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of the PLA, MPP, and nanocomposites were measured using a Perkin Elmer Frontier FT-IR spectrometer with a universal attenuated total reflectance (ATR) polarization accessory.

2.3.4. Transmission electron microscopy (TEM)

Thin cross section films of the PLA and its nanocomposites were cut by a Lecia FC-7 microtome at room temperature. The thin films (thickness is around 100 nm) were then lifted onto copper grids and viewed by a JEOL JEM1400 TEM at 80 kV.

2.3.5. Scanning electron microscopy (SEM)

The surfaces of UL-94 burnt and unburnt samples, the char layers after cone calorimeter and the cross-sections of molded and printed impact samples were imaged using a JEOL JSM7600F SEM with a Schottky electron gun. The elemental distribution of phosphate was detected using an energy dispersive X-ray spectroscopy (EDXS) accessory of the SEM. A layer of gold with thickness around 10 nm was coated on the sample surface to increase electrical conductivity.

2.3.6. Rheology measurements

A Bohlin Gemini HR Nano rheometer was used to estimate the rheology performance of the PLA and its nanocomposites. All the samples were heated up to 180 °C on a 20 mm aluminum cup for frequency sweeping (0.01 Hz–100 Hz). The measurements are conducted in oscillatory shear mode with the strain amplitude set at 2.5%.

2.3.7. Mechanical tests

Tensile properties of both hot press molded and 3D printed samples were measured using an Instron 5542 (Instron Co., Grove City, PA) with the extension rate set at 2.5 mm/min according to ASTM D-638, type M. The impact strength of molded and printed samples was evaluated by Izod impact tests which were conducted based on ASTM D-256. The result for each sample represented the average value of 10 specimens.

3. Results and discussion

3.1. Flame retardancy of nanocomposites

3.1.1. Flame tests

The results of UL-94 tests for PLA and its nanocomposites are listed in Table 1 which shows that the neat PLA failed to pass all burning tests. PLA did not self-extinguish even after 30 s, and heavy dripping was also observed throughout the time of application of