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Effects of ethyl cellulose on the crystallization and mechanical properties of poly(β-hydroxybutyrate)

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ABSTRACT

Ethyl cellulose (EC) was blended with poly(β-hydroxybutyrate) (PHB), aiming at controlling crystallization and mechanical properties of PHB. The obtained PHB/EC blend is an immiscible system, and the discrete EC phase behaves dual characteristics in the PHB matrix, as the viscoelastic droplets during processing, and as the rigid filler particles during shear flow. This is confirmed by the rheological tests. The presence of EC domains acts as the tackifier, sharply increasing system viscosity from 1000 Pa s to 5000 Pa s, and as a result, has large influence on the spherulite morphology of PHB and its crystallization kinetics. The PHB spherulite growth rate reduces in the presence of inert EC, accompanied by decreased degree of crystallinity and reduced lamella defects. These affect the mechanical properties of PHB strongly, together with reinforcing effect of EC itself. At the lower content level, EC can act as both reinforcement and toughener. The presence of 1 wt% EC enhances the tensile strength of PHB by about 22%, from 27.5 MPa to 33.3 MPa, accompanied by 15% increase of impact strength. This work provide an easy way to control the structure and properties of PHB using EC.

1. Introduction

Recently bio-based polymers are being engineered for target applications in different industries for relieving environmental concerns caused by disposal of non-degradable plastics [1]. Poly(β-hydroxybutyrate) (PHB) as a naturally occurring thermoplastic polyester has attracted much attention as a candidate alternative of traditional plastics [2–7]. However, PHB has high degree of crystallinity and fast crystallization rate, and as result, is a relatively brittle material with lower degradation rate, [8,9] which restricts its further application. Moreover, the molecular weight of PHB is commonly not high enough, and therefore PHB shows low melt intensity during processing. This is also against extending its final applications.

Common ways to tailor crystallization or to improve the final properties of PHB are hybridization with nanoparticles [10–12], and copolymerization with other monomers [13], as well as preparation of PHB based blends [14]. Among all these methods, blending PHB with other biodegradable polymers such as poly(butylene succinate) (PBS) [15–18], poly(ε-caprolactone) (PCL) [19] and poly(lactic acid) (PLA) [20–22], is the most practical and economical one to well tailor crystallization, degradation and PHB properties. Therefore, the structure and properties of this kind of PHB-based bio-blends have been extensively studied.

Very recently, cellulose based material has attracted much attention because of the wide raw material resources and environmental-friendly characteristic. [23–28] As one of the typical cellulose derivatives, ethyl cellulose (EC) is thermoplastic, with high mechanical intensity and good heat-resistance, as well as thermal stability [29–32]. Green polymer blends with high performance can be fabricated by mixing EC with biodegradable polymers [28]. The presence of EC can affect the crystalline morphology [33] and the crystallization rates of polymer matrices [34,35], and even changes the miscibility and interfacial properties of the immiscible blends [36], and finally to control or modulate final properties of the polymer matrices [8,29].

EC has already been blended with PHB to control PHB properties by the physical or chemical approaches. Iqbal et al. [37,38] developed a novel enzyme based way to graft poly(3-hydroxybutyrate) [P(3HB)] onto the ethyl cellulose (EC) under a mild and ecofriendly environment and they suggested that P(3HB)-g-EC could be a potential candidate for various biotechnological applications, such

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as tissue engineering and packaging. Chan et al. [39] blended PHB with EC and found that the presence of EC reduced PHB crystallinity and promotes its degradation under physiological conditions. Those reported studies mainly focus on the evaluation of bio-properties and bio-applications PHB/EC blends. To extend the potential application fields of this blend material, it is necessary to make a deep insight into the fundamental aspects around its structure-property relationship.

In this work, therefore, the phase structure and spherulite morphology of PHB/EC blend were studied in terms of thermal, rheological and mechanical analyses. The effect of discrete EC phase on the PHB spherulite growth and morphology was explored in detail because the final properties of PHB are mainly determined by its supermolecular structure, which is in turn controlled by crystallization. The main objective of this work is to establish the relationship between structure and properties of PHB/EC blend materials, and to provide useful guide on the property control of biodegradable polymers using thermoplastic cellulose derivatives.

2. Experimental

2.1. Materials

Poly(β-hydroxybutyrate) (PHB, brand series ENMAT Y3000) was purchased from Tianan Biologic Materials Co. Ltd., P. R. China, with a melt flow index (MI) of 15–30 g/10 min (190 °C/2.16 kg, ASTM D1238) and the density of 1.25 g/cm^3. Its number average molecular weight (M_n) is about 40,000. Ethyl cellulose (EC) with a degree of substitution (DS) of 2.17 was purchased from Sinopharm Chemical Reagent Co. Ltd., P. R. China, The number-average molecular mass (M_n) and weight-average molecular mass (M_w) are 5265 and 7366 (PDI = 1.40), respectively.

2.2. PHB/EC blend preparation

The PHB/EC blends (PHBEC*s*, where *s* is the weight ratio of EC) were prepared by melt mixing by a Haake Polylab Rheometer (Thermo Electron Co., USA) at 180 °C and 50 rpm for 5 min. For better comparison, the neat PHB was also processed by rheometer to keep the same thermal histories with the blend. All materials were dried under vacuum at 60 °C for 24 h before using. The sheet samples for the morphological and rheological measurements were then obtained by compression molding at 15 MPa and 180 °C. The standard rectangle specimens (80 mm × 10 mm × 4 mm) and the dog-bone shaped specimens (32 mm × 4 mm × 2 mm) were prepared by injection molding for the mechanical property testing. The injection was performed on a Haake mini-jet machine (Thermo Electron Co., USA) at cylinder temperature 180 °C and mold temperature 40 °C, with injection pressure 600 bar and holding pressure 500 bar.

2.3. Characterizations

2.3.1. Differential scanning calorimetry (DSC)

The nonisothermal crystallization of the neat PHB and its blends was detected using a differential scanning calorimeter (NETZSCH DSC-204F1, Germany). The sample weighing about 5 mg was first heated from room temperature to 200 °C and held for 5 min to eliminate residual thermal histories, then cooled to the room temperature, and again heated to 200 °C, during which the thermal enthalpies were recorded. All experiments were performed under nitrogen at the heating/cooling rates of 5 °C min^{-1}.

2.3.2. Hot stage polarized optical microscope (HSPOM)

The spherulite morphology of PHB was detected using a polarized optical microscope (POM, Leika DMLP, Germany) equipped with a hot stage (Linkam LTM350, England). The sample was first heated from room temperature to 200 °C at the rate of 20 °C min^{-1} and held for 5 min to eliminate residual thermal histories, and then cooled to the predetermined crystallization temperature (T_c) rapidly, and held for the spherulite morphology observation.

2.3.3. Melt rheological measurements

Rheological measurements were performed on a rheometer (Haake RS600, Thermo Electron Co., USA) using a parallel plate geometry with diameter of 20 mm. The sheet samples were molten at 180 °C for 5 min to eliminate the residual thermal history, and then experienced shear flow immediately. The dynamic strain sweep measurements were performed firstly to determine a common linear viscoelastic region. Then, the dynamic frequency sweep was applied on those samples at the strain level of 5%.

2.3.4. Field emission scanning electron microscope (FE-SEM)

The phase morphology of PHBEC*s* were investigated using a S-4800 field-emission scanning electron microscope (Hitachi, Japan) with a 15 kV accelerating voltage. The fractured surface of PHBEC*s* was coated with gold using an SPI sputter coater before observation.

2.3.5. Mechanical property tests

The tensile properties of the samples were determined by an Instron Mechanical Tester (Instron Co., USA) according to ASTM D638 at a crosshead speed of 1 mm min^{-1}. The impact properties were tested in accordance with ASTM D256. All values reported here represent an average value of the results for tests run on five specimens.

2.3.6. Surface property characterizations

The surface parameters of the two polymers used in this work were determined by the contact angle measurements. The surface energy of a solid or a liquid consists of two components, the dispersive and the polar components [40]:

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{1}$$

and the relations between contact angle and surface energy can be described by the Owens-Wendt method [41]:

$$\gamma_l\left(1+\cos\theta\right) = 2\left(\gamma_s^d\gamma_l^d\right)^{1/2} + 2\left(\gamma_s^p\gamma_l^p\right)^{1/2} \tag{2}$$

where γ_l and γ_s are the surface energy of liquid and solid, respectively; and γ_s^d, γ_s^p, γ_l^d and γ_l^p the dispersive and the polar components of solid and liquid, respectively; while θ is the contact angle. If the contact angles of at least two liquids, usually a polar and a nonpolar liquid [42] with known γ_l^d and γ_l^p parameters, are measured on a solid surface, the γ_s^d and γ_s^p parameters as well as the surface energy γ_s of that solid can be calculated.

Contact angle tests were performed with an OCA40 apparatus (Dataphysics Co Ltd., Germany). Static contact angles of two test liquids (distilled water and glycerin) were measured by depositing a drop of 3–5 μl on the sample surface and the values were estimated as the tangent normal to the drop at the intersection between the sessile drop and the surface. To avoid solvent evaporation, images were taken within 30 s of drop deposition. The reported contact angle values here are the average of at least five tests at different spots of the surface. The surface parameters of the tested samples were then calculated and the results are listed in Table 1. Here, the literature values of surface parameters for the test liquids (20 °C) were used [43]. Using those parameters, the values of interfacial tension between the two polymers can be calculated according to the harmonic-mean equation [44].

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left[\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d+\gamma_2^d} + \frac{\gamma_1^p\gamma_2^p}{\gamma_1^p+\gamma_2^p}\right] \tag{3}$$