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Flame-retardant recycled bamboo chopstick fiber-reinforced poly(lactic acid) green composites via multifunctional additive system

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ABSTRACT

In this study, recycled bamboo chopstick fiber and nano-clay are utilized to reinforce poly(lactic acid) (PLA) biodegradable plastic. The chopstick fiber and nano-clay are surface modified with a coupling agent and grafted onto the side chains of the PLA to enhance the compatibility between the reinforcements and the PLA, and to improve the mechanical properties of the PLA. Moreover, ammonium polyphosphate (APP) and expandable graphite (EG) are added as flame-retardants. The results show that the UL-94 flame test of the composites achieves a V-1 or V-0 grade according to the different composition of the flame-retardants. SEM analysis reveals that the interfacial adhesion of the composite is effectively enhanced after the surface modification of the fiber. The increments of tensile and impact strengths of the composites reach 14.5% and 5.5%, respectively. Thermal analyses show that the thermal stability is significantly improved, and the increment of heat distortion temperature can reach 102%. The resulting green composites are not only flame retardant, but also have good thermal and mechanical properties.

1. Introduction

Intumescent flame retardant (IFR) systems have attracted great attention because they are halogen-free and effective. They are usually composed of an acid source, blowing agent and a carbonic source. The char produced from the synergistic interaction of these ingredients protects underlying materials from heat and oxygen [1]. To further decrease the flammability of poly(lactic acid) (PLA) for wider applications, flame-retardant IFR/PLA composites have been widely studied [2–8]. In Wang et al.'s study [8], microencapsulated ammonium polyphosphate (MCAPP) was added to PLA/starch biocomposites. Their results showed that the peak of the heat release rate and the total heat release of the biocomposites decreased dramatically as compared with pure PLA. The TGA results indicated that the addition of MCAPP to PLA could improve the char yields and the thermal stability of the char at a high temperature as compared with neat PLA. The char residue on the surface is mainly composed of carbon/pyrophosphate and/or polyphosphate compounds and some holes. This char layer can inhibit heat transmission and retard inner PLA degradation.

However, the fire-resistance of IFR alone was insufficient, and expandable graphite (EG) was found to be a highly efficient synergistic additive [1]. In Murariu et al.'s study [9], commercially available EG was added to PLA. They found that the flame-retardant properties of this composite resulted in a large decrease in the maximum rate of the heat release and the HB rating in UL-94 tests. However, the tensile strength of the composites (38 ~ 50 MPa) was decreased as compared with neat PLA (70 MPa). Zhu et al. [1] investigated the synergistic effect between EG and ammonium polyphosphate (APP) on flame-retardant PLA. PLA composites with a 15 wt% of APP/EG (1:3) combinations showed an LOI value of 36.5 and a V-0 rating in UL-94 tests, an improvement over composites with APP or EG alone. The results showed that the APP/EG combination could retard the degradation of polymeric materials above the temperature of 520 °C by promoting the formation of a compact char layer. This stable and dense char layer protected the matrix from heat penetrating inside, and prevented further degradation of the materials. The mechanical properties of the composites were not discussed in that study.

In Shukor et al.'s study [10], PLA was blended with kenaf core fiber (25 wt%), polyethylene glycol (15 wt%) and 10, 15 and 20 phr APP, respectively. The kenaf fiber was untreated or treated with 3%, 6% and 9% NaOH solution separately. It was found that APP was very effective in improving the flame-retardant properties, according to the limiting oxygen index measurement, due to the increased char residue at high temperatures. However, the addition of APP decreased the compatibility between the PLA and kenaf fiber, resulting in a significant reduction in the mechanical properties of the PLA composites. Moreover, the compatibility between the PLA and the kenaf fiber was improved by pretreating

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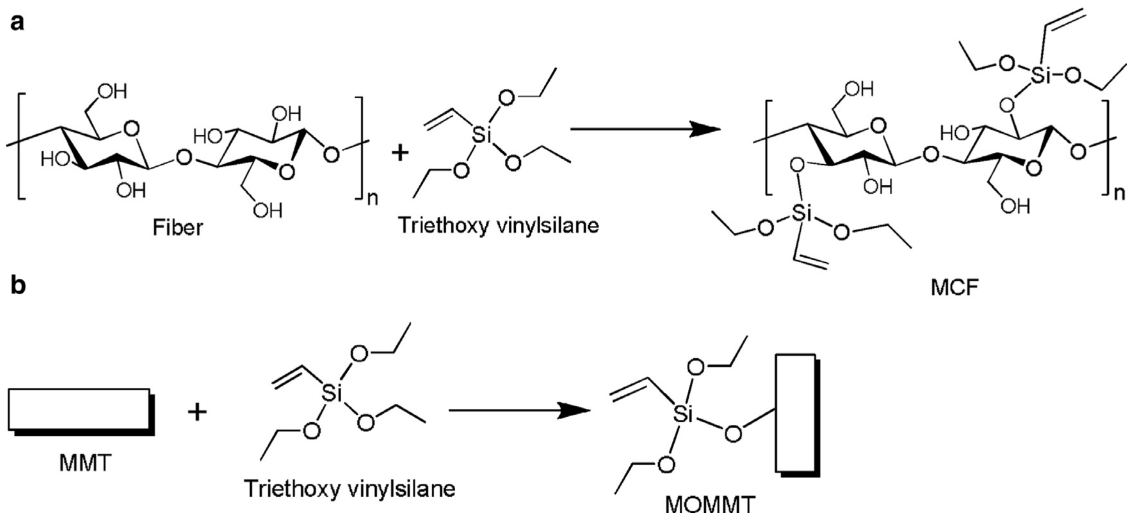

Fig. 1. Reactions of (a) chopstick fiber and (b) MMT with silane coupling agent.

the fiber with NaOH solution. Fiber pretreated using a 6% NaOH solution evidenced better mechanical properties in the resulting composites. Cheng et al. [11] incorporated aluminum trihydrate (ATH) and modified montmorillonite (Cloisite 30B) into PLA to enhance its thermal and mechanical properties. Their results revealed that the thermal oxidative degradation temperature and the activation energy of the nanocomposites were higher than without the addition of ATH and Cloisite 30B. The incorporation of Cloisite 30B into the ATH/PLA composite enhanced the thermo-oxidative stabilization throughout the degradation step. Moreover, the results showed that the high loading of ATH yielded brittle PLA composites; however, replacing a portion of the ATH with Cloisite 30B in the PLA matrix improved this result. Mohapatra et al. [12] also found that Cloisite 30B/poly(butylene adipate-co-terephthalate)/PLA blend composites showed improved thermal properties as compared with pure PLA.

The utilization of disposable chopsticks is very popular [13,14] in Taiwan, China and Japan; they are also one of the major sources of waste in these countries. Incorporating these waste fibers into polymers would not only enhance their thermal and mechanical properties, but would also reduce the cost of the materials; the result would be a green composite [15,16]. According to the literature [11,12,17–19], montmorillonite (MMT) and recycled disposable chopstick fiber (CF) enhance not only the mechanical properties of the polymers, but also the thermal properties and flame retardancy. Moreover, a better content of MMT and natural fiber, around 5 and 30 phr, respectively, was found. Therefore, 5 phr of MMT and 25 phr of CF were incorporated into the APP/EG/PLA composites in this study to improve the mechanical and thermal properties of the composites. The expectation was that the flame-retardant PLA composite would evidence better mechanical properties.

2. Experimental

2.1. Materials

The poly(lactic acid) (PLA, PLA2003D^{TM}) used in this experiment was supplied by Nature-Works LLC, and the ammonium polyphosphate (APP, $n = 1000$) by Chembridge International Corp., Taiwan. The expandable graphite (EG) was supplied by International Carbide Technology Co. Ltd., Taiwan, and the montmorillonite “Kunipia F” clay (MMT) by the Kunimine Co. of Japan. The dicumyl peroxide (DCP) was supplied by Aldrich Co. The recycled disposable chopstick fiber (CF) obtained was subjected to various chemical surface modifications as follows. A favorable process of alkaline treatment for the plant fibers was adopted from a previous study [17,18]. The alkali-treated fibers were chopped and screened to obtain an average length of 2–4 mm, and then these fibers and MMT were treated with a silane coupling agent (triethoxy vinylsilane, supplied by Dow Corning Co.) to obtain the modified fibers and MMT (MCF and MOMMT), as shown in Fig. 1.

2.2. Preparation of flame-retardant PLA samples

The test specimens of the flame-retardant PLA composites for the tensile, impact, heat-distortion temperature and UL-94 measurements were prepared using an injection molding machine. 25, 5 and 0.2 phr of the MCF, MOMMT and DCP with different EG and APP content (13 and 4, 23 and 4, and 13 and 8 phr) was added, respectively, and noted as 13E-4A, 23E-4A and 13E-8A. All materials were dried in a vacuum oven at 80 °C for 24 h before use. Immediately after drying, the PLA was melt blended with other ingredients. In this mixing stage, the conjugation reactions (Fig. 2) were designed to graft the MCF and MOMMT onto the side chains of the PLA.

2.3. Measurements

2.3.1. FT-IR spectroscopy analysis

The infrared spectra were obtained with an FTIR spectrometer (PERKIN ELMER Paragon 500) with a resolution of 2 cm^{-1} that scanned 50 times from 300 to 4000 cm^{-1} at room temperature. All film samples were taken using the conventional NaCl disk method.

2.3.2. Morphology analysis

A Hitachi scanning electron microscope (SEM; model S-3000 N) was used to evaluate the fracture surface of the composites. The acceleration voltage was 3 kV, and the sample surfaces were sputter coated with gold to avoid charging.

2.3.3. Thermal analysis

The thermal behavior was determined using a TA Instruments' TGA Q50 thermogravimetric analyzer (TGA). The samples were scanned from 40 to 1000 °C at a heating rate of 10 °C/min in the presence of a nitrogen flow.