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Influence of polyethylene glycol (PEG) chain length on the thermal behavior of spin-coated thin films of biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)/PEG blends

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ABSTRACT

The influence of the polyethylene glycol (PEG, M_n = 400, 1500, and 3400) chain length on the miscibility and thermal properties of spin-coated films of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx, HHx = 6.9 mol %)/PEG blends was elucidated by using differential scanning calorimetry (DSC) and temperature-dependent infrared (IR) spectroscopy. To extract more detailed information about the spectral variations induced by the temperature, 2D correlation spectroscopy was applied to the temperature-dependent IR spectra of PHBHx/PEG blends. It was found that PEG 400 was completely miscible with PHBHx while PEG 1500 and 3400 were only partially miscible, reflecting that PHBHx/PEG miscibility decreased with the increasing molecular weight of PEG. The amorphous band of carbonyl group of 70/30 PHBHx/PEG 400 blend is resolved into two bands at 1744 and 1754 cm^{-1} in the asynchronous spectrum, which is not observed in the corresponding asynchronous 2D correlation spectra of PHBHx and its blend with PEG 1500 and 3400. This observation suggests that we captured the possible existence of two different types of amorphous state in 70/30 PHBHx/PEG 400 blend and the band at 1744 cm^{-1} is related to the amorphous mixture of PHBHx and PEG 400. Furthermore, 2D correlation analysis and the normalized peak height trends demonstrate that PEG 400 disrupts the crystalline structure of PHBHx, indicating low molecular weight PEG 400 has a clear effect on the thermal properties of PHBHx as well as depressing its melting temperature.

1. Introduction

The poly(3-hydroxybutyrate) (PHB) based copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx) has recently received considerable attention owing to its promising environmental, pharmaceutical and biomedical applications [1–3]. Many studies have been carried on the structure and thermal behavior of PHBHx copolymers using various techniques, such as X-ray diffraction (XRD), differential scanning calorimetry (DSC) and FTIR spectroscopy [4–9]. In comparison with PHB homopolymer, PHBHx copolymer shows a wide range of improved properties including chemical, thermal, and mechanical properties by changing the comonomer 3-HHx content [10,11]. Doi et al. investigated the lamellar crystal structures and thermal properties of PHB homopolymer and its PHBHx copolymer by small-angle X-ray scattering (SAXS) and DSC measurement [6]. They found that the HHx unit content has a great effect on the thermal and mechanical properties of PHBHx while the lattice spacing of PHBHx is essentially the same as that of PHB because HHx units of PHBHx are excluded from PHB crystalline lattice. In addition, PHBHx has excellent compatibility with other biodegradable polymers.

Polymer blending is another convenient method for tailoring the mechanical properties and degradation kinetics of PHBHx copolymer for various applications. Polyethylene glycol (PEG), which is a water-soluble polyether, has good biocompatibility and hydrophilicity, as well as rapid degradability. We have previously investigated the thermal behavior of PHBHx (3-HHx content of 10.0 mol %)/PEG 1500 blends using 2D IR correlation spectroscopy [12,13]. It was found that the intensity of PEG band changed first, and the intensity of the crystalline band of PHBHx subsequently changed before that of the amorphous band in the blend system upon heating process. The present study is an extension of our previous PHBHx/PEG studies. PEG polymers are available in a wide

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range of molecular weights, ranging from 200 to several millions. It is well documented that PEG with different molecular weight exhibit different properties [14–17]. In this study, we focused on the effect of PEG molecular weight on the miscibility and thermal behavior of spin-coated films of PHBHx/PEG blends.

2. Experimental section

2.1. Materials

Biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyhaxanoate) (PHBHx) copolymers with 6.9 mol % 3-HHx content was supplied by the Procter & Gamble Company, Cincinnati, OH. The polymer was purified by dissolving in hot chloroform followed by filtration and subsequent precipitation in hexane. The same process was repeated and re-precipitation in methanol, then vacuum dried at 60 °C. Polyethylene glycol (PEG) (number average molecular weight, M_n = 400, 1500 and 3400) was purchased from Sigma–Aldrich Co., Ltd and used without further purification.

2.2. Preparation of spin-coated films

1 wt % 70/30 PHBHx/PEG blends with different molecular weight of PEG were prepared by dissolving them together in chloroform. The spin-coated films of PHBHx and PHBHx/PEG blends were prepared by spinning their corresponding solution onto a Pt-coated silicon wafer at 3000 rpm for 60 s, respectively, and subsequently placed under vacuum at 60 °C for 4 h to completely remove the residual solvent. The thickness of spin-coated film of PHBHx and 70/30 PHBHx/PEG blends was ca. 100 nm.

2.3. Differential scanning calorimetry (DSC) measurement

DCS measurements were performed using a TA Instruments Q1000 with a Universal Analysis 2000. The DSC thermograms of PHBHx/PEG blends were measured over a temperature range of −60 to 180 °C at heating and cooling rate of 10 °C/min. The glass transition temperature (T_g) and melting point (T_m) of PHBHx/PEG blends were obtained from the second heating process.

2.4. FTIR measurement

The infrared reflection absorbance (IRRAS) spectra were collected at a 2 cm^{-1} resolution with a Bruker IFS 66v/s spectrometer equipped with a liquid nitrogen-cooled MCT detector. The spin-coated film of PHBHx/PEG blend was set on the Bruker A513 reflection attachment with an angle of incidence of 80°, which includes a heating block attachment. A total of 64 scans were co-added for each IR spectral measurement. The temperature was increased at a rate of ca. 2 °C/min. After changing the temperature, the spin-coated film was maintained at that temperature for 10 min to make the samples equilibrate.

2.5. 2D correlation spectroscopy

Synchronous and asynchronous 2D correlation spectra were obtained using home-made software based on the MATLAB R2010a program (The Mathworks Inc., Natick, MA, USA), where the red and blue lines in the 2D correlation spectra represent positive and negative cross peaks, respectively.

3. Results and discussion

Miscibility of PHBHx/PEG blends was studied by using DSC. Fig. 1 shows the DSC thermogram of PHBHx and PHBHx/PEG blends

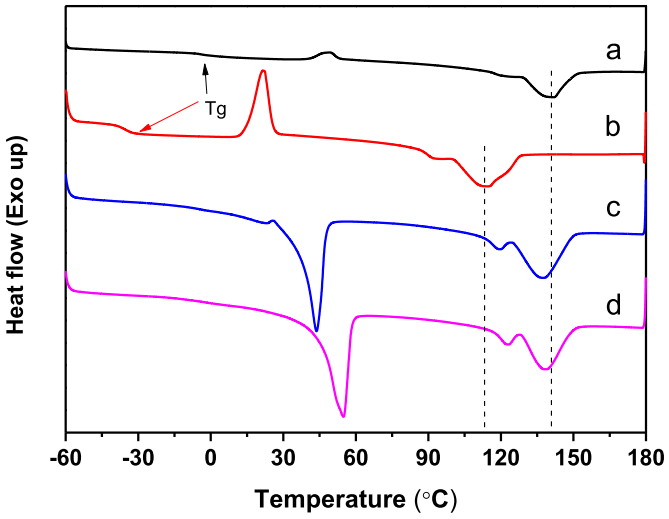

Fig. 1. The second heating process of DCS trace of neat PHBHx (a), 70/30 PHBHx/PEG 400 blend (b), 70/30 PHBHx/PEG 1500 blend (c), and 70/30 PHBHx/PEG 3400 blend (d) with heating rate of 10 °C/min.

in the second heating process. It can be seen from Fig. 1(a) that neat PHBHx has a T_g of 0.5 °C and double T_m at 120 and 143 °C. In the case of 70/30 PHBHx/PEG 400 blend, a single T_g at −32 °C was observed in Fig. 1(b), which is below the T_g of neat PHBHx, indicating that PHBHx and PEG 400 are fully miscible in the blending ratio of 70/30. Furthermore, it is evident from Fig. 1(b) that blend with PEG 400 significantly depressed the melting point of PHBHx. In contrast, the present of T_m of PEG 1500 and 3400 as well as the lack of clearly identifiable T_g of PHBHx in Fig. 1(c) and (d) suggest that PEG 1500 and PEG 3400 are partially miscible with PHBHx. On the other hand, PEG 1500 and PEG 3400 do not show much change in the T_m of PHBHx crystals in the blend samples. Therefore, this result suggests that PHBHx/PEG miscibility increase with the decreasing molecular weight of PEG.

IR spectroscopy is very sensitive to the conformation and local molecular environment of polymers. Monitoring changes in different IR characteristic bands enable us to follow the variation in segmental conformation and chain packing in response to temperature change. Fig. 2 shows the temperature-dependent IRRAS spectra of spin-coated films of PHBHx and 70/30 PHBHx/PEG blends with different molecular weight of PEG recorded during the heating process from 30 to 150 °C. It can be seen from Fig. 2 that the carbonyl band of PHBHx at low temperature consists of two components, centered at 1751 and 1724 cm^{-1}. They correspond, respectively, to the carbonyl group existing in the amorphous and crystalline state. PEG shows no absorption in the region of 1900–1600 cm^{-1}. Therefore, any changes in this region can be directly attributed to those in the environment of the carbonyl group of PHBHx, such as the presence of PEG. Furthermore, it is evident from Fig. 2 that the intensities of bands at 1724, 1295 and 1136 cm^{-1} decrease with increasing temperature, whereas those of bands at 1751 and 1195 cm^{-1} increase. Similar trends of band intensity changes were observed in both spectra of neat PHBHx and its blends.

To explore more deeply the thermal behavior of PHBHx with the addition of different PEG molecular weight, we performed 2D correlation analysis. Since the melting behavior of PEG 1500 and 3400 were observed in region of 3000–2800 and 1500–1000 cm^{-1} during the heating process, the C=O stretching region was selected to investigate the influence of PEG on the thermal property of PHBHx. Fig. 3 displays the synchronous and asynchronous 2D correlation spectra of PHBHx and 70/30 PHBHx/PEG (PEG = 400,