

Mechanical Enhancement of Hemp/PBS Biodegradable Composites by Nanoclay

－Fabrication of PBS/Nanoclay Composites－

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1 Introduction

From the last decade of 20th century one of the rapidly growing areas for the use of plastics is packaging. Traditionally, these packaging materials are made from polyolefins, like polypropylene (PP), polyethylene (PE) and polystyrene (PS)^[1], which are non-biodegradable, leading to serious ecological problems. Therefore, the development of biodegradable materials with controlled properties is demanded. Poly(butylene succinate) (PBS), being a commercially available biodegradable polymer, has attracted much attention recently years.

In the effort to increase the mechanical properties of biodegradable polymer, continuous natural fibers, such as kenaf, bamboo and hemp fibres, has been used as the reinforcement to prepare “green composites”^[2,3]. However, continuous fibres increase only the fibre-dominant properties of the composites, such as longitudinal tensile properties. The matrix-dominant properties, such as in-plane shear properties, longitudinal compressive strength, transverse tensile properties, remain almost same with the unreinforced polymer^[4]. Thus, nanoclay and natural fibre reinforced hybrid green composite is studied in this project to improve both fibre-dominant and

matrix-dominant mechanical properties.

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 methods^[5]. 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 loading^[6]. 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 compatibility^[7].

In this paper, melt intercalation method was employed to produce the PBS/nanoclay composites. The dispersion degree of nanoclay in the PBS matrix was investigated by X-ray diffraction.

2 Experiments

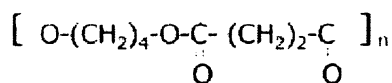
2.1 Materials

Aliphatic polyester poly(butylene succinate) (PBS) was supplied by Showa HighPolymer Co. (Japan) under the trade name Bionolle (grade #1020). The

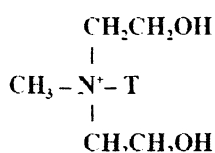
ナノクレイによるHEMP/PBS生物分解性複合材料の力学性能向上
－ PBS/ナノクレイ複合材料の成形 －

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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 $-32\text{ }^\circ\text{C}$, $76\text{ }^\circ\text{C}$ and $115\text{ }^\circ\text{C}$, respectively.



(a)



(b)

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

Cloisite 30B, an organically modified montmorillonites, supplied by Southern Clay Products (USA), were used as the reinforcement. The chemical structure of the organ-modifier is presented in Figure 1(b). The average diameter is around $7\text{ }\mu\text{m}$ and the interlayer space is 1.85 nm ($d_{001} = 1.85\text{ nm}$), as released by the company.

2.2 Nanocomposite fabrication

Before processing, PBS pellets and nanoclay were kept in a ventilated oven at $70\text{ }^\circ\text{C}$ 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 $150\text{ }^\circ\text{C}$ 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 $70\text{ }^\circ\text{C}$ for more than 12 h to remove water.

Dried PBS/nanoclay pellets were then converted into sheets with a thickness of 1.5 to 2 mm by a hot press. The mould feed with proper amount of nanocomposite pellets was heated at $170\text{ }^\circ\text{C}$ with minimal compressive pressure for 15 min to melt the nanocomposites. Then a pressure of 5 MPa was applied for 1 min to release the bubbles. After cooling, the composite sheet was fabricated.

2.3 Characterization

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 ($\lambda = 0.154056\text{ nm}$) with a step size of 0.004° and at a scanning rate of $0.1^\circ/\text{min}$, working at 40 kV 20 mA. The scanning 2θ is 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.

3. Results and Discussions

To fabricate the PBS/nanoclay nanocomposite with good dispersion state, different times of extrusion were performed and the dispersion degree was observed by XRD. Figure 2 shows the results of 2 wt% PBS/nanoclay nanocomposites 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 2θ for the XRD machine) or possibly disappeared.

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 2θ peak position of as-received nanoclay is $4.895 \pm 0.063^\circ$, which is corresponding to the interlayer spacing of 1.8 nm, agreed with the data released by the company. When the 2θ peak is equal to 2° , the interlayer spacing is calculated as 4.41 nm. The disappeared peak of PBS/nanoclay nanocomposites means that the nanoclay has been either completely exfoliated or well intercalated that the interlayer spacing is higher than 4.41 nm. Figure 2 and some repeating experiments show that the spectrum are essentially same for 2 wt% PBS/nanoclay nanocomposites extruded by different times. So, it seems the melting intercalation method is effective in fabrication a well dispersed PBS/nanoclay composites and more times extrusion do not make any obvious differences.

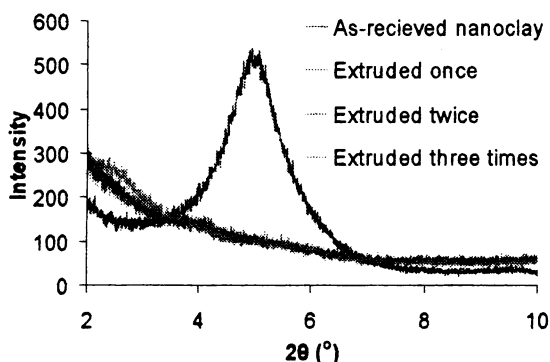


Fig. 2 XRD results of as-received nanoclay powder and 2 wt% PBS/nanoclay nanocomposites extruded by different times.

The melting intercalation mechanism is schematically shown in Figure 3. There are three cases after the melting 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 distributed in the matrix like those conventional particles. The XRD peak will remain the same position. For most cases, the clay particles has 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. Sometimes, when the interaction between clay and matrix is tremendous, not only the peak disappears but also the morphology of nanocomposites changes. All the silicate layers exfoliate and become single layered randomly dispersed high aspect ratio platelets.

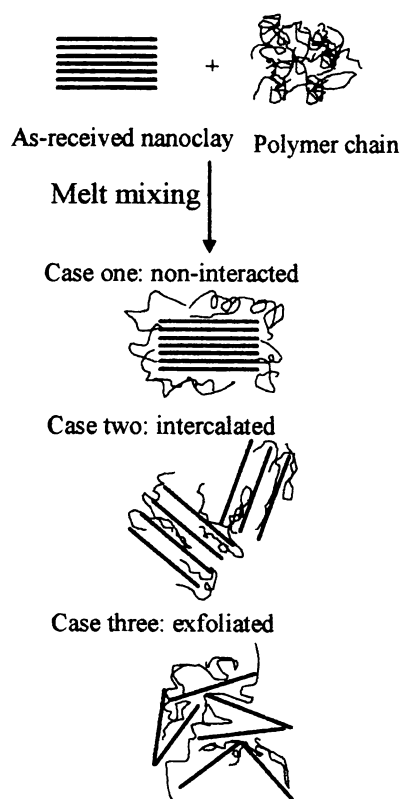


Fig. 3 Schematically drawing of melting intercalation mechanism.

For our as-prepared PBS/nanoclay composites, the XRD peak disappeared, so there are two possibilities: 1) the PBS intercalated into clay gallery and the interlayer spacing was increased to higher than 4.41 nm; 2) The nanoclay was completely exfoliated. To be able to identify the situation, the morphology of the nanocomposites has to be investigated by transmission electron microscope in the future. Based on the results available

currently, it seems the compatibility between clay and PBS is satisfactory.

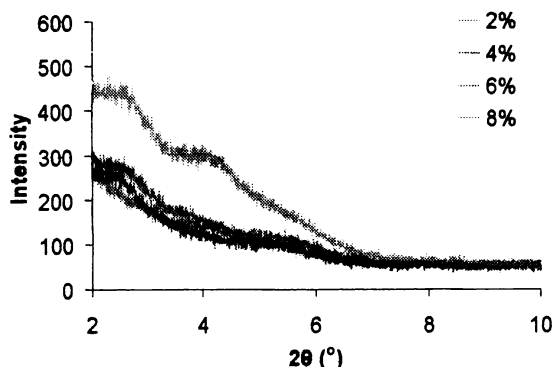


Fig. 4 XRD spectrum of PBS/nanoclay nanocomposites with different clay content.

Figure 4 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 peaks appear, which means the dispersion of clay is satisfactory when the clay content is up to 6 wt%. However, for the PBS composites containing 8 wt% nanoclay, the peak appears 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 spacing, respectively. Compared to the nanocomposites containing lower clay content, the interlayer spacing of clay decreases, because the intercalation of polymer chain into clay gallery is restricted. 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 clay. So, the spectrum clearly indicates that the dispersion of clay become more difficult when the clay content is 8 wt%. As proved by large amount of literatures^[4,6,7], the poor dispersion of clay may result in an poor mechanical, thermomechanical and barrier properties, so it is preferable to keep the clay content lower than 6 wt% in our

future study.

4. Future works

As mentioned above, the transmission electron microscope can help the identification of the composite morphology. The mechanical properties of PBS/nanoclay composites will be tested. Then, the PBS/hemp/nanoclay hybrid nanocomposite will be fabricated and characterized.

「References」

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