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In situ copolymerization of butylene succinate with twice functionalized organoclay: Thermal stability

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Abstract

Biodegradable composites consisting of poly(butylene succinate) (PBS) and layered silicate were prepared by *in situ* condensation polymerization of 1,4-butane diol and succinic acid in the presence of organoclay containing epoxy groups (TFC) and titanium(IV) butoxide as a catalyst. The intercalation and exfoliation of the clay layers in the biodegradable polyester was examined by X-ray diffraction and transmission electron microscopy. The role of the epoxy groups of TFC was investigated for the improvement of the interfacial interaction between clay and polymer matrix. The PBS/TFC composite has higher degree of exfoliation of the silicate layers than in PBS/Cloisite25A (C25A) one. In this study, the improved thermal stability was attributed to the enhanced interfacial interaction between PBS and TFC through a chemical reaction of the epoxy groups with the end groups of the PBS. Thermal stability of the nanocomposites was studied by thermogravimetric analysis, from which activation energy of thermal degradation was determined by the Kissinger's method and the Flynn–Wall–Ozawa one. The activation energy increased in the order of PBS/C25A < PBS < PBS/TFC indicating that the nanocomposite with exfoliated clay platelets was more thermally stable than that with intercalated clay platelets.

Keywords: Thermal stability; Organic–inorganic hybrid nanostructures; Biopolymers; Polymers reinforced; Polymerization

1. Introduction

Research into biodegradable polymers has gained considerable momentum in recent years, due to the increasing attraction for environmental, biomedical and agricultural applications [1]. However, the full-scale commercialization of aliphatic polyesters has not yet been realized, because of their excessively high cost and poor mechanical properties compared with those of general synthetic plastics. The utilization of clays as reinforcements for biodegradable nanocomposites was found to result in a remarkable improvement in strength and toughness [1]. In the polymer/clay nanocomposites, intercalated structures show regularly alternating layered silicates and polymer chains in contrast to exfoliated structures in which the individual clay layers are delaminated and dispersed in the polymer matrix [2–7]. A strong polymer–clay interaction destroyed and dispersed the clay layers, whereas a weak interaction preserved the clay tactoids [8–11]. The concept of coupling the functionalized clay sheet chemically with the polymer or polymer precursor can be useful in promoting the stress transfer to the reinforcement phase to improve the mechanical properties of the nanocomposite [8–11].

The twice functionalized organoclay (TFC), which is an organoclay containing epoxy groups, was synthesized and found to have a high degree of exfoliation in a polymer matrix as a result of a chemical reaction between the epoxy groups and the polymer [7,12]. In this study, PBS/TFC composites were prepared by the *in situ* polymerization. The epoxy functional group of TFC was expected to encourage chemical bonding of the TFC layers with the end groups of PBS, and thus better dispersion of the clay platelets in the polymer matrix. In addition, attention has been directed to obtain activation energy of thermal degradation from the thermo gravimetric analysis of PBS and its nanocomposites.

2. Experiment

2.1. Materials

1,4-Butanediol (BD) and succinic acid (SA) were provided from Aldrich without further purification. The organically

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modified clay, Cloisite25A (C25A), was purchased from Southern Clay Product Inc. and was purified by dissolution in ethanol at 70 °C for 4 h. The silane coupling agents, (glycidoxypropyl)trimethoxy silane (GPS) was supplied by Aldrich. Titanium(IV) butoxide (TNBT, Aldrich) was used as received to catalyze the condensation polymerization reaction.

2.2. *Synthesis of twice functionalized organoclay (TFC)*

After 3.5 g of the GPS was hydrolyzed at pH 4.0 for 4 h with acetic acid in ethanol/deionized water mixture, 10 g of C25A was added and then the mixture was heated with reflux at 70 °C for 24 h [7]. The chemical reaction between C25A and the silane compounds takes place mainly on the edge of the silicate layers where the concentration of the silanol groups is much higher than that on the plain surface. The reaction product was diluted with *n*-propanol five times to remove the soluble homocondensates, then filtered and repeatedly washed with ethanol at room temperature. The product was dried in an oven under a vacuum at 50 °C for at least 48 h [12].

2.3. *Synthesis of PBS/TFC nanocomposites via in situ polymerization*

BD and SA were added to a three neck reactor that was connected to a vacuum system via a liquid nitrogen trap. The flask was heated in an oil bath to 180 °C under mechanical stirring (300 rpm), and then the reactor was added with TNBT under nitrogen. The reactor pressure was reduced to 1 Torr step by step for 2 h, and then the reaction was continued at 1 Torr and 180 °C for 20 h. After breaking the reactor pressure, the TFC, which had already been dispersed in chloroform, was finally added to the reactor under nitrogen flow. The reactor pressure was again reduced to 1 Torr step by step for 1 h, and then the reaction was continued at 1 Torr for another 29 h. The resulting polymer was solved in chloroform, and then was precipitated twice in excess methanol. The product was dried in a vacuum oven at 60 °C to a constant weight. The PBS/TFC nanocomposite was compression molded in the module with 0.3 mm thickness at 180 °C and the pressure of 1 ton was applied using a Carver laboratory press. From these laminates, the specimens used for the mechanical tests were obtained according to the ASTM D638 standard.

2.4. *Characterization*

X-ray measurement (XRD) was carried out by using Rigaku DMAX 2500 X-ray diffractometer with reflection geometry and Cu Kα radiation (wavelength $\lambda = 0.154$ nm) operated at 40 kV and 100 mA. Transmission electron microscopy images were obtained using CM200 microscope (TEM, JEOL, Tokyo, Japan) operated at an accelerating voltage of 120 kV to observe the nanoscale structures of the various nanocomposites. Thermogravimetric analysis (TGA) was performed with TGA (Q50, Polymer Laboratories, UK). The samples were heated in the temperature range of 30–700 °C at a heating rate of 5, 10, 20 and 40 °C/min, with a controlled flow rate of dry nitrogen at 60 cm^3/min. The thermal stability of the nanocomposites was quantified by the activation energy of thermal degradation, which could be conveniently determined from the TGA data by using the equations proposed by Kissinger [13] and Flynn–Wall–Ozawa [14,15]. The tensile properties were tested on Instron 4665 ultimate tensile testing machine (UTM). The cross speed was set at 10 mm/min. At least 10 specimens were tested and the resulting values were averaged.

3. Results and discussion

If the silane molecules penetrated into the clay interlayer spacing and the grafting reaction took place inside the gallery, the interlayer spacing of TFC would be larger than that of C25A. However the d_{001} peak of TFC was almost the same as that of C25A as shown in Table 1. A possible explanation is that the silane molecules reacted mainly at the edges of the clay crystalline sheets where the content of the silanol groups was much higher than that on the plain surface of the clay sheets [16–18]. Therefore it can be said that the grafting reaction occurred mainly outside the interlayer of the clay [19,20].

Two kinds of the organoclay, TFC and C25A, were synthesized in this study to examine the effects of the epoxy groups on the XRD pattern of the PBS/clay composites, as shown in Fig. 1 and Table 1. When PBS *in situ* polymerizes with 2 wt% of TFC, the resulting nanocomposite was abbreviated as PBS/TFC2. In the same context, PBS/C25A2 represents PBS nanocomposite with 2 wt% of C25A. The intercalation of the polymer chains would increase the interlayer spacing compared with that of the clay, which would shift the XRD peak toward a lower angle. The d_{001} peak of PBS/TFC1 and PBS/TFC2 has almost same diffraction angle. When PBS/TFC2, the d_{001} spacing expanded from

Table 1
Properties of PBS/layered silicate nanocomposites

Sample	Composition (wt/wt)	d_{001} spacing of clay (Å)	Modulus (MPa)	Stress (MPa)
PBS	–		397 ± 12.3	33.8 ± 0.2
C25A	–	18.5	–	–
TFC	–	18.5	–	–
PBS/C25A1	99/1	26.5	499 ± 15.7	33.4 ± 1.4
PBS/C25A2	98/2	26.7	533 ± 16.4	33.3 ± 1.7
PBS/TFC1	99/1	28.5	584 ± 20.1	32.2 ± 0.3
PBS/TFC2	98/2	28.6	687 ± 14.9	34.9 ± 2.2