Structural characteristics and enhanced mechanical and thermal properties of full biodegradable tea polyphenol/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) composite films

H. X. Xiang, S. H. Chen, Y. H. Cheng, Z. Zhou, M. F. Zhu*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, and College of Materials Science and Engineering, Donghua University, 201620 Shanghai, P.R.China

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Abstract. Full biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) composite films were prepared with 5–40 wt% green tea polyphenol (TP) as toughener. The effects of mixing TP on mechanical properties, thermal properties and hydrophilic-hydrophobic properties of composite films were investigated. Tension test results show that the incorporation of TP in the PHBV matrix can enhance the toughness of the composite films. Differential scanning calorimetric (DSC) studies show that there is a single glass transition temperature and the lower melting point temperature. Fourier transform infrared (FT-IR) results confirm that the intermolecular hydrogen bonding interactions in composite films. Contact angle measurements show that the hydrophilicity of TP/PHBV composite films can be controlled through adjusting the composition of TP.

Keywords: biodegradable polymers, poly(hydroxybutyrate-co-hydroxyvalerate), tea polyphenol, mechanical properties, thermal properties

1. Introduction

Recently, bacterial polyester poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) has been arising much attention in the field of biomedical and environmental friendly materials because of its good biocompatibility, biodegradability as well as thermoplastic properties. However, the wide application has been restricted by the poor mechanical properties and narrow processing window [1]. Therefore, a significant amount of work has been devoted to improving mechanical and thermal properties of PHBV via PHBV-based polymer blends and composites [2]. This work mainly covers four aspects: nanoparticles/PHBV composites, traditional petrochemical-based materials/PHBV composites, biodegradable

petrochemical-based polymer/PHBV composites, and bio-based materials/PHBV composites.

In nanoparticles/PHBV composites, inorganic nanoparticles mainly include oxide [3], nitride [4], mineralization materials [5, 6], carbon materials or minerals [7], and layered double hydroxides [8, 9]. Organic nanoparticles mainly include cellulose nanocrystal [10], chitosan nanocrystal and starch nanocrystal [11]. The introduction of nanoparticles is helpful for improving the physical properties and processing properties of PHBV through increasing the nucleation density and decreasing the spherulite size. In petrochemical-based materials/PHBV composites, the additive components consist mainly of non-biodegradable polyolefin [12], polyurethane

*Corresponding author, e-mail: zhumf@dhu.edu.cn
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elastomer [13] polyaniline [14]. These blending composites can improve physical properties by some extent and reduce the cost, but also there are some problems in compatibility. So Sadik improved the interfacial and mechanical properties of the immiscible PP/PHBV and PE/PHBV blends by pre-formed copolymer EVOH-g-PHBV [12]. In bio-based materials/PHBV composites, thermoplastic starch, cellulose, polycaprolactone [15], xyloglucan [16], polylactic acid [17], PBAT [18] and poly(butylene succinate) [19] are widely applied to fully biodegradable products [20, 21].

In the method of toughening PHBV, bisphenol A (BPA) as one prominent modifiers, it deters the biodegradability and biocompatibility of PHBV. In order to solve the environmental pollution fundamentally, bio-based materials/PHBV composites are the main direction. As a bio-based material, tea polyphenol (TP) deriving from natural tea leaves is a kind of phenolic compound which contains multiple hydroxyl groups [22]. So fully biodegradable TP was chosen to replace BPA. The major component of TP is catechin, and its chemical structure is shown in Figure 1. This structure provides a large amount of phenolic hydroxyl groups in proton-donating TP and allows it to take advantages of inhibiting bacterium, cancer, tumors.

Herein, fully biodegradable TP/PHBV composite films were prepared via solution blending and spin coating method with hydrogen bonding interaction with 5–40 wt% green TP as proton donor and biopolyester PHBV as proton acceptor. The tensile properties of composite films were studied to investigate the toughening effect of TP on PHBV matrix. The physical properties, thermal properties, crystalline structure and morphology were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), polarization optical microscopy (POM) and wide angle X-ray diffraction (WXR).

Figure 1. Chemical structure of TP

2. Experimental

2.1. Materials

PHBV with 1.09 mol% 3-hydroxyvalerate (HV) [$M_n = 1.16 \cdot 10^4 \text{ g} \cdot \text{mol}^{-1}$, $M_w/M_n = 2.30$] was obtained from Tianan Biologic Material Co., Ltd. (Ningbo, China). Tea polyphenol (TP) (polyphenols $\geq 98\%$, catechin $\geq 80\%$, EGCG $\geq 60\%$, caffeine $\leq 1.0\%$) was purchased from Xuancheng Baicao Plant Industry and Trade Co., Ltd (Xuancheng, China). Chloroform and dioxane were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received.

2.2. Preparation of TP/PHBV composite films

First, PHBV was completely dissolved in chloroform at 60°C in a three-necked flask with a magnetic stirrer. Then, the TP dioxane solutions with different mass fractions (5, 10, 20, 30 and 40 wt%) were mixed and stirred with the PHBV solution at room temperature for 6 h, respectively. Finally, these solutions were cast into films by an applicator. The solvent was allowed to evaporate slowly at room temperature for 48 h, and the resulting films were further dried under vacuum drying oven at 25°C for another 48 h.

2.3. Characterization

The tensile properties of TP/PHBV composite films were measured by an INSTRON 5969 electronic universal material testing machine (Instron Corporation, USA). Tensile specimens with 10 mm in width and 10 μm in thickness were drawn at a strain rate of 1 mm/min. The gauge length was 50 mm, and five replicates were run for each sample.

The hydrogen bond interactions between TP and PHBV were characterized by FT-IR spectrometer (Thermo Nicolet 8700, USA). These tests were carried out by the DTGS-MCT-A double-detector.

The crystalline structures of TP/PHBV composites were obtained with a D/Max-2550 PC diffractometer (Japan). All the samples were allowed to set aside for two weeks at room temperature to reach equilibrium crystallization. CuK_α X-ray source was used with a wavelength (λ) of 0.154 nm. The angle of incidence varies from 5 to 60° by steps of 0.02° . In order to directly understand the mobility of molecular chain of TP/PHBV composites, the crystal growth behaviors and crystalline morphologies of different composites were observed by DM2500P polarizing optical microscope with LINKAM

LTSE350 hot stage (Leica, Germany), and the radial growth rate of spherulites was calculated by data processing software. The samples were sandwiched between two cover slides and kept at 200°C for 2 min and then cooled down to a desired isothermal crystallization temperature with a cooling rate of 30°C/min. The growth rate of spherulite was calculated by the recorded photographs which are taken at constant time intervals.

The melting and crystallization behaviors of TP/PHBV composites were carried out by DSC (Q20, USA) with nitrogen as purging gas. Samples were firstly put on the 200°C hot stage for 4 min, waited until it was fully molten and put it into liquid nitrogen. Then the thermal properties of these samples were tested. The samples were heated from –50 to 200°C at a rate of 10°C/min.

The contact angles of the PHBV film and TP/PHBV composite films were measured via 322 W contact angle analyzer (Thermo Cahn, USA) at room temperature. About 2 μ L deionized water was dropped on the film surface for the tests at a contact time of 5 s. Five independent determinations at different sites of the film were averaged.

3. Results and discussion

3.1. Mechanical properties of TP/PHBV composite films

The stress-strain curves, tensile strength, and elongation at break of TP/PHBV composite films with various TP contents are shown in Figure 2. The toughness of TP/PHBV composite films increases sharply with an increase content of plant polyphenol TP. When the TP content increases from 0 to 20 wt%, the elongation at break of TP/PHBV composite films improved from 1.5 to 36.5%, with an increasing ratio of 2430%. This occurs because of the hydrogen bonding interaction between phenolic hydroxyl groups in TP and carbonyl ester groups in PHBV, which may delay the failure of PHBV under the tensile stress. TP also acts as a low molecular weight plasticizer, when the TP content is lower than 5 wt%, the tensile strength of composites tends to increase from 14.0 to 14.6 MPa. Meanwhile, the strain and elongation at break both increases by 5%. However, when the TP content exceeded 10 wt%, the tensile strength of the composite films decreased rapidly. This type of variation trend also appeared in the results of fracture work for TP/PHBV composite films. When TP content increased up to

Figure 2. Stress-strain curves (a), tensile properties (b) and fracture work (c) of TP/PHBV composite films with various TP contents

20 wt%, the elongation at break of composite films reached the maximum value of 36.5%, while the tensile strength decreased to 6.6 MPa. These results show that the incorporation of TP in the PHBV matrix can enhance the toughness of the composite films. When TP content exceeded 30 wt%, the tensile strength and elongation at break of TP/PHBV composite films fell notably.

3.2. Thermal properties of TP/PHBV composites

The mechanical properties of polymer materials are significantly dependent on the glass transition tem-

perature (T_g). Because the T_g of PHBV is lower than room temperature, so secondary crystallization of its products often occur easily during storage, and resulting in the decrease of its mechanical properties. So green TP is used to improve its T_g . DSC melting curves of PHBV and TP/PHBV composites is shown in Figure 3. The thermal parameters, such as T_g , cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpies (ΔH_{cc}), melting enthalpy (ΔH_m), is shown in Table 1. The degree of crystallinity (X_{DSC}) is also calculated by Equation (1) [23] to examine the changes caused by TP additives:

$$X_{DSC} = \frac{\Delta H_f}{(1 - \phi_{TP})\Delta H_f^0} \cdot 100\% \quad (1)$$

where X_{DSC} is the degree of crystallinity of PHBV and its composites, ϕ_{TP} is the weight fraction of TP, ΔH_f is the measured melting enthalpies and ΔH_f^0 is the enthalpies of 100% crystalline PHBV, which is chosen as 146.6 J g^{-1} for PHB.

In Figure 3 and Table 1, with the TP content increasing from 0 to 40 wt%, the T_g improved from 1.8 to

56.4°C, increasing by 54.6°C. The cold crystallization temperature increased from 43.4 to 109.5°C, and the melting temperature decreased from 174.6 to 157.7°C. These maybe occurred by the formation of the intermolecular hydrogen bonding interaction. As an effect of adding TP component on PHBV, its composites showed a single glass transition temperature and the lower melting point temperature. Moreover, the T_g was increased accordingly. The crystallinity of TP/PHBV composites also calculated by the change of enthalpies and are also shown in Table 1. The crystallinity of composites decreases with the increase of TP content. The decrease of crystallinity maybe influenced by hydrogen bonding interaction between PHBV and TP, which restricts the motion ability of molecular chain.

Figure 4 shows the crystallize patterns of PHBV and TP/PHBV composites at 40°C, respectively. In Figure 4a, the pure PHBV spherulites display the well-known Maltese cross extinction pattern and the concentric extinction rings with the radial growth rate of $1.08 \mu\text{m/s}$. When the TP contents was 5 wt%, ‘Maltese cross’ extinction pattern also appeared in composite, however the banded pattern changed to radial pattern. Moreover, the spherulite radius and the radial growth rate decreased with an increase of TP content. When the TP content reached 20 wt%, spherulite formation can't be observed resulting from the arrangement and the growth modes of spherulites lamellar layers, which are depending on polymer aggregate structure at the same isothermal crystallization temperature and degree of supercooling. The banded spherulites for PHBV generate band pattern of dark and light, which can be related to twisting period of the spherulites radial growth corresponding to extinction spacing, and the adjacent lamellar layers keep

Figure 3. DSC melting curves of PHBV and TP/PHBV composites

Table 1. Thermal parameters of PHBV and TP/PHBV composites

Sample	T_g [°C]	T_{cc}^a [°C]	ΔH_{cc} [J·g ⁻¹]	T_m [°C]	ΔH_m [J·g ⁻¹]	X_{DSC}^b [%]	X_{WXRDC}^c [%]
Pure PHBV	1.81	43.28	36.13	174.61	89.12	61.04	53.03
5 wt% TP/PHBV	6.36	53.08	37.83	169.89	80.34	57.92	48.83
10 wt% TP/PHBV	12.81	69.64	39.16	169.01	73.88	56.23	41.32
20 wt% TP/PHBV	24.80	99.74	37.76	163.88	50.43	43.18	40.72
30 wt% TP/PHBV	45.67	109.45	—	157.69	1.05	1.03	38.05
40 wt% TP/PHBV	56.35	—	—	—	—	—	31.64
Pure TP	—	—	—	—	—	—	8.19

^a T_{cc} is the cold crystallization temperature.

^bDetermined from DSC enthalpy parameters.

^cDetermined from WXRDC spectra

Figure 4. Crystalline morphology and radial growth rate of the spherulites of PHBV (a) and TP/PHBV composites (b) 5 wt% TP/PHBV, (c) 10 wt% TP/PHBV and (d) 20 wt% TP/PHBV at a constant temperature of 40°C

the same period and phase to twist. In the TP/PHBV composites, TP component as organic rigid toughening material plays the role of the proton-donating

material. The intermolecular hydrogen bonding interaction restricts molecular chain motion on PHBV component, and break coordination effect of

lamellae layers of the PHBV spherulites radial growth. As a result, banded spherulite patterns were replaced by radial patterns.

3.3. Hydrophilic-hydrophobic properties of TP/PHBV composites

In order to preliminary study on the application of TP/PHBV composite films, contact angle with water of pure PHBV film and TP/PHBV composite film with various TP contents are shown in Figure 5. The contact angle of TP/PHBV composite films showed a decreasing trend with the increase of TP content, from 97.3 to 54.2°. It can be explained by the hydrophilic interaction for phenolic hydroxyl groups in natural polyphenol TP. In the TP/PHBV composite films, some phenolic hydroxyl groups were exposed on the film surface and changed the surface tension of composite film, which accounted for the improvement of its hydrophilicity. On the other side, biocompatible TP has strong sterilizing

Figure 5. Contact angle of pure PHBV film and TP/PHBV composite films with various TP contents

function, which should be attributed to the α -phenyl-benzopyran structure in TP. With the combination of above advantages, it is expected that the TP/PHBV composites possess some promising applications in biomedical fields.

3.4. Intermolecular interactions of TP/PHBV composites

For a better understanding of the hydrogen bonding interaction between TP and PHBV, the FT-IR was used to observe the change of absorption peaks of characteristic groups. Figure 6 shows the FT-IR spectra of TP/PHBV composites, with the stretching vibrations of hydroxyl ($\nu_{\text{O-H}}$) and carbonyl ($\nu_{\text{C=O}}$) groups. All the characteristic absorption peaks of PHBV and TP appear in TP/PHBV composites, while the positions of hydroxyl and carbonyl stretching vibration peaks have changed. TP shows one broad band, centered at 3380 cm^{-1} , which attributed to the phenolic hydroxyl stretching vibration. For pure PHBV, only a weak peak band centered at 3440 cm^{-1} is observed in this region, which should be attributed to the stretching of the chain-end hydroxyl groups [24]. In Figure 6b, a new band appears at about 3250 cm^{-1} which presumably was induced by the formation of inter-molecular hydrogen bonding between TP and PHBV.

To illustrate hydrogen bonding interaction, the carbonyl ($\nu_{\text{C=O}}$) stretching vibration band in the range from 1660 to 1800 cm^{-1} was analyzed. As is shown in Figure 6b, the peak band around 1722 cm^{-1} should be attributed to the crystalline region of the carbonyl group of PHBV, which is very clear for neat PHBV, and the peak at around 1746 cm^{-1} to the amorphous region of the carbonyl group [22, 25,

Figure 6. FT-IR spectra of TP/PHBV composites (a), hydroxyl stretching region and carbonyl stretching region in the range of 3800–3000 and 1800–1650 cm^{-1} (b)

26]. When the PHBV is blended with TP, a new band appears at lower wave-number about 1688 cm^{-1} . This new band is assigned to the hydrogen-bonded carbonyl groups. With the increase of the TP content, the carbonyl peak position for parts of crystalline region of the carbonyl group is shifting from 1722 to 1728 cm^{-1} , whereas that parts of the free C=O group is almost invariable. This suggested that the hydrogen bonding interaction is formed between the phenolic hydroxyl and carboxyl groups, which is consistent with the results of hydroxyl ($\nu_{\text{O-H}}$) stretching vibration band.

3.5. Crystalline structure of TP/PHBV composites

The physical properties of polymer composite films not only depend on the intermolecular force but also on the degree of crystallinity. The effect of addition TP component on PHBV crystal structure was characterized by WAXD, and the patterns of PHBV and TP/PHBV composites are shown in Figure 7. The diffraction peaks of (020), (110), (021), (101), (111), (121), (040) and (002) for PHBV crystal face appeared in WAXD patterns. And the TP did not significantly affect the diffraction peak position of TP/PHBV composites. This indicates that the introduction of the TP component in composites doesn't change the crystal structure of PHBV. From Figure 7 and Table 1, the crystallinity of PHBV component decreases with an increase in TP content, reducing from 53 to 32%. The decrease of crystallinity maybe influenced by hydrogen bonding interaction between PHBV and TP, which is consistent with the results discussed in DSC.

Figure 7. XRD patterns of PHBV and TP/PHBV composites

4. Conclusions

Biodegradable TP/PHBV composites were prepared with green TP and bacterial polyester PHBV. The intermolecular hydrogen bonding interactions in composites were confirmed through the shift of hydroxyl ($\nu_{\text{O-H}}$) and carbonyl ($\nu_{\text{C=O}}$) stretching vibration peaks. By adding TP components to PHBV matrix, the mechanical and thermal properties of TP/PHBV composite films were improved. Compared with pure PHBV, the elongation at break increased 24 times, meanwhile, the glass transition temperature and cold crystallization peak temperature increased by almost 45 and 45°C , respectively. The hydrophilicity of TP/PHBV composites can be controlled through adjusting the dosage of TP. Therefore, the result of this composite system will have an important effect on broadening the green plant polyphenol application and expanding the modification methods for preparing fully biodegradable environmental-friendly bacterial polyester materials.

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