Preparation and Characterization of Poly(hydroxybutyrate-co-hydroxyvalerate)–Organoclay Nanocomposites

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ABSTRACT: This study describes the microstructure and thermal and mechanical properties of poly(hydroxybutyrate-co-hydroxyvalerate) (PHB/HV)–organoclay nanocomposites prepared by melt intercalation using Cloisite 30B, a monotallow bis-hydroxyethyl ammonium-modified montmorillonite clay. X-ray diffractometry and transmission electron microscopy analyses clearly confirm that an intercalated microstructure is formed and finely distributed in the PHB/HV copolymer matrix because PHB/HV has a strong hydrogen bond interaction with the hydroxyl group in the organic modifier of Cloisite 30B. The nanodispersed organoclay also acts a nucleating agent, increasing the temperature and rate of crystallization of PHB/HV; therefore, the thermal stability and tensile properties of the organoclay-based nanocomposites are enhanced. These results confirm that the organoclay nanocomposite greatly improves the material properties of PHB/HV. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 525–529, 2003

Key words: organoclay; nanocomposites; biodegradable; crystallization

INTRODUCTION

The development of commercially viable biodegradable plastics is an important effort toward the preservation and revitalization of our global environment because plastics compose an estimated 18% by volume of solid waste. A class of biodegradable plastics receiving considerable attention is poly(hydroxyalkanoates) (PHAs), in particular poly(3-hydroxybutyrate) (PHB) and copolymers poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB/HV).[1–6] Although PHAs are biodegradable (microorganisms are able to rapidly degrade PHB and PHB/HV to carbon dioxide and water[3]), their rate of chemical hydrolysis is slow. This combination of properties is advantageous. These plastics are produced by microbes (including soil bacteria, estuarine microflora, blue green algae, and various photobiological systems) as a natural part of their metabolism.[4] Although the proportion of PHA in cells typically is <30%, under fermentation conditions of carbon excess and nitrogen limitation, PHA can comprise as much as 70% of the dry cell weight.[5] The typical feedstock for PHB production is glucose. When proprionic acid is added to the growth medium during conditions of nitrogen limitation, the polymer produced is the PHB/HV copolymer. Bacterially produced PHB/HV copolymers have been demonstrated to be randomly sequenced.[7]

PHB has attracted some commercial interest because it possesses properties similar to synthetic thermoplastics, such as poly(propylene); however, PHB is rarely used commercially because of its brittle behavior and lack of melt stability.[3] These drawbacks have furthered interest in PHB/HV copolymers, which are tougher and have greater melt stability.[4] However, crystallization rates of PHB/HV copolymers are very slow compared with the time scale of most industrial molding and fabrication processes. Slow crystallization rate is related to slow nucleation rate and to slow linear growth rate resulting from inclusion of, for example, HV units in the PHB crystalline lattice.[8]

The development of commercial applications for PHB/HV copolymer requires improving crystallization and processing behaviors, reducing overall cost, and further enhancing mechanical properties. One approach for overcoming these limitations is to incorporate the silicate layer into the polymer and create polymer–clay nanocomposites. The main advantage of nanocomposites is that enhanced mechanical properties can be obtained with a small amount of clay because of the large contact area between polymer and clay and because the layered structure of clay with a high aspect ratio provides outstanding barrier properties that can not be found in polymer composites filled with glass fiber.[8] More importantly, clay is environmentally friendly, naturally abundant, and economical. Nanocomposites have been synthesized using various methods, including solution intercalation,

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$$\begin{array}{c} T \\ | \\ H_3C \longrightarrow N^+ \longrightarrow CH_2CH_2OH \\ | \\ CH_2CH_2OH \end{array}$$
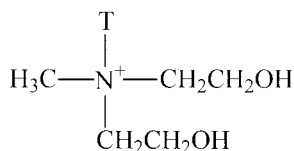
Tallow (~65% C18, ~30% C16, ~5% C14) CEC=90meq/100g

Figure 1 Chemical structure of the cation in Cloisite 30B.

in situ polymerization, or melt intercalation, for many polymeric systems ranging from thermoplastic to thermosetting polymers. Among the preparation methods, melt intercalation is considered the promising approach for the fabrication of nanocomposite because of its versatility, its compatibility with current polymer processing equipment, and its environmental friendliness due to the absence of use of any solvent.

In this study, we fabricated and characterized the biodegradable PHB/HV–organoclay nanocomposite to realize the combination of the biodegradability of PHB/HV with enhanced mechanical and crystallization behaviors and high stability afforded by the organoclay. The PHB/HV nanocomposites prepared by melt intercalation were characterized by X-ray diffractometry (XRD) and transmission electron microscopy (TEM) for microstructure determination, and by differential scanning calorimetry (DSC) for analysis of crystallization behaviors. The tensile test and thermogravimetric analysis (TGA) measurements were also performed.

EXPERIMENTAL

Materials

Biodegradable PHB/HV copolymer (Biopol D300G) in the form of granules containing ~6% HV content, with a melt flow index (MFI) of 8 g/10 min (based on ASTM 1238-906; 2.1 kg loaded at 170°C), was used. Cloisite 30B (organoclay), which is organically modified montmorillonite (MMT), was chosen as the clay for the nanocomposites. A product of Southern Clay Company, Cloisite 30B contains ammonium cations (e.g., methyl tallow bis-2-hydroxyethyl ammonium); the chemical structure of these ammonium cations is shown in Figure 1.

Preparation of PHB/HV Nanocomposites

Cloisite 30B organoclay and PHB/HV copolymer were dried under a vacuum at 80°C for at least 24 h. Then, 0, 1, 2, and 3% weight ratios of organoclay and PHB/HV copolymer (D300G, 30B-1, 30B-2, and 30B-3, respectively) were dry mixed before melt blending. The melt-blending process was carried out in a Brabender Mixer at 165°C and 50 rpm for 15 min. The

mixed nanocomposites and PHB/HV copolymer were taken out of the mixer, cooled at room temperature, and then cut into small pieces to prepare specimens for characterizations.

Characterization

The dispersed state of the silicate layers in the matrix polymer was evaluated by XRD and TEM. XRD spectra were obtained with a Rigaku X-ray generator (CuKα radiation, with $\lambda = 1.5406$ Å) with a 2θ scan range of 0 to 10° at room temperature. The specimens of nanocomposite for XRD measurement were obtained in sheet form using a hydraulic press at 165°C. The TEM images were obtained with a Jeol JEM-2000EX TEM. The specimens were cut into ultrathin slices at room temperature with a Reichert-Jung Ultracut Microtome. No staining process was used.

Crystallization and melting behaviors of nanocomposites were investigated by DSC (TA Q-100). The samples first were heated from room temperature to 200°C at a rate of 20°C/min under a nitrogen atmosphere and held in the melt state for 5 min to destroy any residual nuclei. Then, the samples were cooled at various cooling rates (i.e., 1, 5, 10, and 0°C/min). The thermograms of these samples were analyzed to estimate the crystallization kinetics. The samples crystallized at 10°C/min cooling rate were heated again at a rate of 10°C/min to obtain the melting endotherms.

A TGA test for thermal stability of nanocomposites was performed with a Dupont TA 2200. The samples were heated from room temperature to 400°C at 10°C/min under a nitrogen atmosphere.

Tensile strength (σ_b), Young's modulus, and elongation at break (ε_b) were measured as the mechanical properties of the nanocomposite. Tensile tests were performed with a universal tensile machine (Instron UTM) according to the test method of ASTM D 1708. Five specimens for each sample were tested at the crosshead speed of 5 mm/min, and averaged values were used. The specimens for the mechanical test were made by injection molding in a Mini Max molder (CSI) at 165°C.

RESULTS AND DISCUSSION

Microstructure of Nanocomposites

The microstructure of nanocomposites is demonstrated by the enlargement degree of *d*-spacing distance. The *d*-spacing distances can be determined by the diffraction peak and the position of d_{001} in the XRD pattern. The values of the latter can be determined by the Bragg equation ($2d_{001}\sin\theta = \lambda$), where d_{001} is the interplanar distance of (001) diffraction face, θ is the diffraction position, and λ is the wavelength. In our practice, it is believed that the greater the *d*-spacing
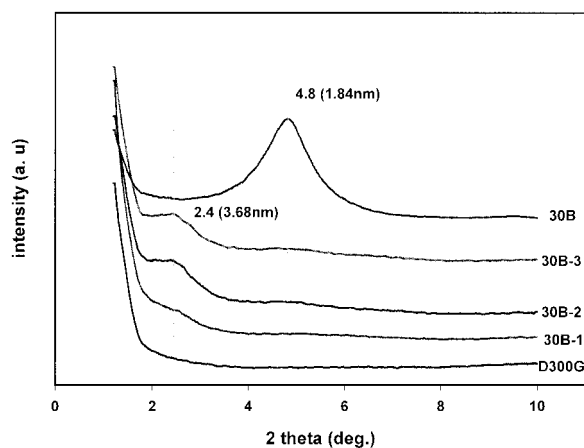
Figure 2 XRD patterns of PHB/HV–clay nanocomposites with various Cloisite 30B contents.

distance, the greater the interaction of polymer molecular chains with clay layered silicate. That is to say, the interaction of polymer molecular chains with the silicate layer can be expressed relatively by the d-spacing distance of d_{001}.

The XRD patterns of the PHB/HV–organoclay nanocomposites with varying amounts of Cloisite 30B are shown in Figure 2. The d-spacing for PHB/HV–organoclay nanocomposites with 2 and 3 wt % Cloisite 30B increased from 1.84 nm ($2\theta = 4.8°$) for the original Cloisite 30B (30B) to 3.68 nm ($2\theta = 2.4°$) for the nanocomposites, which clearly indicates that PHB/HV copolymer chains are intercalated into the silicate layers. This phenomenon is attributed to the favorable interaction between PHB/HV and Cloisite 30B that originates from the strong hydrogen bonding between the ester carbonyl group of PHB/HV and the hydroxy group in the gallery of Cloisite 30B, as shown the chemical structure in Figure 1. Other researchers reported similar results in polymer–clay nanocomposite preparation; for example, strong polar interactions, especially hydrogen bonding, critically affects the formation of intercalation and exfoliated hybrids via polymer intercalation.[10–12]

The TEM micrographs presented in Figure 3, which show the typical result of a TEM bright field-image of PHB/HV copolymer in which dark entities are the cross section of intercalated silicate layers, confirm the XRD results just presented. The TEM image of the PHB/HV–organoclay nanocomposite with 3 wt % organoclay (30B-3) exhibits good dispersion of clay in the polymeric matrix and stacked and intercalated silicate layers with large anisotropy.

Crystallization of Nanocomposites

The effect of the clay content on the crystallization behavior of PHB/HV copolymer was studied by DSC cooling scans; these results are shown in Figure 4 and

Table I. Both the nanocomposites and the PHB/HV copolymer have only one exothermic peak, but the peak form and peak temperature of the nanocomposites differs from those of the PHB/HV copolymer matrix. The presence of the silicate layers in the nanocomposites increases the crystallization temperature of PHB/HV. It can be concluded that the clay increases the crystallization rate and has a strong heterophase nucleation effect on the polymer matrix. The nanoscale silicates act as nucleating agents, facilitating the heterogeneous crystallization process. The fact that the silicates are well dispersed leads to an increased number of sites available for nucleation, thereby enhancing the crystallization rate and altering the kinetics. The DSC melting point (T_m) of the nanocomposites occurs at a lower temperature than that of PHB/HV copolymer, which may be related to a reduction in crystallite size in the presence of nanodispersed layers.[13,14]
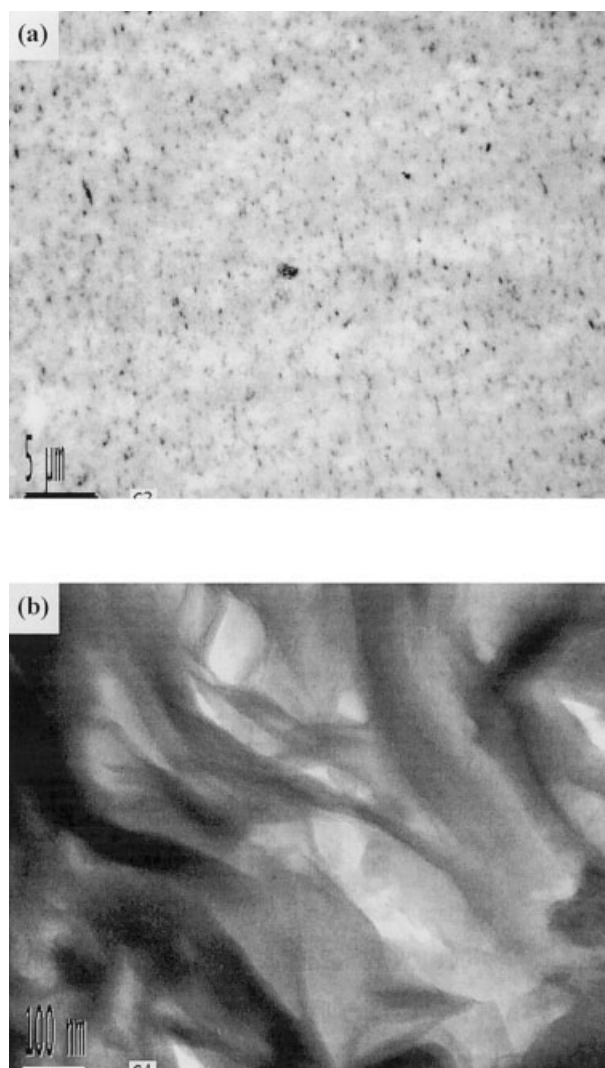

Figure 3 TEM images of PHB/HV–clay nanocomposite with 3 wt % Cloisite 30B.
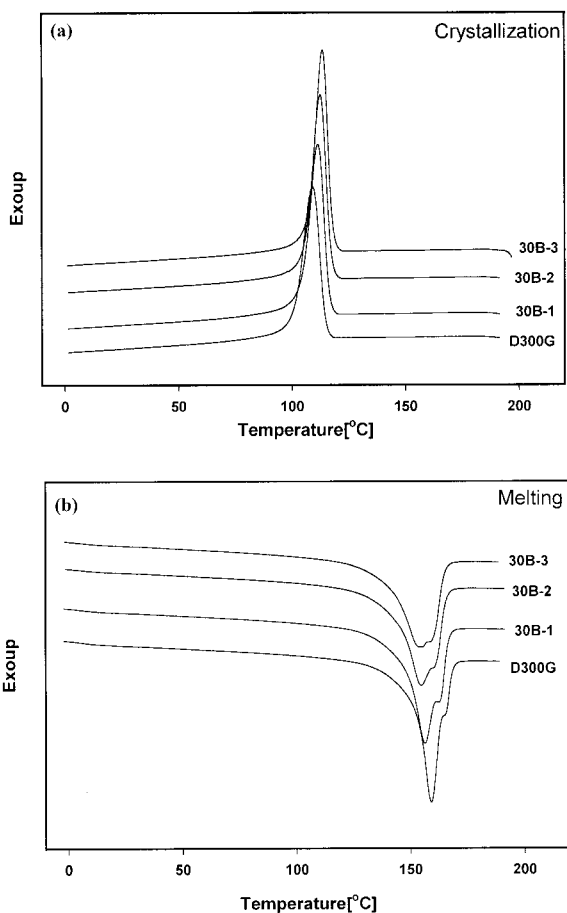
Figure 4 Crystallization and melt behavior of PHB/HV–clay nanocomposites with various Cloisite 30B contents at a scan rate of 10°C/min.

Figure 5 Crystallization behavior of PHB/HV and PHB/HV–nanocomposite with 2 wt % Cloisite 30B at various scan rates.

The nonisothermal crystallization behaviors of PHB/HV copolymer and nanocomposites at various cooling rates are presented in Figure 5. The crystallization temperature (T_c) shifts, as expected, to lower temperature with an increasing cooling rate for both pure PHB/HV copolymer and the nanocomposites. A shorter time for the polymer to crystallize at the higher cooling rate indicates that the crystallization occurred at a lower temperature. This result suggests that the motion of polymer molecules could not follow the cooling temperature when the specimens are cooled quickly. When comparing T_cs of pure PHB/HV copolymer and the
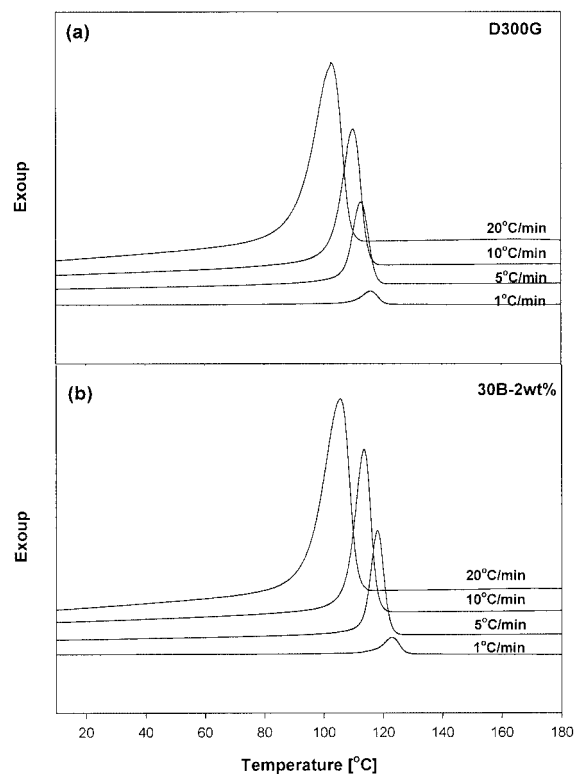
nanocomposite with 2 wt % clay (30B-2) for a given cooling rate, that of the nanocomposite is higher than that of pure PHB/HV copolymer. This difference indicates that the addition of organoclay into PHB/HV increases the crystallization rate of PHB/HV. This change is because the silicate layers of organoclay easily interact with the PHB/HV chain segments; therefore, the crystallization of PHB/HV can occur at a higher temperature. This result is clear evidence of the nucleating effect of the organoclay in PHB/HV; that is, the layers of organoclay act as heterogeneous nuclei during the nonisothermal crystallization process. Given the slow crystallization rate of PHB/HV, the addition of organoclay has the positive effect of enhancing the crystallization rate.

TABLE I
Thermal and Tensile Properties of PHB/HV–Organoclay Nanocomposites

Sample[a]	T_c (°C)	T_m (°C)	Young's modulus (MPa)	σ_b (MPa)	ε_b (%)
D300G	109.2	159.1	481	31	8.5
30B-1	111.4	156.4	555	32	7.6
30B-2	113.1	154.7	730	35	7.7
30B-3	115.2	154.3	795	33	5.6

[a] D300G denotes the PHB/HV copolymer; 30B-1, 30B-2, and 30B-3 denote the PHB/HV–Cloislite 30B nanocomposites with 1, 2, and 3 wt % ratios of organoclay to PHB/HV copolymer, respectively.
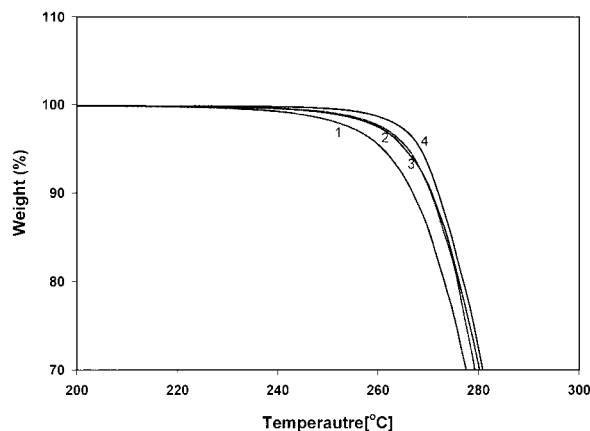
Figure 6 TGA thermograph of PHB/HV–clay nanocomposites with various Cloisite 30B contents.

Thermal Stability

The silicate layers of clay in the polymer matrix are believed to increase the barrier properties by creating a maze or tortuous path that retards the progress of gas molecules through the polymer matrix. Thermal stability of nanocomposites was assessed by TGA at a heating rate of 10°C/min under N_2 flow, and the results are shown in Figure 6. The weight loss due to the formation of volatile degradation products was monitored as a function of temperature. The 3% weight loss of pure PHB/HV copolymer started at 252°C, and that of the nanocomposites with 1 and 2% organoclay (30B-1 and 30B-2, respectively) increases to 259°C. The nanocomposite with 3% organoclay (30B-3) has a much higher weight loss temperature of 263°C. The increase in thermal stability observed for nanocomposites may be related to the nanodispersion of the silicate layers. The well-dispersed and layered structure of clay in the polymer matrix is thought to be an effective barrier to the permeation of oxygen and combustion gas, which improves the thermal stability.

Mechanical Properties

Tensile properties [i.e., Young's modulus (E), stress at break (σ_b), and elongation at break (ε_b)] were measured and are reported in Table I. The tensile strength (E) is greatly improved with only a little increase in the stress at break (σ_b) for the PHB/HV copolymer–organoclay nanocomposites (30B-1, 30B-2, and 30B-3) compared with the PHB/HV copolymer alone (D300G). Even at low clay content (i.e., 3 wt % organoclay; 30B-3), E is significantly increased from 480 MPa to >790 MPa. Small amounts of nanodispersed clay act as effective reinforcing filler to enhance the me-

chanical properties of the PHB/HV copolymer. This improvement is also attributed to the strong hydrogen bonding between PHB/HV copolymer and Cloisite 30B, indicating the importance of the strong interaction between polymer and organoclay for the formation of nanocomposites with fine dispersion, as seen in the XRD and TEM results.

CONCLUSIONS

PHB/HV–organoclay nanocomposites were prepared by a melt intercalation method using Cloisite 30B as the organoclay. An intercalated structure was formed due to the strong hydrogen bond interaction between PHB/HV and the organoclay. The nanodispersed organoclay increased both the temperature and rate of crystallization of PHB/HV, indicating that the organoclay was an effective nucleating agent in the polymer matrix. Moreover, the nanocomposites showed a significant increase of tensile properties, with good thermal stability. Given the very slow crystallization behavior and poor mechanical properties of PHB/HV copolymer, the fabrication of an organoclay nanocomposite is an effective way to extend the applications of the biodegradable PHB/HV copolymer. The effect of organoclay on the biodegradability of PHB/HV should be analyzed further in a future report.

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