Research Article

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Fabrication and characterization of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) modified with nano-montmorillonite biocomposite

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Abstract: In this study, a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) modified with nano-montmorillonite biocomposite (MMT/PHBH) was fabricated by solution-casting method. The results showed that the addition of MMT increased the crystallinity and the number of spherulites, which indicated that MMT was an effective nucleating agent for PHBH. The maximum decomposition peak of the biocomposites moved to a high temperature and residue presented an increasing trend. The biocomposites showed the best thermal stability at 1 wt% MMT. Compared with PHBH, 182.5% and 111.2% improvement in elastic modulus and tensile strength were obtained, respectively. Moreover, the oxygen permeability coefficient and the water vapor permeability of MMT/PHBH biocomposites decreased by 43.9% and 6.9%, respectively. It was also found that the simultaneous enhancements on the crystallizing, thermal stability, mechanical, and barrier properties of biocomposites were mainly caused by the formation of intercalated structure between PHBH and MMT.

Keywords: poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), nano-montmorillonite, mechanical properties, barrier properties

1 Introduction

With the aggravation of plastic pollution and the consumption of petroleum resources, biopolymers have attracted more attention as a substitute for petroleum synthetic materials (1,2). Among the numerous kinds of biodegradable polymers, polyhydroxyalkanoates (PHAs), synthesized by a variety of bacteria from renewable resources and a natural polymer biomaterial (3), is considered the most promising representative of the eco-friendly polymers. As an alternative to traditional plastics, PHAs with biodegradability have been widely used for packaging, coating applications, and adhesives (4).

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is the best-known type of PHAs (5). However, the application of PHBH is limited because of high crystallinity, poor thermal stability, and narrow processing windows (6). Recently, some studies have been reported for improving the performance of biopolymer, especially nanofillers (7). Nanofillers exfoliate interfacial area and surface energy which affects the overall properties of the composites. Several methods have been used for production of biopolymer nanocomposites including solution intercalation (4), *in situ* polymerization (8), and melt intercalation (9). As efficient nanofillers, nanoclays have received great deal of attention, as they are cost-efficient, chemically and thermally stable (10). Moreover, it has large *d*-spacing, in which more polymer chains are allowed to enter the interlayer spacing. Thus, it forms a strong bond with the polymer matrix, which results in a well mechanical performance (11). The high aspect ratio clay layer structure provides excellent barrier properties (12,13).

In this study, a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) modified with nano-montmorillonite biocomposite (MMT/PHBH) was fabricated by solution-casting method. To investigate the effects of MMT on PHBH, the changes in the physical properties and structural characteristics of MMT/PHBH biocomposites were examined by changing the nanofiller concentration. Moreover, the crystallization behavior of the biocomposites was characterized

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using positive hot-stagemicroscopy. The effects of biocomposite formation on mechanical, thermal properties, water vapor, and oxygen permeability were also presented.

2 Materials and methods

2.1 Materials

PHBH contained 11 mol% 3-HH ($M_w = 6 \times 10^5$) and was purchased from Japan Kaneka Co., Ltd. Nanometer montmorillonite was produced by Zhejiang Fenghong new materials Co., Ltd. Anhydrous ethanol and 95% ethanol were produced by Tianjin Fengchuan chemical reagent technology Co., Ltd. Trichloromethane and dichloromethane were produced by sinopsin chemical reagent Co., Ltd.

2.2 Preparation of MMT/PHBH biocomposite

The solution-casting method was applied for preparation of the biocomposites as it ensures optimal dispersion of the nanofillers, and therefore, ensures maximum interaction of the filler and matrix. First, MMT was dissolved by the addition of 50 mL chloroform, magnetically stirred for 15 min, sonicated by the ultrasonic processor for 0.5 h to obtain a transparent solution. Then, 1.5 g purified PHBH was added to the solution and magnetically stirred for 30 min until the PHBH dissolved. Finally, the resultant solution was cast at 35°C onto a glass plate. After being dried, the MMT/PHBH biocomposite was vacuum-dried at

65°C for 12 h to completely remove residual chloroform solvents. The content of nano-MMT (based on PHBH) in biocomposite is 1, 3, 5, and 7 wt% and labeled as 1 wt% MMT/PHBH, 3 wt% MMT/PHBH, 5 wt% MMT/PHBH, and 7 wt% MMT/PHBH, respectively.

2.3 Characterization of MMT/PHBH biocomposite

FT-IR spectra were recorded on a TENSOR 27 FTIR Spectrometer (Brock spectrometers, Germany) with the wave number range of 400–4,000 cm^{-1} . SEM (Nanosem 430, FEI, U.S.) was used to analyze surface and cross-section morphology of the samples. The X-ray diffraction (XRD) of biocomposite was performed to test the crystallinity use X-ray diffractometer (D/max-2500, Rigaku Corp., Japan) in Cu-K α radiation at 40 kV and 100 mA. The crystallization behavior of the biocomposite was characterized using positive hot-stagemicroscopy (POM, DM4000, Leica, Germany).

2.4 Thermal stability

TGA was performed on thermogravimetric analyzer (TGA Q500, TA Instruments, U.S.) in a dynamic nitrogen atmosphere.

2.5 Mechanical properties

Mechanical properties of film samples were measured using an Instron Universal Testing Machine (Model

Figure 1: (a) FTIR spectra of PHBH, MMT, and MMT/PHBH biocomposites; (b) the local magnification curve of FTIR spectra.

3369, Instron Engineering Corp., USA) according to ASTM Method D 882-2010. The sample length and width were 175.00 and 10.00 mm, respectively.

2.6 Water vapor transmission rate and oxygen permeability

Water vapor transmission rate (WVTR) was conducted according to GB-T1037-1988 standard method. WVTR was carried out at 38°C and 90% relative humidity. The values were the average of three measurements. Oxygen permeability was evaluated using a gas permeability tester (GDP-C, Brugger, Germany). The diameter of the film used for the test was more than 120 mm and there were no defects such as holes and cracks, and so on.

3 Results and discussion

3.1 FT-IR analysis

Figure 1a shows the FT-IR spectra of PHBH, MMT, and MMT/PHBH biocomposites. The band at $1,717\text{ cm}^{-1}$ was

the characteristic peak of stretching vibration of C=O (14). With MMT content increasing, the intensity of C=O peak first increased and then decreased and began to shift toward lower wave number (Figure 1b). This was due to hydrogen bonding interaction between the hydroxyl group of MMT and the carbonyl group of the PHBH (15). The peaks at $2,976$, $2,932$, and $2,873\text{ cm}^{-1}$ were assigned to the C–H stretching vibration peaks of $-\text{CH}_3$. With increased MMT addition, the intensity of peaks at $2,976$, $2,932$, and $2,873\text{ cm}^{-1}$ decreased, indicating that the PHBH chains intercalated between the silicate layers of MMT; the restriction effect of the layers decreased in peak intensity (16–18). In addition, it was also found that the 1 wt% MMT/PHBH has the highest intensity at $1,118\text{--}916\text{ cm}^{-1}$ and corresponded to Si–O stretching vibration peak.

3.2 Morphological analysis

SEM images of the surface and cross-section of the PHBH and the MMT/PHBH samples are shown in Figure 2. The surface of 1 wt% MMT/PHBH was uniform, smooth, free of pores, and compact. For 3 wt% MMT/PHBH, the surface was slightly rough but had no pores. Generally, in the MMT/PHBH biocomposites, good dispersion of nano-

Figure 2: Scanning electron microscopy images of the surface and cross-section of PHBH and MMT/PHBH biocomposites: (a) PHBH, (b) 1 wt% MMT/PHBH, (c) 3 wt% MMT/PHBH, (d) 5 wt% MMT/PHBH, and (e) 7 wt% MMT/PHBH.

MMT at 1–3 wt% loading was obtained (Figure 2b and c). As the filler content was increased (5–7 wt%), the size of the agglomerates increased and the surface of the biocomposites showed increased surface porosity and roughness; this was especially evident in the 7 wt% MMT/PHBH biocomposite.

The cross-section of PHBH shows an undulating and uneven morphology with a distinct porous structure. A white layer (red circle shows nano-MMT layer) was found for 1 wt% MMT/PHBH, 3 wt% MMT/PHBH, and 5 wt% MMT/PHBH biocomposite; this indicated that some PHBH molecular chains were successfully intercalated to the nano-MMT layer by solution intercalation (19), which is consistent with the results in XRD. From the cross-sectional morphology of 1 wt% MMT/PHBH and 3 wt% MMT/PHBH biocomposites, it can be seen that the distribution of MMT in the composites was relatively uniform, and the section was dense. With the content of MMT increasing (more than 5%), the interface of MMT and PHBH was clear due to the relatively weak interfacial binding force. Moreover, the cross-sectional structure of biocomposite was loose and the combination of the two phases was poor. It was also found that the dispersibility of MMT in the polymer matrix deteriorated, resulting in significant agglomeration and stress concentration.

3.3 XRD analysis

The crystallinity of MMT/PHBH biocomposites is shown in Figure 3. The XRD patterns of PHBH possessed two characteristics peaks at 13.4° and 16.9° , assigning to (020) and (110) planes, respectively. The MMT exhibited a single (001) diffraction peak at 4.75° and two more diffraction peaks at 7.14° and 19.75° , simultaneously (16). The diffraction peak of MMT (001) in MMT/PHBH biocomposites decreased because of the polymer chain incorporated inside the MMT galleries resulting in some expansion of silicate layers. The expansion behavior was due to decrease in the degree of coherent layer stacking (20). The lowering and displacement of the peaks indicated that PHBH and nano-MMT form a disordered intercalated structure.

XRD characterization of nano-MMT and MMT/PHBH biocomposites was conducted, and the data were summarized in Table 1. The interlayer spacing d_{001} of nano-MMT was 1.86 nm. Compared with MMT, MMT/PHBH biocomposites have the larger interlayer spacing (1.94–2.13 nm), proving that in the composite process some molecular chains of PHBH infiltrated into the silicate

Figure 3: The X-ray diffraction pattern of MMT, PHBH, and MMT/PHBH biocomposites.

layers of MMT and formed intercalated biocomposite (21). Nevertheless, because of the agglomeration of nano-MMT, the interlayer spacing of d_{001} decreased when the content of nano-MMT was more than 5% in biocomposites. It can be seen from Table 1 that PHBH had no obvious characteristic diffraction peak between 3° and 10° ; the PHBH/MMT nanocomposite only shows a (001) characteristic diffraction peak of nano-MMT. This showed that PHBH and nano-MMT formed a disordered intercalation structure. With the increase in the amount of nano-MMT added, the peak position of the (001) diffraction peak shifted to a small angle by a certain distance due to the expansion of the interlayer spacing of nano-MMT. In addition, due to the unevenness of the spacing of the nano-MMT layers in the PHBH/MMT nanocomposite, the half-value width was widened, showing a wider diffraction peak. Compared with PHBH, the crystallinity of PHBH/MMT nanocomposite increased, and with the increase of nano-mmt addition, the crystallinity of PHBH/MMT nanocomposite increased first and then decreased. It showed that the addition of MMT could promote PHBH crystallization and acted as an effective nucleating agent.

3.4 Polarized optical microscopy

Figure 4 shows POM images of the PHBH and MMT/PHBH biocomposites. In PHBH, the crystal had a characteristic band and a dense cross texture. The large and perfect spherulites in Figure 4a were observed because of the sufficient growth space. After adding nanofillers, the spherulite dimension in MMT/PHBH significantly became

Table 1: The X-ray diffraction data of MMT, PHBH, and MMT/PHBH biocomposites

Samples	2θ	Half-peak width	d_{001} (nm)	Diameter (nm)	Crystallinity (%)
MMT	4.75	0.62	1.86	12.73	—
1 wt% MMT/PHBH	4.15	0.53	2.13	14.71	50.54
3 wt% MMT/PHBH	4.34	0.68	2.04	11.59	51.44
5 wt% MMT/PHBH	4.44	0.56	1.99	14.16	50.32
7 wt% MMT/PHBH	4.54	0.57	1.94	13.88	47.43
PHBH	—	—	—	—	46.67

smaller; meanwhile, the nucleation density was far higher than that of PHBH as the content of nano-MMT was less than 3 wt% (Figure 4b and c), suggesting the nucleation effect of MMT. Smaller spherulites could be observed in 1 wt% MMT/PHBH and 3 wt% MMT/PHBH biocomposites, implying that the nano-MMT particles were stripped in the polymer matrix to form an intercalation structure with the polymer (18). Mohamed El-Hadi and Ahmed reported that

the reduction of spherulite size is the main reason for the toughness of the material (22), which was an agreement with the mechanical properties results. When the content of nano-MMT exceeded 5 wt% (Figure 4d and e), the density of spherulites decreased slightly and the size increased. It may be due to too many spherulites colliding with each other, inhibiting the growth and reducing the crystallization rate of samples (3).

Figure 4: The POM images ($\times 200$) of spherulite growth during isothermal crystallization at 60°C after different time at 0, 5, 10, and 15 min for: (a) PHBH, (b) 1 wt% MMT/PHBH, (c) 3 wt% MMT/PHBH, (d) 5 wt% MMT/PHBH, and (e) 7 wt% MMT/PHBH.

Figure 5: TGA (a) and DTG (b) curves of PHBH and MMT/PHBH biocomposites.

3.5 Thermal stability analysis

The TGA and DTG curves of PHBH and MMT/PHBH biocomposites are shown in Figure 5. As shown in Figure 5a, all samples appeared single-stage thermal decomposition. The PHBH exhibited a high thermal decomposition rate. The decomposition of PHBH commenced at 200°C and was completed at 260°C. Compared with PHBH, the initial thermal decomposition temperature of MMT/PHBH biocomposite increased. It was attributed to the excellent dispersion of nano-MMT in the polymer matrix, resulting in the interaction force and compatibility with PHBH enhancing. Meanwhile, the thermal parameters T_5 and T_{max} were higher than that of PHBH, as shown in Table 2, indicating the improvement of the thermal stability of the PHBH by adding the MMT. The initial degradation temperature (T_5) and peak temperature (T_{max}) of biocomposites increased first and then decreased as the nano-MMT content increased. It was believed that this was due to the increased thermal conductivity of the samples, which resulted in the improvement of the heat conduction (23). With the increase of nano-MMT content, the char yield of biocomposite presented an increasing trend, indicating

that the polymer chain was successfully intercalated into the silicate layer and the dispersion of nano-MMT limited the movement of molecular chains (24). It can be seen from Figure 5b that the maximum decomposition peak of the biocomposites moved to a high temperature (25). With the nano-MMT content increased, the T_{max} of MMT/PHBH gradually decreased. Compared with PHBH, the T_{max} of 1 wt% MMT/PHBH increased by 22.44°, demonstrating that the compatibility of MMT with the matrix was one of the key factors to improve the performance of the nanocomposites (26).

3.6 Mechanical properties

The effect of nano-MMT on the mechanical properties of MMT/PHBH biocomposites is shown in Figure 6. With the increase of nano-MMT, the tensile strength and elongation at break of MMT/PHBH biocomposites first increased and then decreased and reached the maximum at 1 wt% MMT/PHBH. Compared with PHBH, the tensile strength and elongation at break of biocomposites increased by

Table 2: The TGA data of PHBH/MMT biocomposites with different MMT contents

Samples	T_5	T_{10}	T_{30}	T_{50}	T_{max}	Char yield (%)
PHBH	203.85	213.01	224.85	230.77	230.53	10.36
1 wt% MMT/PHBH	233.43	238.52	247.94	253.52	252.97	23.81
3 wt% MMT/PHBH	228.94	234.28	243.52	250.51	246.11	22.57
5 wt% MMT/PHBH	225.09	230.34	240.24	248.31	241.65	14.68
7 wt% MMT/PHBH	222.77	227.60	236.18	239.01	238.05	38.08

T_5 , T_{10} , T_{30} , and T_{50} represent the degradation temperatures at 5, 10, 30, and 50% mass loss, respectively; T_{max} represents the maximum mass loss temperature observed in DTG thermograms.

Figure 6: Tensile strength, elongation at break, and elastic modulus of MMT/PHBH biocomposites.

111.2% and 21.1%, respectively. It was attributed to the hydrogen bonding network formed between MMT and PHBH, restraining the movement of the PHBH molecular chain (27–29). Meanwhile, elastic modulus increased from 368.4 MPa for PHBH to 1,040.7 MPa for 3 wt% MMT/PHBH with an increase of 182.5% and then decreased to 895.5 MPa for 7 wt% MMT/PHBH, which was higher than that of PHBH. When the addition amount of nano-MMT was 0–3 wt%, nano-MMT had good dispersibility in the matrix of PHBH and PHBH intercalated into the silicate layer of MMT for improving the mechanical properties of the biocomposites (30). However, when the addition amount of MMT was more than 3%, the tensile strength and modulus of biocomposites decreased, attributing to the poor dispersion and the agglomeration of nano-MMT in biocomposites (31), which

Figure 7: Blocking performance of MMT/PHBH (a) oxygen permeability coefficient; (b) water vapor permeability coefficient; (c) the tortuous zigzag diffusion path in PHBH and MMT/PHBH nanobiocomposite when used as a gas barrier.

caused incomplete intercalation of the nano-MMT layers in the PHA matrix (32).

3.7 Water vapor transmission rate and oxygen permeability

Figure 7 shows the oxygen permeability coefficient and water vapor permeability of MMT/PHBH biocomposites. As the nano-MMT content increased, the oxygen permeability coefficient and water vapor permeability of MMT/PHBH biocomposites first decreased and then increased. Compared with PHBH, the oxygen permeability coefficient of MMT/PHBH decreased by 43.9%, and the water vapor permeability decreased by 6.9% when the nano-MMT content was 1 wt%. According to Fukushima et al., gas barriers' properties were dependent on the types of biopolymers and nanoclays up to critical nanoclay concentration, which in this study was 1 wt% of nano-MMT. Improvement in gas barrier properties was due to the concept of the tortuous path which occurred due to good dispersibility of nanoclays inside matrix (33). When impermeable nano-MMT was incorporated into PHBH matrix, gas molecules were forced to wiggle or diffuse around the PHBH in a random walk instead of taking a straight line path that is perpendicular to the film surface. This resulted in a longer path for gas diffusion through the film in the presence of nano-MMT (34). When the gas passed from one side through the biocomposite, the gas molecules first adsorbed and dissolved on the surface. These molecules then gradually diffused into the interior, passed through the entire biocomposite, and reached the other side (15). Figure 7c shows that the silicate layers of nano-MMT were arranged at random and the polymer intercalation layer entered into the MMT layer, which made the silicate layer forming a more tortuous diffusion path and improved the barrier performance of biocomposites (35). However, the agglomeration of nano-MMT appeared because of the increased nano-MMT (36), which caused the partial loss of the enhancement and the increased amount of gas molecule transmission. Meanwhile, from the cross-sectional morphology, it was also found that the 5 wt% MMT/PHBH and 7 wt% MMT/PHBH biocomposites were loose and had more holes, which increased the penetration of gas molecules.

4 Conclusions

In this study, a biocomposite of MMT/PHBH was fabricated by the solution-casting method. The addition of

MMT significantly improved the crystallization properties, thermal stability, and mechanical and barrier properties of the biocomposite. The results show that the polymer chain was successfully intercalated into the silicate layer of nano-MMT to form an intercalation composite structure. It also confirmed nucleating agent role of nano-MMT particles clearly. Compared to PHBH, the tensile strength and elastic modulus of biocomposite increased by 111.2% and 182.5%, respectively, as the addition of the MMT increased. Besides, the oxygen permeability coefficient and the water vapor permeability of MMT/PHBH biocomposite decreased by 43.9% and 6.9%, respectively.

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