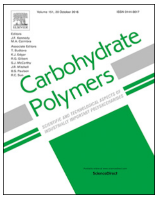
Carbohydrate Polymers 195 (2018) 79–88

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Green poly(β-hydroxybutyrate)/starch nanocrystal composites: Tuning the nucleation and spherulite morphology through surface acetylation of starch nanocrystal

Guorui Zhang[a], Defeng Wu[a,b,*], Wenyuan Xie[a,b], Zhifeng Wang[c], Chunjiang Xu[a]

[a] *School of Chemistry & Chemical Engineering, Yangzhou University, Jiangsu, Yangzhou, 225002, PR China*
[b] *Provincial Key Laboratories of Environmental Engineering & Materials, Jiangsu, Yangzhou, 225002, PR China*
[c] *Testing Center, Yangzhou University, Jiangsu, Yangzhou, 225002, PR China*

ARTICLE INFO

Keywords:
Starch nanocrystal (SNC)
Surface acetylation
Poly(β-hydroxybutyrate) (PHB)
Nanocomposite
Nucleation
Spherulite

ABSTRACT

Starch nanocrystal (SNC) particles were used as the filler to prepare green composites with biodegradable poly (β-hydroxybutyrate) (PHB). An interesting way to tune the nucleation and banded morphology of composites by the surface acetylation of SNC was proposed. Pristine SNC acts as the nucleating agent, while acetylated SNC as the antinucleation one to PHB. This role switching is due to improved polymer-particle compatibility after surface acetylation of SNC particles. The banded structure of PHB spherulites degrades evidently in the presence of two kinds of SNC particles, showing decreased ring-band space, with deteriorated periodicity and increased flocculation of peak-to-valley height. But the two kinds of composites have different mechanisms on the degradation of their ring-bands because the two kinds of SNC particles, pristine SNC and acetylated one, have different influences on the PHB spherulite growth rates and system undercooling. This work also opens a new window for the applications of SNC particles.

1. Introduction

Polysaccharide nanocrystals reinforced poly(β-hydroxybutyrate) (PHB) composites are very interesting because both the polymer and the filler particles are bio-originated and biodegradable. Therefore, this kind of green composites has attracted increasing attention in recent years (Panaitescu, Frone, & Chiulan, 2016; Reddy, Vivekanandhan, Misra, Bhatia, & Mohanty, 2013). Cellulose nanocrystal (CNC) is the most common one in the family of polysaccharide nanocrystals. It has been reported that CNC could be used as good agent to regulate crystallization kinetics and spherulite morphology of PHB (Chen et al., 2015; Chen, Wu, Tam, Pan, & Zheng, 2017; Yu, Qin, & Zhou, 2011), and to improve thermal and hydrophilic properties of PHB (Arrieta et al., 2014; Yu et al., 2011), or to optimize phase structure of the PHB based blends with other kinds of biodegradable polyesters (Arrieta et al., 2014). Therefore, hybridization with CNC is a promising way to tailor structure and properties of PHB materials.

Starch nanocrystal (SNC) is another kind of interesting polysaccharide nanocrystals. It is derived from the starch, through acid hydrolysis or physical treatments to remove amorphous phase in the onion-like starch granules (Corre & Angellier-Coussy, 2014; Corre, Bras, & Dufresne, 2010). Therefore, SNC shows different shape from rod-like CNC. It is commonly platelet-like, and the platelet size strongly depends on the starch resources (Kim, Park, & Lim, 2015; Xie, Pollet, Halley, & Avérous, 2013). Similar with CNC, SNC also shows high modulus and strength, with good biodegradability and biocompatibility. Thus, it has been suggested as the promising filler for polymers, too. Some polymers, especially the biodegradable/biocompatible aliphatic polyesters, including polylactide, poly(butylene succinate) and poly(ε-caprolactone), have been used to prepare the biocomposites with SNC (Lin, Huang, Chang, Anderson, & Yu, 2011; Xie et al., 2013). However, the work is still very limited up to now, and no literature reports are found on the PHB/SNC composites, which means that there is large space to be filled around the structure and property studies of this system.

Similar with other biodegradable aliphatic polyesters, PHB is also semicrystalline, and its final performance, such as mechanical properties and biodegradation rates, is highly dependent of its crystallization histories (Avella, Martuscelli, & Raimo, 2000; Reddy, Ghai, Rashmi, & Kalia, 2003). The reported work revealed that the spherulite morphology and growth kinetics of PHB depended strongly on the presence of CNC particles and their surface properties in PHB/CNC systems (Chen et al., 2015; Chen et al., 2017). This indicates that hybridization with SNC might also have large influence on the crystallization of PHB because SNC has similar bulk and surface properties with CNC. This is

---

[*] Corresponding author at: School of Chemistry & Chemical Engineering, Yangzhou University, Jiangsu, Yangzhou, 225002, PR China.
E-mail address: dfwu@yzu.edu.cn (D. Wu).

https://doi.org/10.1016/j.carbpol.2018.04.079
Received 14 February 2018; Received in revised form 20 April 2018; Accepted 21 April 2018
Available online 22 April 2018

of great interest and worthy of study because it may provide new way to control PHB crystallization, or even opens a new window for the applications of SNC. Thus, in this work, the crystallization behavior of PHB composites were studied in terms of SNC loadings and its surface properties. Two kinds of SNC particles, including the pristine and the acetylated ones, were used as the filler. Their roles played during nucleation and spherulite growth of PHB were explored then. The interactions between particles and polymer in those two systems was further detected, aiming at making a full insight into the relations between phase compatibility and banded morphology of PHB spherulites in the PHB/SNC composite systems.

2. Experimental

2.1. Material preparation

Poly(β-hydroxybutyrate) was a commercial product purchased from Tianan Biologic Materials Co. Ltd., P. R. China, with a brand name of ENMAT Y3000. Its number average molecular weight (M_n) and melt flow index (MI) and are about 40,000 and 20 g/10 min (190 °C/2.16 kg, ASTM D1238), respectively (provided by supplier). The industrial corn starch was purchased from Suchow Ouyang Chemical Technology Co. Ltd., P. R. China. It has A-type crystalline structure, with the average particle size of 15 μm (measured by the scanning electron microscopy and reported in the previous work (Xu, Chen, & Wu, 2018)).

The acid hydrolysis of starch was employed here to prepare the SNC suspension (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). Detailed route can be found elsewhere (Xu et al., 2018). As-obtained platelet-like SNC particles are A-type crystallites, with the average platelet sizes of 80.6 ± 6.8 nm, and the average thicknesses of 8.3 ± 2.6 nm. Their transverse modulus is 4.5 ± 0.8 GPa. The acetylation of SNC particles and the preparation of PHB composites followed a continuous route developed for the preparation of the acetylated cellulose nanocrystal filled polylactide composites (Xu et al., 2016), without any freeze drying step. Details can be found in the previous work (Xu et al., 2018).

The degree of substitution (DS) of acetylated SNC was determined by the ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) analysis. Detailed method can be found in the reports by Teramoto and Shibata (Teramoto & Shibata, 2006). The calculated value of DS of the SNC acetylated in this work is about 1.82, which is of middle level (this acetylation level had no evident influence on the particle sizes and thickness, but decreased degree of crystallinity of SNC particles to a certain degree, reducing their transverse modulus a little (Xu et al., 2018; Xu, Wu, Lv, & Yan, 2017)). The PHB composites with the thickness of about 300 μm were prepared by the casting of suspensions (using chloroform as the solvent, casted at 20 °C and vacuum-dried at 35 °C then to constant mass), then. Hereafter the composite samples with pristine and acetylated SNC particles are referred as to PSN*s* and P*a*SN*s*, respectively, where *s* is particle weight content.

2.2. Characterizations

2.2.1. Transmission electron microscopy (TEM)

The dispersion of pristine and acetylated SNC particles in PHB matrix were detected using a JEM-2100 transmission electron microscope (JEOL Co., Japan) with 120 kV accelerating voltage. The samples were microtomed (~100 nm) for the observation.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The particle-polymer interactions in the composite samples were detected using an X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Scientific Co., USA) equipped with an Al anode XR50 source operated at 200 W. The overview spectra were recorded with 20 eV at 0.05 eV steps under the pressure $< 3.0 \times 10^{-7}$ mbar.

2.2.3. Rheological characterizations

Rheological tests were performed on a DHR-2 rotational rheometry (TA Co., USA) with the 20 mm parallel plate fixtures. The step shear flow was applied at 200 °C, and the steady viscosities and stresses were recorded within the rate region of 10^{-4}–$10^{2}\,s^{-1}$.

2.2.4. Differential scanning calorimetry (DSC)

The crystallization and melting behaviors were examined by a differential scanning calorimeter (DSC-204F1, Netzsch Co., Germany). The sheet sample (about 5 mg) was heated from room temperature to 220 °C and held for 5 min, then cooled to the room temperature, and again heated to 220 °C. The heating/cooling rates were 1, 3, 5, 7, 10 °C min^{-1}. All experiments were performed under nitrogen.

2.2.5. X-ray diffraction (XRD)

The crystalline structure of PHB and its composite samples was determined using an X-ray diffractometer (AXS D8 ADVANCE, Bruker Co., Germany) with a rotating anode generator operated at 40 kV and 40 mA. The scan ranged from 5° to 80°, with the rate of 2° min^{-1}.

2.2.6. Small-angle X-ray scattering (SAXS)

The lamellar structure was determined by a small-angle X-ray scattering instrument (AXS GmbH, NanoStar, Bruker Co., Germany) with a Vantec-2000 2D detector. The incident X-rays of CuKα radiation (1.54 $A(o)$) were monochromated by a cross-coupled Göbel mirror. All tests were performed at the room temperature, and the 1D SAXS profiles were collected by integration of 2D pattern, shown as normalized intensity (I) versus q ($q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of the X-rays and 2θ the scattering angle). The 1D correlation function ($K(z)$) defined by Strobl and Schneider (Strobl, & Schneider, 1980) was plotted by

$$K(z) = \frac{1}{2\pi^2}\int_0^\infty I(q)q^2\cos(qz)dq \tag{1}$$

where $I(q)$ is the absolute scattering intensity collected from the SAXS tests, and z the direction along which the electron density is measured.

2.2.7. Polarized light microscope (PLM)

The spherulite morphology was recorded using a polarized light microscope (Leika DMLP, Germany) with a hot stage (Linkam LTM350, England). The samples were heated from room temperature to 200 °C at the rate of 10 °C min^{-1} and held for 5 min, and then cooled rapidly to the predetermined crystallization temperature (T_c) for the following observation. All sheet specimens had almost the same thickness (~100 μm) and for each observation, a new specimen was used. The banded structure was then analyzed using Image J (version 1.42q) software.

3. Results and discussion

3.1. Different roles of pristine SNC and acetylated one to PHB nucleation

The thermograms of PHB and its composite samples are shown in Fig. 1. It is of great interest that the two kinds of SNC particles, acetylated SNC and pristine one, play fully different roles during crystallization of PHB (Fig. 1a). It is seen that PSN3 shows the crystallization temperature (T_c) of about 99.5 °C, increased by about 9 °C relative to the neat PHB (90.5 °C) (Table 1). This indicates that the pristine SNC acts as the nucleating agent to PHB, increasing its T_c evidently. Similar role has also been reported on some other polysaccharide particles, such as the pristine CNC and/or microcrystalline cellulose (MCC), during crystallization of PHB (Chen et al., 2015, 2017; Yu et al., 2011). The acetylated SNC, however, plays opposite role. It is seen that the T_c of PHB reduces in the presence of acetylated SNC (Fig. 1a), and clearly shows a monotonous downward trend with