Effect of halloysite nanotube loading on structure, mechanical and thermal properties of poly (l-lactic acid)/poly-(butylene succinate) blend

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Abstract. Poly (l-lactic acid) (PLA)/poly-(butylene succinate) (PBS)/Halloysite Nanotubes (HNT) composites were prepared via melting compounding in a twin-screw extruder. The effects of HNT addition on mechanical properties, thermal properties of PLA/PBS blends were investigated. The structure of ternary composites was studied by Transmission Electron Microscopy (TEM) and the results revealed that a small incorporation of HNT dispersed well in the two polymers. Ternary composites presented improved tensile strength and elongation at break at low loading levels of HNT. Dynamic Mechanical Analysis (DMA) results showed that the addition of HNT significantly increased storage modulus of PLA/PBS composites. The differential scanning calorimetry analysis indicated that HNT can serve as nucleating agent for PLA in ternary composites, which lead to decreased cold crystallization temperature and increased crystallinity of PLA.

1. Introduction

Due to increasing environmental concerns, biodegradable polyesters are receiving considerable attention. In competition of biodegradable polyester, the polymers (PLA and PBS) originated from renewable resource have been extensively investigated due to environmental protection [1]. In particular, PLA has attractive properties, such as good strength, good biocompatibility and barrier properties [2]. For these reasons, PLA is expected to be an interesting candidate for biomaterials and construction materials in near future [3]. However, PLA’s poor flexibility, high price and low heat resistance are major obstacles for the possibility of commercial applications, particularly for packaging industries [4-6]. In this respect, Adding polycaprolactone (PCL) [7] and poly (butylene succinate) PBS [8-10], which are more tough and still biodegradable polyesters, into PLA could overcome the brittleness of PLA. Specially, researchers found much valuable information in PLA/PBS blends. Zhao et al [11] reported that elongation at break in PLA/PBS blends was considerably higher than that of pure PLA, but with an acceptable loss of strength. Furthermore, the crystallization of PLA was enhanced after the addition of PBS even though PBS was in a molten state. Takagi et al [12] and Shibata et al [13] found that the cold-crystallization of PLA was enhanced after adding PBS.

However, some studies [12-14] concluded that phase separation led to probable deterioration in some properties, since PLA was immiscible with PBS. Adding nanoparticles into PLA/PBS blends was an effective way of improving the compatibility of PLA and PBS [15-17]. In order to improve the interfacial bonding between PLA and PBS, numerous modification methods were introduced. However, the procedures were neither easy to handle nor environmental-friendly. Because it was toxic.
in modification nanoparticles such as Carbon Nanotube (CNT) [18], these nanocomposites could not be directly utilized in biomedical area.

The use of Halloysite nanotube (HNT) does not add risk to the environment because it is a green filler and a natural product. As demonstrated elsewhere [19], the composition of HNT and kaolin were resemble. HNT had a predominantly hollow tubular structure with nanoscale lumen. Its structure was relatively high length-to-diameter ratio, and low hydroxyl group density on their surface. Unlike other nanostructured clays that must be exfoliated, HNT did not require exfoliation. Furthermore, HNT provided strength increase without the loss of ductility [20]. In addition, its use did not cause any potential risks to environment as other nanofillers potentially did [18]. Compared to the CNT, HNT was easily available, abundant, rather cheap and eco-friendly. Given to these characteristics, HNT has been regarded as a promising competitor and alternative to both CNT and OMMT. Many HNT nanocomposites were prepared and studied by researchers [21-23]. Murariu [21] reported that the addition of HNT can result in an increase of thermal and mechanical properties at a small loading. Excellent tensile properties and good impact properties were observed in PLA /HNT nanocomposites with a content of 3–12 wt.% nanofiller [21]. However, from recent literatures, the application of HNT in PLA/PBS and how HNT affects the properties of PLA/PBS composites have not been reported. Further research in the effect of HNT on PLA/PBS properties will help in the development of several properties of PLA/PBS composites.

In this article, our major work is on the effect of HNT addition on tensile properties, dynamic mechanical properties, and thermal properties of PLA/PBS blends. Previous work [23] revealed that excellent properties were obtained when PLA/PBS weight ratios was 70/30 wt.%. Therefore, PLA/PBS/HNT composites having fixed composition of PLA and PBS of 70% and 30% (weight ratio) with various HNT loadings are prepared.

2. Experiment

2.1. Materials

PLA with a commercial grade 4032D used in the study has a specific gravity 1.25 g/cm$^3$, which was supplied by Natural Works LLC (USA). The PLA has a glass transition temperature about 60°C. It has a melting temperature about 163°C. Additionally, PBS (BIONOLLE #1903MD) was supplied by Showa High Polymer (Japan). It has density=1.26 g/cm$^3$ and a melting temperature of ~115°C. Halloysite nanotube (HNT) was obtained by Aldrich. It has nanotubes length=1–3 um, pore volume=1.26-1.34 ml/g. Before processing, HNT was dried at 80°C for 10 h in vacuum, whereas polymers were dried for 8 h.

2.2. Preparation of polymer blend and blend-clay composites

After dried, PLA/PBS (70 wt.%/30 wt.%) pellets were premixed. The ratio was determined because it resulted in a good balance of properties. Importantly, PLA was our target polymer, whose properties need to be improved. Different kinds of HNT (1, 3, 6, 9 wt.%) were blended with premixed polymer in a plastic bag. A BRABENDER counter-rotating twin-screw extruder was used to prepare composites by means of melt blending. The extruder is from Germany with a screw diameter of 25 mm and a length/diameter ratio of 20:1. The temperatures from feeding port to die were 160, 170, 195, 195, 195, 175, and 175°C. The screw speed was set at 100 rpm. A water bath was introduced to cool the composites extrudate from the die. Then, the extruded blends into pellets was cut by a pelletizer. Next, more than 4 h at 80°C was needed to dried these extruded pellets. After then, the pellets were made into sheets of 150 mm x 80 mm x 2 mm by compression molding mold at 190°C. Finally, the sheets were prepared into the samples for TEM, tensile properties, dynamic mechanical properties and dynamic rheological test. The dried pellets from the fresh extruder at the exit of die were prepared for differential scanning calorimetry analysis specimens. It is noted that B0, B1, B3, B6 and B9 represented the blends with 0, 1, 3, 6, 9 wt.% HNT contents, respectively.
2.3. Characterization

2.3.1. TEM. The dispersion of nanoparticles in composites was evaluated by Transmission Electron Microscopy (TEM) at an acceleration voltage of 200 kV. TEM is a JEOL field emission transmission electron microscopy named JEM-100XII. Before testing, a Leica EMUC6/FC6 microtome was used to make circular sheet into ultrathin sections with a thickness of ~100 nm.

2.3.2. Tensile test. An INSTRON universal machine (model 5566, USA) was used to evaluate tensile properties of ternary composites. All samples were tested at room temperature in accordance with GB/T 1040.2 (2006), and had the same tension mode with a single-strain rate of 5 mm•min⁻¹. Final data were determined in an average of five independent tests.

2.3.3. Dynamic mechanical analysis (DMA). NETZSCH DMA labelled 204C was introduced to evaluated dynamic mechanical properties of neat PLA/PBS and PLA/PBS/HNT blends. All samples were tested in tensile mode at temperature ranged from −65°C to +150°C with a heating rate of 3°C/min, and then with a frequency of 1 Hz and oscillation amplitude of 0.04 mm. The measurements was fixed at the same condition. The storage modulus and the loss modulus were obtained from DMA test. Specimen dimensions in test were approximately 1×5×32 mm (thick-width-length).

2.3.4. Differential scanning calorimetric (DSC). A NETZSCH DSC 204 F1 analyzer from Germany was used to evaluate thermal properties. All samples were tested at a weight of 6-10 mg with DSC protocol. In DSC protocol, samples were heated from room temperature to 210°C in a nitrogen atmosphere at a heating speed of 10°C/min, and the temperature of 210°C was maintained for 5 min, then declined to room temperature at a cooling rate of 10°C/min. A second heating scan monitored was determined between room temperature to 210°C at a rate of 10°C/min. Melting temperature (T_m), melting enthalpy (ΔH_m), glass transition temperature (T_g) and cold crystallization temperature (T_c) were obtained from the second heating mode. The fractional crystallinity (χ_c) was determined by the following equation:

$$\chi_c(\%) = \frac{\Delta H_c - \Delta H_0}{\Delta H_0 \times \text{wt.}\%} \times 100\%$$

Where χ_c was the crystallinity of polymer (PLA or PBS) in the composite, ΔH_c represented the cold crystallization enthalpy, ΔH_m represented the melting enthalpy, ΔH_0 represented the theoretical enthalpy for a fully crystalline, and wt.% represented the polymer weight fraction in HNT composites. According to previous work in our team, ΔH_0 for PBS [24] and PLA [25] had been assigned to be 200 J/kg and 93 J/kg, respectively.

3. Results and discussion

3.1. Morphology of PLA/PBS/HNT ternary composites

Obviously, polymer properties are evidently influenced by the dispersion of nanoparticles. A well dispersion of HNT nanoparticles is the desire thing, which will significantly influence thermal, tensile properties of PLA/PBS/HNT ternary composites.

The morphology of ternary composites was mainly evaluated by TEM analyses. Figures 1(a)-1(d) represents typical TEM pictures of PLA/PBS/HNT ternary composites. From the picture, HNT well dispersed in samples with 3 wt.% and 6 wt.% HNT loadings. When increasing the loading of HNT to 9 wt.%, the individually separated HNT and aggregated HNT coexisted in the sample. The results revealed that HNT well dispersed in some samples without complicated surface-treatment procedure.
3.2. Tensile properties and dynamic mechanical properties

Tensile strength and the elongation at break of PLA/PBS/HNT composites were showed in figure 2. In figure 2, tensile strength of ternary composites initially increased before 6 wt.%, and then monotonically declined with the introduction of more HNT. Specially, tensile strength was improved by almost 130% separately at 6 wt.% HNT loading than that of blank PLA/PBS blend (31.48 MPa). However, at high HNT loading (9 wt.%), tensile strength significantly decreased to 33.64 MPa while it was higher than that of pristine blend without HNT. Regarding to the elongation at break of ternary composites, the elongation at break climbed sharply to 17.86 wt.% at 6 wt.%, which was nearly 2 times better than that of blank PLA/PBS (9.78 wt.%), whereas a dramatic reduction occurred in ternary composite filled with 9 wt.% HNT.

There are some works reporting reinforcing effect for PLA/PBS blend when adding different nanoclay. For example, PLA/PBS with four organically modified pristine montmorillonites were prepared and researched [26]. Blends with pristine montmorillonite and nanoclay (C25A) showed poor mechanical properties. However, the maximum of the elongation at break and yield strength of PLA/PBS with organically modified clay (C20A) were obtained at organically modified clay content of 2 wt.%, which were 18%~5% increment compared with blank PLA/PBSA respectively [26]. For example, both the elongation at break and tensile strength of the PLLA/PBS blend decreased precipitously as a result of nanoclay (C25A) incorporation [15]. These results revealed that the structural characteristics of nanoparticles, dispersion state as well as interfacial interactions caused the different reinforcing effects in clay composites. Comparing with nanoclay, HNT without modification methods showed good reinforcing properties for PLA/PBS. The excellent reinforcing of HNT for PLA/PBS could owe to the uniform distribution of HNT and the interfacial interaction between HNT and polymers [27]. However, in the case of PLA/PBS with 9 wt.% HNT loading, tensile strength and elongation at break started to decrease, whereas they were higher than those of blank PLA/PBS. This decline was ascribed to aggregated HNT (as shown in TEM test), which could be the stress-centralized points during loading process.

Figure 1. TEM images of PLA/PBS/HNT composites: (a) B3, (b) B6, (c) B9. (d) B9 in 200 nm scale. The red circle in (c) represents HNT aggregates.
Figure 2. Tensile strength and the elongation at break of ternary blends with different HNT loadings.

Figure 3. Temperature dependence of storage modulus for polymer ternary blends (Samples B0, B3, B6, each having 0, 3, 6 wt.% HNT respectively).

Figure 3 represents the temperature dependencies of storage modulus for pure PLA/PBS and the ternary blends obtained by the addition of 3 wt.% and 6 wt.% HNT. All investigated samples for storage modulus presented similar behaviors with the increase of temperature. Specially, storage modulus decreased gradually before 40°C, and then followed by a dramatic decline in the ranges of 40-60°C. The storage modulus of PLA/PBS composites was significantly enhanced by the incorporation of HNT. The interactions between polymer matrix lead to the rise. Thus, HNT could restrict the mobility of polymer chains adsorbed on HNT’s surface, resulting in the formation of a stiffened interphase [27].

3.3. Thermal properties

Figure 4. DSC thermograms of neat polymer, ternary composites.

Figure 4 reveals DSC thermograms of pure PLA/PBS and HNT composites during a second heating scan. As seen from figure 4, two melting endotherm peaks were discernible for neat PBS while a single one was found for ternary composites. The corresponding data are collected in table 1. Firstly, from these DSC results, it comes out that PLA in blank PLA/PBS composite showed a broad cold crystallization exothermic peak at about 103.6°C. Here, PLA’ crystal is not perfect in cold crystallization because of the lower crystal ability of PLA chain, and the imperfect crystals form in cold crystallization would reorganize into more orderly crystal structures [28]. Furthermore, $T_{cc}$ of
PLA shifted to a lower temperature after the introduction of HNT. On introduction of 6 wt.% HNT into the blend, the $T_{cc}$ of sample B6 decreased to a lower temperature of nearly 97.2°C, which was 6.4°C lower than that of sample B0. This is because of the nucleating effect of HNT in PLA cooling crystallization process. The heterogeneous nucleation increases the crystallinity of PLA. Similar heterogeneous nucleation of nanosized particles for PLA were found [29-32].

Table 1. DSC data of PLA/PBS/HNT blends.

| Blend samples (PLA/PBS/HNT) | PLA component | PBS component |
|-----------------------------|---------------|--------------|
| $T_{m1}(^\circ C)$ | $T_{cc}(^\circ C)$ | $\Delta H_m$ (J/g) | $\chi_c$(%) | $T_{m2}(^\circ C)$ | $\Delta H_m$ (J/g) | $\chi_c$(%) |
| Pure PLA | 168.5 | 99 | 18.46 | 38.71 | 21.77 |
| B0 | 163.8 | 103.6 | 15.92 | 20.01 | 113.4 | 6.28 | 10.01 |
| B3 | 168.2 | 104.3 | 16.41 | 22.67 | 113.4 | 13.78 | 22.97 |
| B6 | 167.5 | 97.2 | 10.31 | 27.12 | 113.4 | 8.447 | 14.08 |
| B9 | 167.4 | 98.7 | 13.31 | 28.02 | 113.4 | 9.774 | 16.29 |

As seen from DSC data, however, for the PBS component, $T_{m2}$ of ternary blends were same with $T_{m2}$ of blank PLA/PBS, indicating that HNT had little influence on $T_{m2}$ of the ternary blends. The melt enthalpy of PBS component in ternary blends grew with the addition of HNT, though the increasing trend was not consistent.

4. Conclusions
PLA/PBS/HNT ternary blends were successfully obtained by direct melt mixing via a twin-screw extruder, and their structure, mechanical properties, thermal properties were studied. Results revealed that a small incorporation of HNT dispersed well in the two polymers. Both tensile strength and elongation at break for ternary composites were significantly improved due to the HNT incorporation. DMA results revealed HNT significantly enhanced the storage modulus of PLA/PBS composites. DSC analysis illustrates that HNT can act as nucleating agent in process of PLA crystallization of ternary composites, leading to the decrease of cold crystallization temperature and the increase of PLA crystallinity.

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