Carbohydrate Polymers 87 (2012) 784–789

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Chitin nanocrystals grafted with poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and their effects on thermal behavior of PHBV

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ARTICLE INFO

Article history:
Received 7 February 2011
Received in revised form 28 July 2011
Accepted 23 August 2011
Available online 30 August 2011

Keywords:
Chitin
Nanocrystal
Graft
Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

ABSTRACT

Chemically modified chitin nanocrystals were synthesized by grafting poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) onto chitin backbone via chlorination. Acetyl amino group was maintained in the reaction. The chemical structure and morphology of PHBV grafted chitin nanocrystals were characterized by Fourier transform infrared, Transmission electron microscopy and X-ray photoelectron spectroscopy. Contact angle measurement showed that the lipophilicity of chitin was improved by the surface modification. The effects of original chitin and PHBV-graft-chitin nanocrystals on the crystallizing and melting behavior of PHBV were studied by differential scanning calorimeter (DSC). The results indicated that both unmodified and modified chitin nanocrystals suppressed crystallization of PHBV. The melt point of PHBV was increased after being mixed with nanofillers.

1. Introduction

Novel biopolymer composites (biocomposites) based on biodegradable and renewable materials have received an increasing interest over the last decades. Nanofillers have been effectively used in biocomposites as reinforcing agents. Polysaccharide nanocrystals including cellulose, starch, and chitin show superior properties as reinforcing reagent for biocomposites due to their biocompatibility, non-toxicity and low cost (Sashiwa & Aiba, 2004). Chitin nanocrystals have attracted attention as they exhibit a unique cationic structure among the three main polysaccharides (Li, Revol, & Marchessault, 1997). Recently, chitin nanocrystals have been used to reinforce many polymeric matrices, such as natural rubber (Nair & Dufresne, 2003), poly(S-*co*-BuA) (Paillet & Dufresne, 2001), poly(vinyl alcohol) (Jirawut, Ratana, & Pitt, 2006), polycaprolactone (Morin & Dufresne, 2002) and so on. However, like all the other nanoparticles, chitin nanocrystals self-aggregate easily, which leads to low efficiency of reinforcement in nanocomposites. Additionally, the hydroxyl groups on the surface of nanocrystals are immiscible with hydrophobic polymer matrices. A potential solution is reducing the reactivity of its surface hydroxyl groups by surface chemical modification. Indeed, polysaccharide nanocrystals bearing a high concentration of hydroxyl groups in each glucose residue offer various possible coupling reaction sites. Surface modification improves the hydrophobicity of polysaccharide nanocrystals and thus their dispersion and compatibility with polymer matrices (Dufresne, 2008). Many lipophilic chains have been used for this purpose, for instance, stearic acid chloride (Thielemans, Belacem, & Dufresne, 2006), alkenyl succinic anhydride, phenyl isocyanate (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005) and polycaprolactone (Feng et al., 2009).

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) can be produced by a wide variety of microorganisms (Köse et al., 2003). It is a biodegradable and biocompatible polymer which has been used in medical applications, such as scaffolds and drug delivery (Chen & Wu, 2005). PHBV has high elastic modulus but it is very brittle. PHBV has a comparatively low crystallization nucleation density, and its secondary crystallization of the amorphous phase can take place at the ambient temperature during storage. The solidification process tightly constrains the amorphous chains between the crystals, making the material brittle (Li, Lai, & Liu, 2003). Therefore, reinforcing and toughening PHBV with biocompatible materials is frequently carried out, such as using natural fibers (Bhardwaj, Mohanty, Drzal, Pourboghrat, & Misra, 2006; Reinsch & Kelley, 1997), hydroxyapatite (Doyle, Tanner, & Bonfield, 1991), and starch (Keller & Owen, 1996).

In this study, we aimed to solve the above two problems simultaneously. PHBV with long alkyl chain is hydrophobic (Wang, Wang, & Cao, 2009). In theory, the lipophilicity of chitin should be improved by surface grafting of PHBV. On the other hand, although chitin and chitosan can hinder the crystallizing behavior of PHB because of inter-molecular hydrogen bonds between the PHB carbonyls and

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doi:10.1016/j.carbpol.2011.08.066

the chitin hydroxyls (Ikejima & Inoue, 2000), PHBV-graft-chitin nanocrystals may work as reinforcing agent in PHBV matrix. This is because inter-molecular hydrogen bonds would be decreased as the number of hydroxyls of chitin is reduced by modification. In this work, we successfully prepared PHBV-graft-chitin nanocrystals, but found that the novel nanoparticles suppressed the crystallizing behavior of PHBV instead of assisting.

2. Experimental

2.1. Materials

Chitin from shrimp shells was supplied by Aladdin reagent Co., Ltd (Shanghai, China). Chitin nanocrystals were prepared from this material using the method described by Nair and Dufresne (2003); poly(3-hydroxybutrate-*co*-3-hydroxyvalerate) was provided by Tianan Biologic Co., Ltd (Ningbo, China). The 3-hydroxyvalerate (3HV) content of PHBV was 12 mol%. The weight average molecular weight ($\bar{M}_{\mathrm{w}}$) was approximately 380,000 g/mol and the polydispersity index (PDI) was about 1.5. PHBV with low molecular weight was prepared by acid degradation according to the method reported by Yu and Marchessault (2000). After degradation, the $\overline{M}_{\mathrm{w}}$ of PHBV was reduced to 14,570 g/mol, with the PDI of 2.1 as determined by gel-permeation chromatography (GPC). Thionyl chloride and sodium hypochlorite were also supplied by Aladdin reagent Co., Ltd (Shanghai, China), triethylamine by Tianjin Regent Co., Ltd (Tianjin, China). All the other regents, trichloromethane, hydrochloric acid, succinic acid, paratoluenesulfonic acid, dimethyl sulfoxide (DMSO) and absolute ethyl alcohol, were sourced from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Pretreatment of PHBV before grafting reaction

PHBV with low molecular weight was processed by the following method to provide more end-carboxyl groups. PHBV was dissolved in DMSO, followed by adding succinic acid and paratoluenesulfonic acids. The reactant mixture was heated to 75 °C with magnetic stirring for 3 h. Then PHBV was recovered by precipitation in acetone from DMSO, and washed three times by ethyl alcohol and finally centrifuged and vacuum-dried for 24 h.

2.3. Preparation of grafted chitin nanocrystals

PHBV ($\overline{M}_{\mathrm{w}} = 14,568$ g/mol, PDI = 2.1) was firstly dissolved in distilled chloroform in a round-bottomed reaction flask under a nitrogen atmosphere. Thionyl chloride was then injected into the solution. The molar ratio of thionyl chloride to PHBV was 0.5, to avoid crossing links among PHBV long chains. The solution was stirred with a magnetic stir bar at 70 °C for 8 h. The unreacted thionyl chloride was distilled after the reaction. Chitin nanocrystals and drops of triethyl amine were added after that. The reactant mixture under nitrogen atmosphere was heated at 70 °C with magnetic stirring for 24 h. The reaction scheme is shown in Fig. 1.

The resulting mixture including solvent was poured into a separatory funnel and some deionized water was added as extractant. The successfully modified chitin nanocrystals were collected from the interface between the chloroform and water. However, the product contained not only modified chitin nanocrystals but also possibly some unreacted PHBV. Soxhlet extractor was used to obtain the pure PHBV modified chitin nanocrystals. The product was wrapped by a filter paper, and then soaked in the chloroform, which served as extracting agent. The unreacted PHBV was removed after reflux condenser with chloroform for 12 h. After vacuum-drying, the pure PHBV modified chitin nanocrystals were finally obtained.

2.4. Instrumental analysis

A Nicolet 6700 spectrophotometer was used to obtain Fourier transform infrared (FTIR) spectra in transmission mode at a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1}. The background was KBr pellet spectrum. Each spectrum was obtained from a total of 10 scans. TEM images were taken by a Hitachi H-7650 transmission electron microscope at the acceleration voltage of 80 kV. Chitin nanocrystals both before and after modification were dispersed in a 0.5% aqueous solution and negatively stained with 1% uranyl acetate. X-ray photoelectron spectroscopy (XPS) experiments were

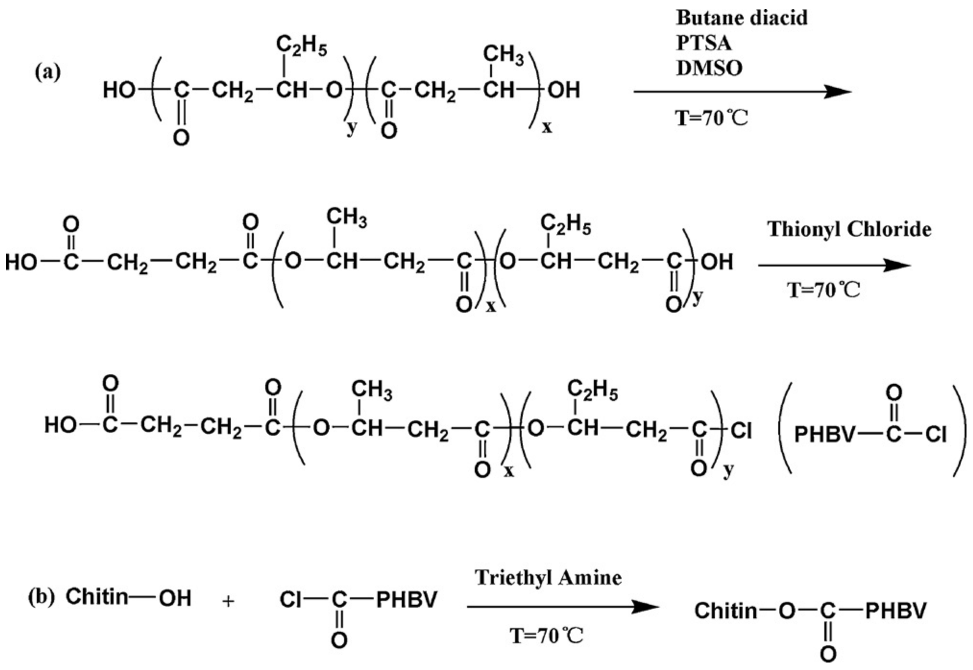

Fig. 1. Reaction schemes for (a) acyl chloride of PHBV and (b) grafting of acyl chloride PHBV to the chitin nanocrystal surface.

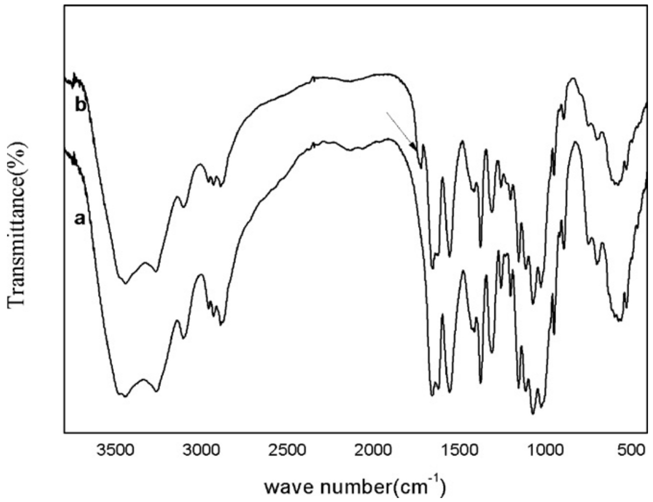

Fig. 2. FTIR spectra of chitin nanocrystals unmodified (a) and modified with PHBV (b).

carried out using AXIS UTLTRADLD (Shimadzu Corporation, Japan), operated at 15 kV under a current of 30 mA. Contact angles were measured at room temperature using a Dataphysics OCA20 Contact Angle System. Liquid drops were dropped at the speed of 0.1 μL s^{-1} onto the “pellet”. The pellet was produced by pressing naked or modified chitin nanocrystals on a tablet machine. The thermal properties of the polymers were determined by Differential Scanning Calorimeter (METTLER TOLEDO DSC I). The thermal history of the samples was removed by scanning from 25 to 200 °C at the heating rate of 50 °C/min. After maintaining at 200 °C for 2 min and then cooling down the sample to −50 °C at the cooling rate of 10 °C/min, the samples were reheated at 10 °C/min to 200 °C. The crystallization temperatures of PHBV were determined by the second scan and the melting temperature by the third scan.

3. Results and discussion

3.1. FTIR analysis

Fourier transform infrared (FTIR) experiments were conducted to determine whether PHBV was grafted onto the chitin nanocrystals. Fig. 2 shows the FTIR spectra of chitin nanocrystals unmodified (a) and modified with PHBV (b). Fig. 1a shows a typical FTIR spectrum of chitin nanocrystals. As shown in Fig. 1b, a distinct absorption peak appears at about 1724 cm^{-1} which can be attributed to the carbonyl stretching ($\nu_{\mathrm{C=O}}$) absorption. The PHBV spectrum has a prominent characteristic absorption peak centered at the same wavelength corresponding to ester function group (–COO–). Therefore the FTIR spectrum confirms that PHBV has been grafted onto chitin nanocrystal surface. The O–H and N–H stretching centered at about 3400 cm^{-1} is one of the characteristic absorptions of chitin. However, no notable reduction around 3400 cm^{-1} was found. The reason may be that, compared with active surface hydroxyl groups, a great amount of internal inaccessible hydroxyl groups limit the visibility of the signal decrease. The peaks at 1655 cm^{-1} and 1560 cm^{-1} are attributed to the amideⅠband and amideⅡband.

3.2. Morphology

The morphologies of unmodified and modified chitin nanocrystals were examined using TEM (Fig. 3). Fig. 3a shows the TEM images of unmodified chitin nanocrystals. The nanocrystals are rod like in shape, and their average length and width are measured to be about 150 and 20 nm, respectively. The chitin nanocrystals are generally believed to aggregate as a result of hydrogen bond interactions due to the surface hydroxyl groups. However, the appearance of the chitin nanocrystals changed after chemical modification with PHBV (Fig. 3b). A large amount of white dots surrounding the chitin blurred the outlines of chitin nanocrystals, which is an indication that PHBV is successfully grafted onto chitin nanocrystals. Moreover, the degree of aggregation of the nanoparticles appears to be reduced after modification.

3.3. XPS spectroscopy

X-ray photoelectron spectroscopy can be used for quantitative analysis of surface modification. As shown in X-ray photoelectron spectroscopy for chitin nanocrystals before and after modification (Fig. 4a), the signals observed around binding energies of 531, 399, and 286 eV correspond to the 1 s orbital electrons of oxygen, nitrogen and carbon, and the signals around 198 and 102 eV can be attributed to 2p orbital electrons of chlorine and silicon, respectively. The chlorine may come from the residual acyl chloride terminal group and the signal of silicon may be attributed to the silicone grease which was used as seal.

Deconvolution results of the C 1s signals of unmodified and PHBV-modified chitin nanocrystals are shown in Table 1, Figs. 4(b) and (c). These results confirm that aliphatic surface replacement of the oxygen-rich chitin surface has taken place. The C–C/C–H proportion (C1) increases while C–N/C–O proportion (C2) decreases. This is due to the grafted PHBV contains higher ratio of alkyl groups to ether groups than the original chitin particles. The decrease of

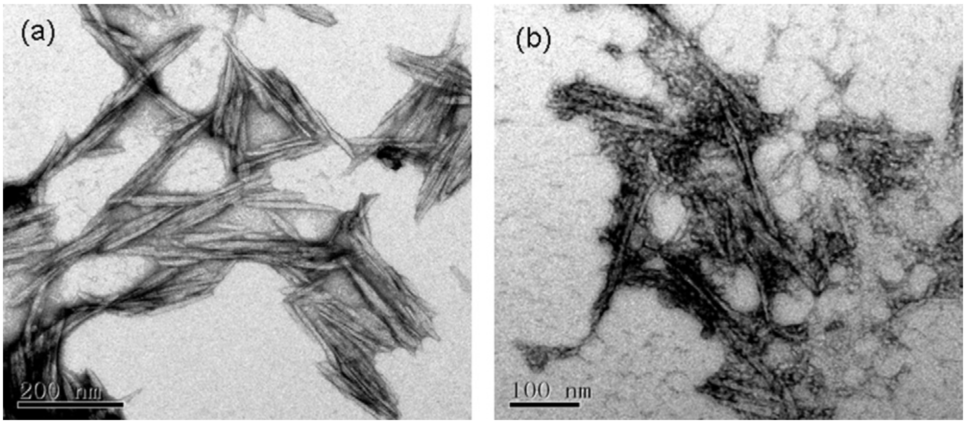

Fig. 3. Transmission electron micrographs of unmodified chitin nanocrystals (a) and chitin nanocrystals surface-modified with PHBV (b).

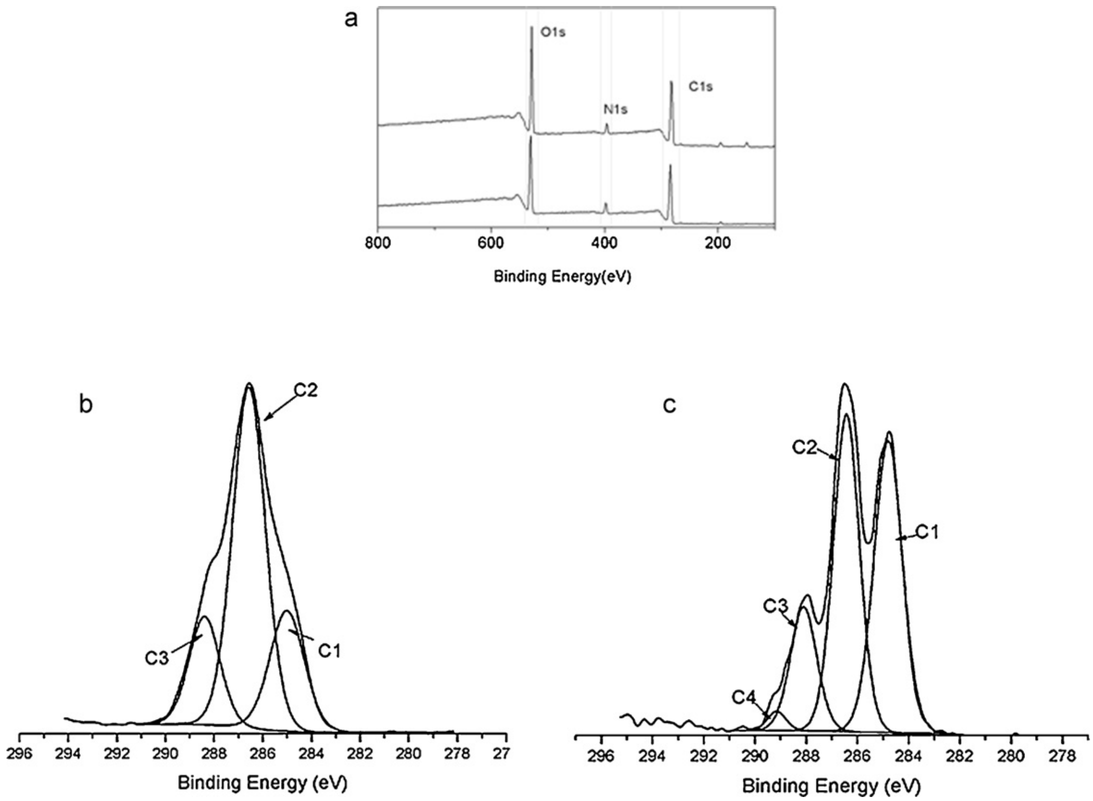

Fig. 4. X-ray photoelectron spectroscopy of chitin nanocrystals unmodified and modified with PHBV (a), and decomposition of the C 1s signal into its constituent contributions for unmodified (b) and modified (c) chitin nanocrystals.

Table 1
Surface functional group composition obtained from the decomposition of the C 1s signal.

	C1 C–C/C–H	C2 C–N/C–O	C3 O–C–O/C═O	C4 O–C═O
BE (eV)	285.0	286.6	288.4	289.2
Chitin	22.4	59.8	17.8	0
Chitin/PHBV	41.2	40.8	16.2	1.8

O–C–O/C═O (contribution C3) and the appearance of ester linkage (contribution C4) confirms surface grafting of PHBV. All of these evolutions in the deconvolution of main carbon signals give additional evidence of the efficiency of the PHBV-grafting of chitin nanoparticles.

3.4. Contact angle

Contact angle measurements of liquid droplets on material surfaces were used to characterize surface properties of modified nanoparticles. It can provide information for the evolution of hydrophilic/hydrophobic character induced by the different functionalizations. Table 2 shows the contact angle (θ) values of unmodified and modified chitin nanocrystals. The value confirms the success of surface chemical modification. An inspection of the θ values indicates a notable increase for water and notable decrease for dioodomethane because of the reduction of chitin's polarity. It has two reasons. Firstly, PHBV is hydrophobic while chitin is hydrophilic, so the long aliphatic chains wrapped around the chitin surface hydroxyl groups. Secondly, the modification on the surface decreased the number of hydroxyl groups. As a result, the number of hydrogen bonds between chitin and water was reduced, indicating that surface was effectively covered although the chitin surface reaction is limited, as shown by the results from FTIR and XPS spectroscopy.

Table 2
Contact angle (θ) values of unmodified and modified chitin nanocrystals.

	θ	
	Water	Diiodomethane
Chitin	33	45
PHBV-g-chitin	70	40

3.5. Thermal behaviors of PHBV after adding original and grafted chitin nanocrystals

Crystallizing and melting behaviors of PHBV added with chitin nanocrystals were evaluated by differential scanning calorimeter (DSC). The DSC cooling thermograms (Second scan) of PHBV/chitin blends containing different weight fractions of original and modified chitin nanocrystals are shown in Fig. 5. Due to the mass fraction of grafted PHBV layer in the whole nanocrystals is very low according to the FTIR and XPS, it is acceptable that the content of modified nanoparticles in the matrix is based on chitin nanocrystals. In Fig. 5, the crystalline temperatures are seen to drop with the increase of original chitin nanocrystal content. The crystallization temperature (T_c) of PHBV with 10 wt% original chitin nanocrystals is approximately 22 °C lower than the T_c of pure PHBV. This is due to the hydrogen bonds between the PHBV carbonyls and the chitin

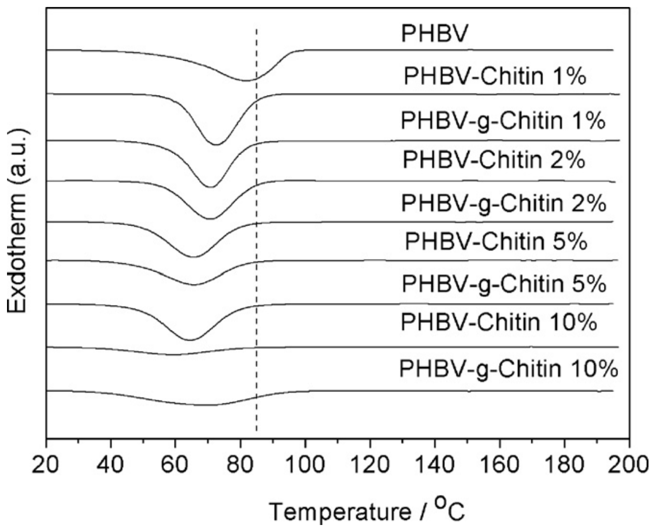

Fig. 5. Crystallization behaviors of PHBV/chitin composites.

hydroxyls. The hydrogen bonds confine the diffusion and migration of polymer chains (Chen, Zhou, Zhuang, & Dong, 2005; Ikejima, Yagi, & Inoue, 1999). With the addition of 1 wt% modified chitin nanocrystals, the T_c of the blend decreased to 65 °C, similar to that of the 2 wt% chitin nanocrystal/PHBV blend. This might be attributed to the better dispersion of modified chitin nanocrystals in PHBV matrix, which results in more hydrogen bonds in the blend. The T_c of PHBV with 2, 5 and 10 wt% modified chitin nanocrystals/PHBV blend are higher than the PHBV containing same percents of original chitin nanocrystals/PHBV blend but it is still lower than that of the pure PHBV with 2, 5 and 10 wt% of nanofillers. These results indicate that the crystallization of PHBV became more difficult. Therefore, the incorporation of modified chitin nanocrystal hinders the crystallization process of pure PHBV. Theoretically, the modified chitin nanocrystal should have a positive effect on the crystallization of PHBV. In our case, the hydrogen bonds between the PHBV carbonyls and the chitin hydroxyls did not decrease sufficiently because the surface modification of chitin nanocrystal was limited. In addition, the PHBV tails grafted onto chitin nanocrystal might have taken part in the crystallization process. The nucleation growth rate could decrease as a result of the restricted mobility of the grafted-PHBV chain.

Fig. 6 shows the melting thermograms of pure PHBV and PHBV blends. Neat and all the composites exhibit triple melting peaks (T_{m1}, T_{m2} and T_{m3}). A weak single melting peak in the range of 137–144 °C (T_{m1}) is observed. Furthermore, the samples show a double melting peak at two higher nearby temperatures (T_{m2} and T_{m3}). PHBV with low molecular weight might cause low lamella thickness melt at much lower temperature (T_{m1}) than the higher molecular weight PHBV. Thereafter, the less well crystallized PHBV crystals melted at a lower temperature (T_{m2}) and subsequently recrystallized, causing the third melting peak (T_{m3}) (Ten, Turtle, Bahr, Jiang, & Wolcott, 2010). This means that the second endothermic peak should be used as the melting temperature of the blend. As shown in Fig. 6, all the melting points of the composites are higher than that of the neat PHBV while there is no significant difference among these composites. One of the factors for the increase of T_m in PHBV composites is that slower PHBV spherulite growth leads to the formation of more perfect crystalline lamella. In other words, the presence of nanofillers gives more time for polymer chains to fully grow crystalline lamella, even if the activity of the polymer chain decrease.

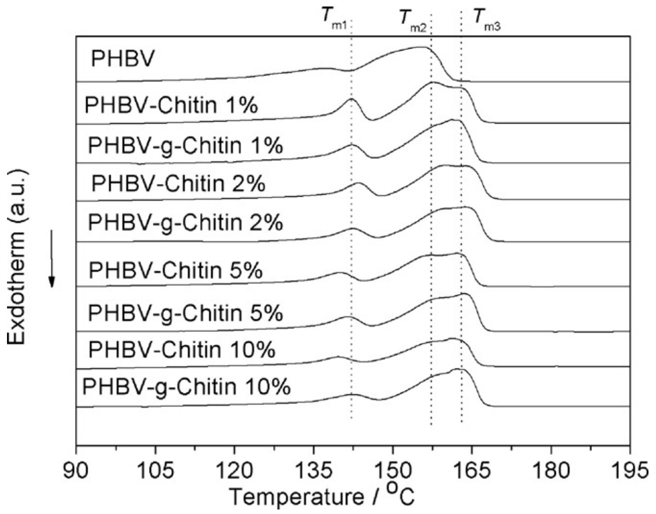

Fig. 6. Melting behaviors of PHBV/chitin composites.

4. Conclusions

The surface modification of chitin nanocrystals with PHBV was successfully carried out using chloridization reaction. FTIR spectroscopy, TEM and XPS characterizations were performed to confirm the modification. Contact angle measurements showed that the lipophilicity of chitin nanocrystals was improved with this method. On the other hand, the novel nanoparticles did not promote the crystallizing behavior of PHBV. Although the surface modification reduced the number of hydroxyl groups of chitin nanocrystals, the intermolecular hydrogen bonds between the PHBV carbonyls and the chitin hydroxyls were still strong enough to limit the crystallization of PHBV. To promote the crystallizing behavior of PHBV with modified chitin nanocrystals, further work is ongoing.

Acknowledgements

This research was supported by Ningbo Natural Science Foundation (Grant Nos. 2010A610193 and 2011A610116), Program for Ningbo Innovative Research Team (2009B21008), Ningbo Key Lab of Polymer Materials (Grant No. 2010A22001).

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