

Fabrication of PBS/Hemp/Nanoclay Hybrid Green Composites

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1 Introduction

As the rapidly growing usage of plastic materials, millions of tons of plastic waste are produced and buried in landfill sites around the world each year. It takes a long time for conventional plastics to degrade, leading to serious ecological problems. Therefore, the development of biodegradable materials with controlled properties is demanded. The potential applications of biodegradable composites include short-term packaging materials, disposable tableware, food packaging and parts of electronic devices. Poly(butylene succinate) (PBS), being a commercially available biodegradable polymer, has attracted much attention in recent years.

The application of biodegradable plastics has been restricted due to their relatively lower strength compared to conventional plastics such as polypropylene and polyethylene. Therefore, continuous natural fibers, such as kenaf, bamboo and hemp fibres, has been used as the reinforcement to prepare "green composites"^{1,2)}. In this study, hemp fibers were selected as a reinforcement of the biodegradable composites due to their high strength and excellent thermal stability.

Nanoclay is organically modified layered silicate, composed of stacked platelets with van der Waals force between the neighboring layers. The thickness of each layer is about 1 nm, diameter from 10 nm to several microns, and the interlayer space around 1 nm depending on the modification methods³⁾. Due to its high aspect ratio and good physical and thermal properties, nanoclay has the potential for exceptional improvements in barrier, flammability resistance, thermal and mechanical properties for polymer composites at very low filler loading⁴⁾. The reinforced properties depend largely on the dispersion degree of silicate platelets within polymer matrix, which in turn is a function of the polymer-nanoclay compatibility⁵⁾.

In this paper, melting intercalation method was employed to fabricate the PBS/nanoclay composites. The dispersion degree of nanoclay in the PBS matrix was investigated by X-ray diffraction. The PBS/hemp/nanoclay hybrid composites were prepared by pultrusion method⁶⁾. Tensile properties of composite materials were also characterized.

2 Experiments

2.1 Materials Aliphatic polyester poly(butylene succinate) (PBS) was supplied by Showa HighPolymer Co. (Japan) under the trade name

Bionolle (grade #1020). The chemical structure is shown in Figure 1(a). The weight-average molecular weight is about 1.4×10^5 . The glass transition temperature, crystallization temperature and melting temperature are -32°C , 76°C and 115°C , respectively.

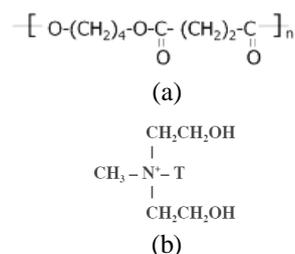


Fig. 1 Chemical structures of (a) PBS and (b) organo-modifier used in Cloisite 30B. T is hydrogenated tallow.

Continuous hemp fibre with a diameter of 120 μm was provided by Hemp Revo, Inc. Cloisite 30B, an organically modified montmorillonites, supplied by Southern Clay Products (USA), was used as the reinforcement. The chemical structure of the organo-modifier is presented in Figure 1(b). The average diameter is around 7 μm and the interlayer space is 1.85 nm ($d_{001} = 1.85 \text{ nm}$), as released by the company.

2.2 Melt intercalation Before processing, PBS pellets and nanoclay were kept in a ventilated oven at 70°C for more than 12 h to eliminate the humidity. The nanoclay and PBS pellets were firstly dry-mixed by shaking them in a plastic bag manually. The mixture was then feed into a single screw extruder, which was operated at 150°C and rotated at 20 rpm. The mixture yielded PBS/nanoclay composite strands after extrusion, which was quenched in a water bath at room temperature to quickly crystallize and make the nanocomposites strand brittle. The color of the strands turned to yellowish, compared to pure PBS. The nanocomposites strands were pelletized by a scissor. Then the pellets was cleaned by DI water in an ultrasonic bath for 10 min, then filtered and washed by acetone. Finally, the pellets were dried at 70°C for more than 12 h to remove water. For comparison, twin screw extruder was also employed to mix PBS and nanoclay.

2.3 Pultrusion method Compared with the common composite production processes, pultrusion offers the advantage of continuous production of profiles with a constant cross-section. Figure 2 schematically shows the

setup of the pultrusion method in this study. Different from the setup employed to produce composites with thermosetting matrix, the pultrusion is connected with a single screw extruder, so that the hybrid composites can be fabricated in one step. The experiment is operated with 150 °C extruder temperature, rotating at 5 rpm, die 120 °C, pulling speed 1 Hz, with 40 yarns of hemp.

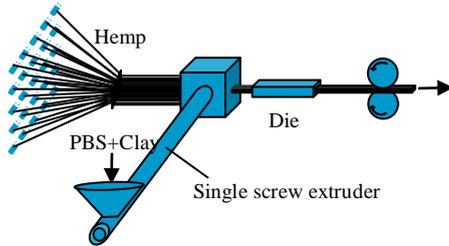


Fig. 2 Schematic drawing of pultrusion method.

Pultruded bars exhibited a poor surface quality, so they were cut into 10 cm long pieces and hot pressed in a mold. Before hot press, they were firstly dried in a vacuum oven at 70 °C for more than 12 h. A polytetrafluoroethylene (PTFE) film was used as a releasing film. A conventional spray release agent was not used because it could get in-between the individual bars and prevent them to melt or weld together. The mold was put into a hot press, having a temperature of 135 °C, and a pressure of 5 MPa was applied over a period of 3 min to ensure a better impregnation of the natural fibers by the PBS matrix. After that the press was cooled to room temperature under constant pressure of 5 MPa. The plates with 2 mm thickness were obtained.

2.4 Characterizations The dispersion degree of nanoclay in PBS matrix was investigated by X-ray diffractometer (XRD, Rint 2000, Rigaku). XRD patterns were obtained using a Cu K α radiation ($\lambda = 0.154056$ nm) with a step size of 0.004° and at a scanning rate of 0.1°/min, working at 40 kV 20 mA. The scanning 2 θ was ranging from 2 to 10°. Every sample was scanned at different spots for 5 times to ensure that the data was averaged and the figures were representative.

The tensile properties of PBS/nanoclay composites and PBS/hemp/nanoclay hybrid composites were characterized according to ASTM D638 and ASTM D3039, respectively, by a universal testing machine (Autograph AG-1, Shimadzu Co. Ltd., Kyoto, Japan) at room temperature. To produce the PBS/clay dog-bone shaped specimens, the dried PBS/nanoclay pellets were molded by an injection molding machine (Matsuda 35F-25K) at 150°C cylinder temperature, 25°C mold temperature, 19.5 MPa injection pressure and 7 mm/s injection speed.

To identify the barrier effect of nanoclay, the

PBS/hemp/clay composites were exposed to distilled water and soil, respectively, conditioned at 60°C and 60% humidity by a Super Xenon Weather Meter SX75 (Suga Test Instrument Co. LTD).

3. Results and Discussions

3.1 Dispersion of nanoclay To fabricate the PBS/nanoclay composite with good dispersion state, different times of extrusion were performed and the dispersion degree was observed by XRD. Figure 3 shows the XRD results of 2 wt% PBS/nanoclay composites extruded for once, twice and three times, which is compared to the spectrum of as-received nanoclay. Based on these observations, PBS/nanoclay composites do not show any obvious peak, which means the interlayer spaces of nanoclay has been significantly increased and the peak position of d_{001} is moved to lower than 2° (2° is the lowest limitation of 2 θ for the XRD machine) or possibly disappeared.

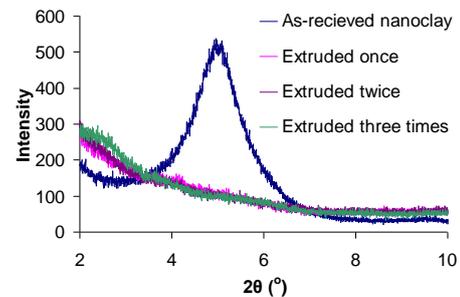


Fig. 3 XRD results of as-received nanoclay powder and 2 wt% PBS/nanoclay composites extruded by different times.

According to Bragg's law:

$$n\lambda = 2d \sin \theta$$

where d is the distance between atomic layers in a crystal, λ is the wavelength of the incident X-ray beam, θ is the angles of incidence of X-ray beam and n is an integer, the 2 θ peak position of as-received nanoclay is $4.895 \pm 0.063^\circ$, which is corresponding to the interlayer spacing of 1.8 nm, agrees with the data released by the company. When the 2 θ peak is equal to 2°, the interlayer spacing is calculated as 4.41 nm. The disappeared peak of PBS/nanoclay composites means that the nanoclay has been either completely exfoliated or well intercalated that the interlayer spacing is higher than 4.41 nm.

The melting intercalation mechanism is schematically shown in Figure 4. There are three cases after the melt mixing of nanoclay and polymer matrix. If the compatibility between nanoclay and polymer is very poor, there is no interaction between them. The clay particles will distribute in the polymer matrix like those conventional particles. The XRD peak will remain

the same position. For most of the cases, the clay particles have been organically modified before mixing with polymer matrix. The compatibility between clay and matrix is improved, so the polymer matrix can intercalated into the gallery space of clay and force the interlayer spacing to increase. Thus, the XRD peaks position move to lower angle or even disappear, depending on the extent of intercalation. Ideally, when the interaction between clay and matrix is tremendous, all the silicate layers are fully exfoliated and become single layered randomly dispersed high aspect ratio platelets.

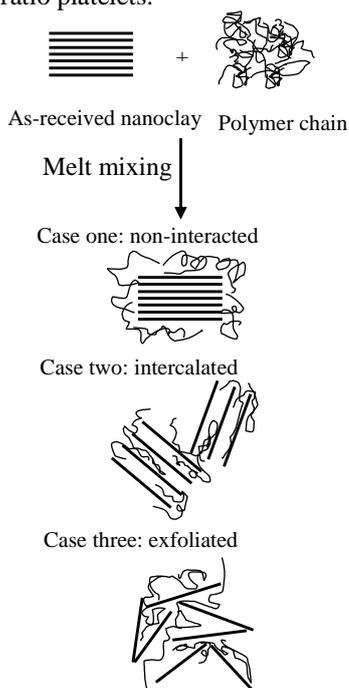


Fig. 4 Schematic drawing of melting intercalation mechanism.

Figure 3 and some repeating experiments show that the spectrum are essentially same for 2 wt% PBS/nanoclay composites extruded by different times. So, it seems the compatibility between nanoclay and PBS is satisfactory. The melting intercalation method is effective in fabricating PBS/nanoclay composites. The dispersion degree of nanoclay is intercalation-exfoliation.

Figure 5 shows the XRD spectrum of PBS/nanoclay composites extruded for once with different clay content. With increase the clay content, the spectrum do not change much for 2 wt%, 4 wt% and 6 wt% PBS/clay composites. The curves are smooth and no obvious peak appears, which means the dispersion of clay is satisfactory when the clay content is up to 6 wt%. However, for the PBS/nanoclay composites containing 8 wt% nanoclay, two peaks appear where 2θ equals to $2.454 \pm 0.114^\circ$ and $4.03 \pm 0.227^\circ$, corresponding to 3.6 nm and 2.148 nm interlayer space, respectively. The intercalation of PBS polymer chain into the

interlayer space of nanoclay is restricted because of the high filler content. Besides, the intensity of the peak also significantly increases for 8 wt% nanocomposites. Although the intensity of the spectrum is affected by many factors, the increased peak intensity can still qualitatively indicate that there are more layers of silicate platelets presented in one clay particle as a result of poor exfoliation of nanoclay. So, the spectrum clearly indicates that the dispersion of nanoclay become rather difficult when the nanoclay content is 8 wt%.

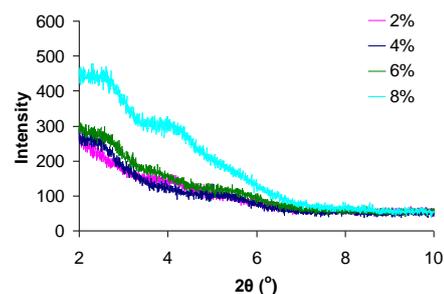


Fig. 5 XRD spectrum of PBS/nanoclay composites with different clay content.

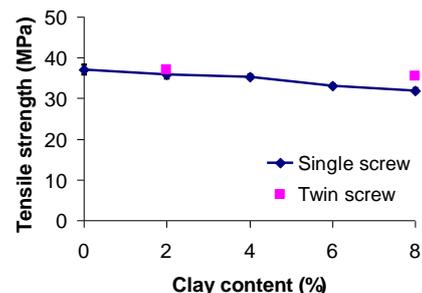
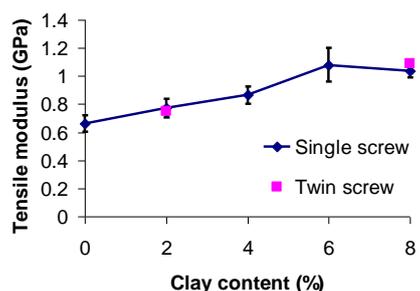


Fig. 6 Tensile properties of PBS/nanoclay composites.

3.2 Tensile properties Figure 6 shows the tensile properties of PBS/nanoclay composites of different clay content extruded by single screw extruder and twin screw extruder. Tensile modulus of nanocomposites increases with clay content and reaches 62.6% improvement with 6 wt% nanoclay. Tensile strength decreases slightly with nanoclay content. Tensile modulus of nanocomposites mainly depend on the modulus of constitute components. Tensile strength is more complex, which depend not only on the properties of

constitute components, but also on the dispersion of nanoclay and interfacial adhesion between nanoclay and PBS. To improve the dispersion of nanoclay and the mechanical properties of nanocomposites, twin screw extruder was employed and the tensile test results in Figure 6 indicates that the tensile strength of 8 wt% composites is 11.3% higher than the one prepared by single screw extruder, due to the improved dispersion of nanoclay. However, the tensile strength of 8 wt% nanocomposite prepared by twin screw extruder is still 4.1% lower than that of pure PBS. The decreased tensile strength may result from the large interface area and moderate interfacial adhesion between nanoclay and PBS.

Table 1. Tensile properties of different materials

	PBS	PBS/clay	PBS/hemp	PBS/hemp/clay
Tensile modulus (GPa)	0.66	0.87	9.9	10.3
Tensile strength (MPa)	37	35.3	107	99.3

Table 1 compared the tensile properties of pure PBS, 4% PBS/clay, 25% PBS/hemp and PBS/25% hemp/4% clay hybrid composites. By adding hemp fibre, the tensile modulus and strength has been dramatically increased. The addition of clay increased only the tensile modulus.

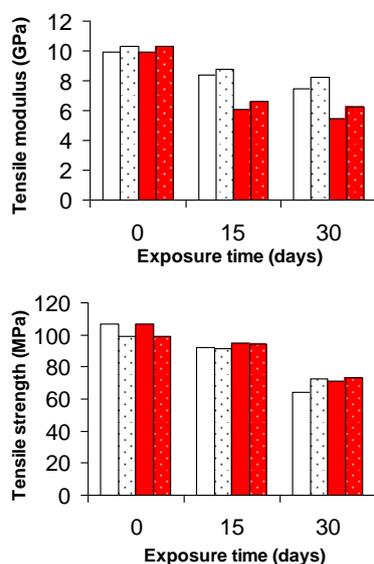


Fig. 7 Residual tensile properties of PBS/hemp/nanoclay composites. (White background: exposed to water; red background: exposed to soil; without dot: without clay, with dot: with clay)

To identify the barrier effect of clay, the residual properties of the PBS/hemp/clay composites were shown in Figure 7, after they were exposed to

water and soil environment. The tensile properties of all the studied composites were decreased after expose. For the hybrid composites, the tensile properties decreased more slowly than PBS/hemp composites because nanoclay acted as a barrier to environment. So, the tensile strength became higher than the composites without clay after expose.

4. Conclusions

Poly(butylene succinate) (PBS)/hemp/nanoclay composites were fabricated by pultrusion method plus melt intercalation. The intercalation and exfoliation of nanoclay in PBS matrix were examined. The tensile properties of PBS/nanoclay and PBS/hemp/nanoclay composites were characterized. The main findings are following:

1. Melt intercalation is an effective way to mix the PBS and clay. A satisfactory dispersion of nanoclay in PBS was obtained when the clay content was less than 8 wt%.
2. Tensile modulus increased significantly with the increase of the nanoclay content. Tensile strength decreased slightly with the increase of the nanoclay content.
3. For the PBS/hemp/nanoclay composites, the tensile properties decreased more slowly than PBS/hemp composites after expose to water or soil, because nanoclay acted as a barrier to environment.

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