



Effect of cellulose nanocrystals on the crystallization behavior and enzymatic degradation of poly(butylene adipate)

Hai-Mu Ye*, Cai-Shui Wang, Zi-Zhe Zhang, Shu-Fang Yao

Department of Materials Science and Engineering, China University of Petroleum, 102249 Beijing, PR China



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ABSTRACT

Cellulose nanocrystals (CNCs) are nature-resourced nanoparticles and have been widely used to improve performance of biodegradable polyesters. Two types of CNCs respectively prepared by sulphuric acid hydrolysis (*a*CNCs) and ammonium persulfate oxidation (*o*CNCs) processes were incorporated into poly(butylene adipate) (PBA) matrix to regulate its crystallization behavior and enzymatic degradation performance. Thermal and X-ray diffraction analysis revealed that both *a*CNCs and *o*CNCs could promote the crystallization ability and lamellar thickening of α -form PBA, while *o*CNCs showed stronger promotion than *a*CNCs. Optical morphology study indicated that both two types of CNCs enhanced the nucleation ability of PBA. Furthermore, the mechanism of crystallization promotion of CNCs on PBA was further discussed and attributed to the “memory effect” in the melt state of PBA/CNCs composites, which was originated from the hydrogen-bonding interaction between CNCs and PBA chains. The enzymatic degradation testing proved that CNCs could slower down degradation rate of PBA and PBA/*o*CNCs composites possessed lower degradation rate than PBA/*a*CNCs composites.

1. Introduction

In recent decades, biodegradable polyesters have attracted great attention due to their widely applicable characteristics in environmental protection and physical health maintenance. Poly(butylene adipate) (PBA) is one of the hottest research aliphatic polyesters because of its easy regulation of polymorphism, which directly decides the degradation performances and mechanical properties, etc. (Minke and Blackwell, 1979, 1980; Gan, Kuwabara, Abe, Iwata, & Doi, 2005; Song et al., 2014). The α -form crystal shows faster enzymatic degradation than the β -form one (Gan et al., 2005), while the β -form crystal has been found to have better mechanical properties than the α -form one (Song et al., 2014). Usually, bulk PBA melt-crystallizes to pure α - or β -form crystals when the temperature is set above 32 °C or below 27 °C, respectively; and a mixture of α - and β -form crystals appears when the temperature is selected between 27 and 32 °C (Gan, Abe, & Doi, 2002; Woo & Wu, 2005). Till now, various manners have been employed to regulate the above temperature-dependent crystal formation behavior of PBA to expand the performance field and uncover the selection mechanism of crystal formation, including nucleating agents (Liang, Pan, Zhu, & Inoue, 2010; Tang, Xu, & Guo, 2015; Yang, Liang, Chen et al., 2017), blending process (Yang et al., 2010; Sun et al., 2011), chain modification (Liang et al., 2010; Zhao & Gan, 2006), etc. Though various methods can effectively control the performances of PBA,

environment-friendly and natural resource additive is still desired for its application.

Cellulose nanocrystals (CNCs) have attracted great attention because of their natural resources, superior mechanical strength, biodegradable property, fruitful surface groups, etc (Habibi, Lucia, & Rojas, 2010). Since the first use of CNCs as reinforcing nanofillers in poly(styrene-*co*-butyl acrylate) (PStBA) (Favier, Chanzy, & Cavaille, 1995), CNCs have been employed as effective additive in various polymer matrices, especially in biodegradable polymers. Such as polylactide (PLA) (Lin, Huang, Chang, Feng, & Yu, 2011; Lizundia, Vilas, & León, 2015; Pal, & Katiyar, 2016), poly(butylene succinate) (PBS) (Hu, Lin, Chang, & Huang, 2015; Lin et al., 2011) and poly(ϵ -caprolactone) (PCL) (Habibi et al., 2008; Zoppe, Peresin, Habibi, Venditti, & Rojas, 2009). CNCs were found to possess enhancements on the mechanical property and thermal stability and improvement on the gas barrier property of polyesters. Furthermore, CNCs had been reported to form specific interaction, e.g. hydrogen bonds, with polyester matrices (Senda, He, & Inoue, 2002; Xu et al., 2013; Zhang, Shi, Ye, Dong, & Zhou, 2018), so it is expected that CNCs can be used to effectively regulate the crystallization behavior and the related properties.

This work tried to provide an environment-friendly and natural resource additive to regulate the structure and properties of PBA, and further presented that the polymorphism of PBA could supply a route to reveal the interaction between different CNCs and PBA. Two types of

* Corresponding author.

E-mail address: yehaimu@cup.edu.cn (H.-M. Ye).

CNCs with different surface groups were prepared and introduced into PBA matrix by solution-cast method. CNCs with various adding content from 0.5% to 2% were incorporated into PBA, and the crystallization behavior of PBA/CNCs composites was in detail studied with differential scanning calorimetry (DSC), polarized optical microscopy (POM), wide angle X-ray diffraction (WAXD), and Fourier transform infrared (FTIR). Furthermore, the effect of CNCs on enzymatic degradation of PBA was evaluated. The result demonstrated that both adding content and surface groups of CNCs influenced the crystallization and degradation of PBA due to different strength of interaction between PBA and two types of CNCs.

2. Experimental section

2.1. Materials

Adipic acid (AA, AR grade), ammonium persulfate (APS, AR grade) and micro-crystalline cellulose (MCC) were purchased from Shanghai Aladdin Industrial Corporation (China); 1,4-butanediol (BDO, AR grade) was obtained from Tianjin Guangfu Fine Chemical Research Institute (China); Concentrated sulfuric acid (H_2SO_4 , 98%) and *N,N*-dimethyl formamide (DMF, AR grade) were provided by Beijing Chemical Plant (China).

2.2. Preparation of PBA and CNC

PBA was synthesized from BDO and AA by a two-step reaction of esterification and polycondensation in molten state, as reported in previous literature (Song et al., 2014). The number average molecular weight (M_n) and polydispersity index (PDI), determined by gel permeation chromatography (GPC, Viscotek, M302 TDA), are 5.7×10^4 g/mol and 1.82, respectively.

CNCs were prepared by two manners: sulphuric acid hydrolysis (Kargazadeh et al., 2012) and ammonium persulfate oxidation (Leung et al., 2011). The sulphuric acid hydrolysis method was conducted as follow: 3.0 g of MCC was treated with 45 mL 60 wt% sulfuric acid at 50 °C for 2 h under strongly magnetic stirring; then the reaction was quenched by diluting with 10-fold deionized water. The system was allowed to stand steady for 2 days to settle the solids, and the top part of transparency solution was decanted off; after decanting, the remaining suspension was washed with fresh deionized water and followed by successive centrifugations (10,000 rpm for 20 min); such procedure was repeatedly several times until the supernatant appeared turbid. Then the concentrated solution system was transferred to a dialysis bag and dialyzed by changing distilled water every 12 h under continuous stirring until the pH value reached 7. The solution system in dialysis bag was then poured into a poly(methyl methacrylate) culture dish and sealed by plastic wrap. After being frozen at -20 °C for 24 h, the specimen was converted to powder product (named as *a*CNCs) by lyophilization at -50 °C for 3 days. The ammonium persulfate oxidation method was conducted as follow: 3.0 g of MCC in 200 mL of 1 mol/L APS was strongly stirred at 50 °C for 16 h, and the obtained solution system was further treated using the same procedures (not include the first step) as described in sulphuric acid hydrolysis method. The CNCs prepared by ammonium persulfate oxidation method was termed as *o*CNCs.

2.3. Fabrication of the PBA/CNCs composites

PBA/CNCs composites were prepared as follows: DMF which is a good dispersion medium for CNCs (Samir, Alloin, Sanchez, El Kissi, & Dufresne, 2004) and good solvent for PBA was used. 10 mg CNCs were first suspended in 50 mL DMF by ultrasonication (200 W) for 30 min to obtain uniform dispersion system, then a certain amount of PBA was added to the DMF system. Another 60 min of strong agitation was performed to ensure the fully dissolution of PBA. The composites was

dried at 50 °C for 2 days and then dried in vacuum oven at 70 °C for 3 days to remove the residual DMF. The highest adding amount content of CNCs was 2%, making impossible to quantify the effect of the content but not to in detail study the critical saturated content.

2.4. Characterization

The morphology of CNCs specimens was examined by transmission electron microscope (TEM, FEI Tecnai G² F20). A drop (2 μL) of the CNCs diluted aqueous suspension (0.01 wt%) was applied to a carbon-coated copper microscope grid, then it was dried in a vacuum oven at 40 °C for 2 days. Wide angle X-ray diffraction (WAXD) was performed on a Bruker D8 Advance diffractometer (USA) using a Ni-filtered $\text{Cu K}\alpha$ target. The scanning range (2θ) was from 16° to 28° with a step of 0.01°, and the scanning rate was 4°/min. To obtain isothermally crystallized specimens for WAXD measurement, the specimen sandwiched between two glass slides was placed on a hot-stage at 110 °C for 5 min; after that, the specimen was quickly dipped into an oil bath preset at required temperature for 60 min, long enough for the complete crystallization of PBA and PBA/CNCs composites. Then, the cover slide was removed to get an exposed surface for measurement. Differential scanning calorimetry (DSC) measurement was performed on a NETZSCH 204F1 instrument under nitrogen atmosphere equipped with an intercooler. For non-isothermal DSC, the sample was melt-cooled from 110 °C to 0 °C after being held 110 °C for 5 min and, subsequently, reheated to 110 °C; for isothermal DSC, the sample was melt-quenched to the required temperature from 110 °C and held at that temperature until the crystallization process completed. Fourier transform infrared (FTIR) spectra were collected using a Bruker Hyperion FTIR spectrometer in attenuated total reflectance (ATR) mode with a scanning resolution of 4 cm^{-1} . A polarized optical microscope (Leica) was employed to capture spherulite morphology.

For enzymatic degradation, the following procedure was applied: (a) $10 \times 10 \times 0.1$ mm³ films of PBA and PBA/CNCs composites were obtained by hot-press and then isothermal crystallization at required temperatures; (b) 50 μL of lipase solution (lipase from *Pseudomonas* sp., type XIII, 1 mg/mL in 0.1 M phosphate buffer solution) was added to 1 mL of phosphate buffer solution with a piece of film; (c) the reaction mixture was incubated in a vial with shaking water bath at 37 °C, and the degradation rate was calculated by the weight loss in 3 h interval. Before weight measurement of residue, the samples were washed with deionized water until the pH value of filtrate was 7 and then dried in vacuum oven for 2 days.

3. Results and discussion

3.1. Characterization of CNCs

Fig. 1a and b shows the morphology of as-prepared CNCs. Both the *a*CNCs and *o*CNCs possessed the rod-like structure with a diameter of 10–30 nm and length of 50–300 nm. The large distribution range in size was expected, due to the diffusion-controlled nature upon hydrolysis/oxidation (Cao, Habibi, & Lucia, 2009). The reagent molecules first diffused into the amorphous regions of MCC, where the hydrolysis/oxidation processes occurred; then amorphous regions were consumed and CNCs remained; the diffusion degrees of reagent molecules in different parts of MCC whose original state was solid led to different hydrolysis/oxidation degrees, which resulted in the large distribution range of CNCs in size. The characteristic FTIR absorption bands (Fig. 1c) for *a*CNCs were attributed to the hydrogen-bond O–H stretching vibrations at ~ 3400 cm^{-1} , the C–H stretching vibrations at ~ 2900 cm^{-1} , the O–H bending vibrations of absorbed water at 1646 cm^{-1} , the C–OH deformation vibrations at ~ 1030 cm^{-1} , and the C–OH out-of-plane bending vibrations at ~ 667 cm^{-1} (Oh, Yoo, Shin, & Seo, 2005). Compared with *a*CNCs, two obviously different absorption bands at 1733 and 1628 cm^{-1} appeared for *o*CNCs, which were

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