

Mechanical, thermal and degradation properties of poly(*d,l*-lactide)/poly(hydroxybutyrate-*co*-hydroxyvalerate)/poly(ethylene glycol) blend

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ABSTRACT

The mechanical, thermal and biodegradable properties of poly(*d,l*-lactide) (PDLLA), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(ethylene glycol) (PEG) blends were studied. The influence of PEG on the tensile and impact strengths of the blends was investigated. The results showed that the toughness and elongation at break of the PDLLA/PHBV (70/30) blends were greatly improved by the addition of PEG, and the notched Izod impact strength increased about 400% and the elongation at break increased from 2.1% to 237.0%. The thermal and degradation properties of the blends were investigated by differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA), it was found that the thermal stability of PHBV in the presence of PDLLA was improved. The degradation test showed that the addition of PEG could notably accelerate the biodegradation of the blends in the soil at room temperature, and the mass loss is about 20% after 30 days of the storage.

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1. Introduction

Polymers like poly(3-hydroxybutyrate) (PHB), poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) and poly(lactic acid) (PLA) have attracted much attention recently because of their excellent biodegradability and biocompatibility. However, the brittleness and narrow processing window of these polymers restrict their application. Blending of these polymers with other biocompatible polymers has been widely studied to improve their mechanical and thermal properties [1–4].

PLA (including poly(*l*-lactide), PLLA and poly(*d,l*-lactide), PDLLA) have high mechanical strength and modulus with complete biodegradability and biocompatibility which make it suitable for use in biomedical, agricultural and packaging applications. However, the noticeable brittleness and rigidity of PLA restrict its broad application.

Bacterially synthesized PHBV is a crystalline polymer with complete biodegradability and biocompatibility, which is also attractive for applications in the biomedical materials and environmentally friendly materials [5–8]. The resistances to water, gas and high temperature of PHBV are excellent.

And the tensile strength of PHBV at maximum is 28 ± 3 MPa and elongation at break is $9 \pm 3\%$ [9]. PDLLA can improve the mechanical properties of PHBV. Zhang et al. [4] investigated PHB/PDLLA blends

and proved that the blending of PDLLA and PHB was helpful to improve the toughness of PHB and the thermal stability of PDLLA. The crystallization behavior would greatly influence the mechanical properties of both composites. The crystallization of PHB in the blends was affected by the level of addition of PDLLA. Two types of spherulites were observed by Blümm and Owen [10], which showed that PHB and PLLA did not co-crystallize. And spherulites of opposite type could interpenetrate when different spherulites met.

Poly(ethylene glycol) (PEG) is often used as a plasticizer with good biocompatibility and blood compatibility. It is hydrophilic, water-soluble, nontoxic and flexible. Many researches have been done on PLA/PEG [11] and PHBV/PEG [9,12] systems. Stefani et al. [11] found that hydrolytic degradation of lactic acid stereo-copolymers depends much on whether zinc lactate or tin octoate was used to polymerize lactides, and the research showed degradation proceeded faster inside than at the surface. Parra et al. [9] studied the thermal, mechanical, morphological, physical–chemical and biodegradation properties of PHB/PEG blends, and proved the addition of PEG as a plasticizer could not change the thermal stability but decreased the tensile strength and increased the elongation at break of PHB with the increase in the PEG content. In conclusion, the addition of PEG might be helpful to improve some of the mechanical properties without influencing the thermal stability of the original blends.

Ternary blends of PDLLA/PHBV/PEG have not been reported till now. So this work focuses on the mechanical properties, thermal stabilities and degradation properties of PDLLA/PHBV/PEG based on the previous experience.

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2. Experimental

2.1. Material and sample preparation

Biodegradable PHBV copolymer in the form of white powder was provided by Tianan Biologic Material Co. Ltd., Ningbo, China. The content of β -hydroxyvalerate (HV) in the copolymer is 1.13 mol%, as measured by Nuclear Magnetic Resonance (MERCURYplus 400, Varian, Inc., USA). The viscosity-average molecular weight of the copolymer is 130,000, as measured at 30 °C with chloroform as a solvent in an Ubbelohde Viscometer via the equation:

$[\eta] = KM^\alpha$, where $[\eta]$ is the intrinsic viscosity, K and α are parameters, and M is the viscosity-average molecular weight.

Biodegradable PDLLA in the form of yellow translucent granules was made by Natureworks, USA. Its number-average molecular weight (M_n) is 151,400 and molecular weight distribution index (M_w/M_n) is 1.458 ± 0.011 as measured by Gel Permeation Chromatography (GPC, Series 200, Perkin Elmer, Inc., USA).

PEG was supplied by National Medicine Group Chemical Agent Co. Ltd., China with an average molecular weight of 20,000.

Both PHBV and PDLLA were pre-treated in a vacuum oven (0.09 MPa) for 12 h at 50 °C, then the samples were prepared in the Rheocord 90 HAAKE Rheometer (Mess-Technic GmbH, Germany), under the condition of 170 °C \times 40 rpm \times 6 min. Then the samples were sealed and stored at room temperature for 24 h. The mixed samples were compression molded into sheets. The samples were cut into rectangular bars ($63.5 \times 12.7 \times 3.2$ mm³) and dumbbell-shaped specimen, and stored for 24 h at 23 °C before tensile and impact tests.

2.2. Mechanical properties

Tensile and flexural properties were measured using an Instron 4465 (Instron Corp., USA) according to ASTM D638 and D790. Notched Izod impact strength was determined using an impact analyzer (RAY-RAN Test Equipment Ltd., UK) according to ASTM D256. The dumbbell-shaped specimens were 1 mm thick and the speed of the crosshead was 20 mm/min for tensile test and 1.7 mm/min for flexural test at 23 °C. The rectangular bars were used for flexural and impact tests.

2.3. Scanning electron microscopy

The morphologies of fracture surfaces of impact specimens were studied using scanning electron microscopy (S-2150 Hitachi Co., Japan). The impact fracture surfaces were then sputter-coated with a thin gold layer before observation.

2.4. Differential scanning calorimetry

Melting behavior of PHBV, PDLLA and PDLLA/PHBV/PEG blends was investigated by DSC (Pyris 1; Perkin Elmer, Inc., USA). The samples were treated with different processes.

- (1) Sequential scan: PHBV was heated from 20 °C to 200 °C at 20 °C/min under a nitrogen atmosphere, and annealed for 3 min at 200 °C, and then cooled to 20 °C at 50 °C/min, and the process was repeated for 6 times. All the sequential heating curves were tracked.
- (2) Ordinary scan: the samples were heated from room temperature to 200 °C at 20 °C/min under a nitrogen atmosphere and held for 3 min at 200 °C. Then, the samples were cooled to -20 °C at 10 °C/min, and reheated to 200 °C at the same scanning rate. The second heating DSC run curves were marked to estimate the melting behavior according to the analysis in the paper. The crystallinities of blends and PHBV phase were obtained from the following equations:

$$C_{\text{blend}} = \frac{\Delta H_f}{\Delta H_0} \times 100 \quad (1)$$

$$C_{\text{PHBV}} = \frac{\Delta H_f}{\Delta H_0 \times W_{\text{PHBV}}} \times 100 \quad (2)$$

where C_{blend} and C_{PHBV} are the crystallinities of the blend and PHBV in the blend, respectively, ΔH_0 is the thermodynamic enthalpy of fusion per gram of PHB (146.6 J/g) [13], ΔH_f is the apparent enthalpy of fusion per gram of PHBV/PDLLA/PEG blends; W_{PHBV} is the mass content of PHBV in the blends.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of samples was carried out with a Thermogravimetric Analyzer (Perkin Elmer, Inc., USA). The weight of each specimen was about 3 mg and the atmosphere was nitrogen (40 ml/min). The temperature increases at the rate of 20 °C/min. TGA curves were recorded in the process of heating from room temperature to 700 °C.

2.6. Degradation test

To study the degradation of blends in the natural environment, each piece of specimen ($25 \times 25 \times 0.4$ mm³) was buried separately into common garden soil at room temperature without any extra degradation enzyme or bacteria added. Samples were periodically removed from the soil, washed with distilled water for 3 times and dried till a constant weight in a vacuum oven at 40 °C before further analysis by gravimetric measurement.

The surface morphologies of the specimen during degradation test were observed by optical microscopy using a Leica DM LP microscope (Leica Microsystems GmbH, Germany). Photographs of initial and final stages of each specimen were taken.

3. Result and discussion

3.1. Mechanical properties

The mechanical properties of PDLLA/PHBV/PEG blends with different weight-ratios are listed in Table 1. The results indicate that PDLLA is stiff and brittle with high tensile strength, and PHBV is a brittle material with higher flexural modulus but lower tensile and flexural strengths. The mechanical properties of PDLLA/PHBV (70/30) were much better than those of PHBV. The tensile strength, flexural strength and flexural modulus were significantly reduced by the addition of PEG, but the elongation at break increased obviously. At the weight ratio of PDLLA/PHBV/PEG (70/30/20), the elongation at break achieved 237% and the tensile strength was higher than 24 MPa.

Fig. 1 shows the stress-strain curves of the PDLLA and PDLLA/PHBV/PEG blends. Although the tensile strength of PDLLA reached 56 MPa, PDLLA broke before arriving at the yield point with a small strain, indicating the typical brittle behavior, so did PHBV and PDLLA/PHBV blends. Tensile strength and elongation at a break of

Table 1
Mechanical properties of PDLLA/PHBV/PEG blends

| PDLLA/PHBV/PEG | Tensile strength, MPa | Elongation at break, % | Flexural strength, MPa | Flexural modulus, MPa |
|----------------|-----------------------|------------------------|------------------------|-----------------------|
| 100/0/0 | 54.7 | 5.03 | 94.0 | 3655 |
| 0/100/0 | 19.7 | 0.17 | 39.1 | 3646 |
| 70/30/0 | 49.7 | 2.07 | 75.0 | 3507 |
| 70/30/10 | 29.7 | 28.7 | 36.1 | 1127 |
| 70/30/20 | 24.1 | 237.0 | 5.48 | 220 |

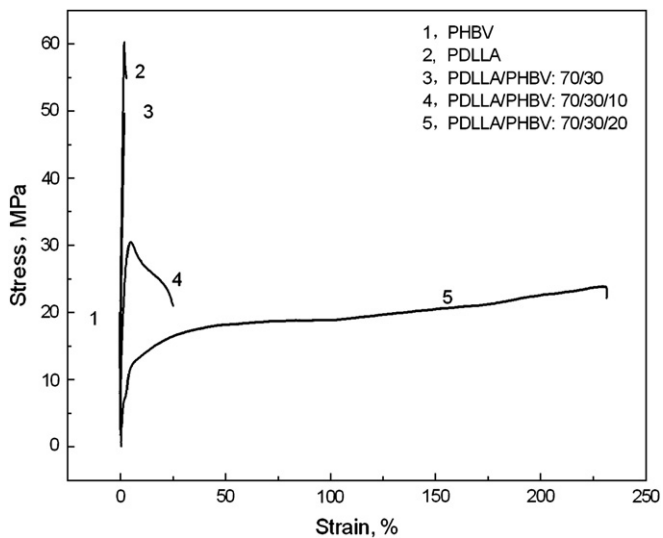


Fig. 1. Stress-strain curves of PDLLA/PHBV/PEG blends.

PDLLA/PHBV (70/30) were lower than those of PDLLA, but there was a great improvement, compared with PHBV. When the weight ratio of PDLLA/PHBV/PEG blend was 70/30/10, its stress-strain behavior changed markedly from that of PDLLA/PHBV, and a thin-neck was formed with notable craze in the tensile process. It yielded at 5% strain and the elongation at break increased to 30%, 6 times higher than that of PDLLA, showing that the toughness increased to a certain extent. There was no yield phenomenon when the weight ratio was 70/30/20. The stress increased rapidly within a small strain in the beginning, then came to a flat stage with increasing strain, which was similar to the forepart stress-strain curves of elastomers. The PDLLA/PHBV/PEG (70/30/10) showed some characters like those of flexible materials.

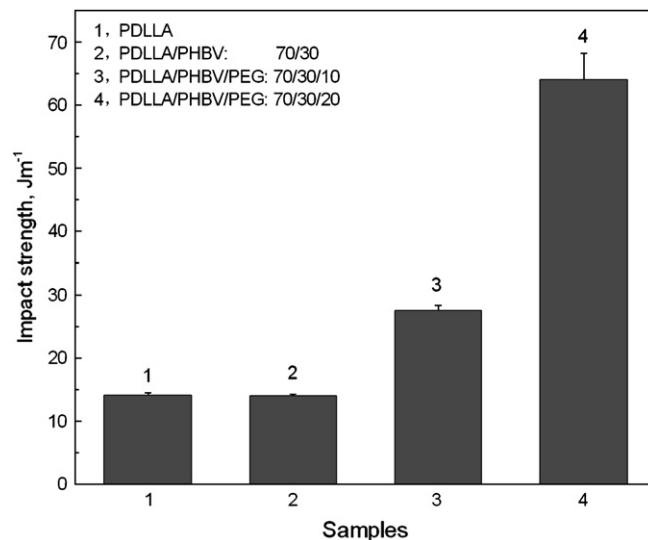


Fig. 2. Impact strength of PDLLA/PHBV blends 1, PDLLA; 2, PDLLA/PHBV (70/30); 3, PDLLA/PHBV/PEG (70/30/10); 4, PDLLA/PHBV/PEG (70/30/20).

The impact strength of PDLLA, PDLLA/PHBV and PDLLA/PHBV/PEG blends with different PEG contents is shown in Fig. 2. The toughness of materials could be depicted by impact strength. PDLLA and PDLLA/PHBV blends have extremely low impact strength, which was obviously enhanced after the addition of PEG, and the impact strength increased with increasing PEG content. It indicates that the addition of PEG could effectively increase the toughness of PDLLA/PHBV blends because the plasticizer of PEG could act as a lubricant and eliminate the impact to one point caused by the strain. The ductile PEG could move among the polymer molecules and transfer the strain to different parts of the material.

The morphologies of the fracture surfaces were investigated by SEM, as shown in Fig. 3. The fracture surface of PDLLA was quite

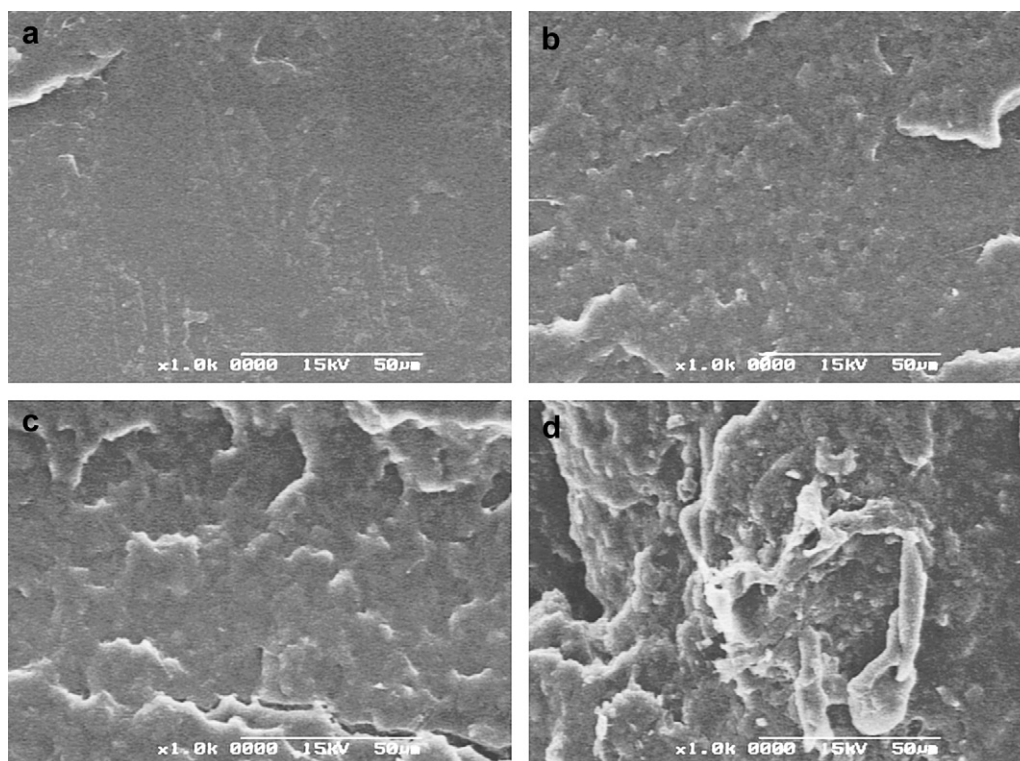


Fig. 3. SEM micrographs of fractured surface of PHBV/PDLLA/PEG blends (a) PDLLA; (b) PDLLA/PHBV (70/30); (c) PDLLA/PHBV/PEG (70/30/10); (d) PDLLA/PHBV/PEG (70/30/20).

smooth and this type of fracture was caused by low energy. Coarseness was observed on the fracture surface of PDLLA/PHBV, and the crack of the blend mainly developed along the same direction, indicating the resistance to the development of cracks was quite low. These two morphologies (Fig. 3a and b) indicate a brittle fracture. The surfaces of impact specimens with PEG were rougher than those without PEG, and cracks developed in different directions, as shown in Fig. 3c and d. It is obvious that shear-yield and plastic deformation formed on the fracture surfaces of blends with PEG, especially for the blend with high content (20 phr, Fig. 3d). Plastic deformation and different directions of cracks needed more energy in fracture and thus the materials with PEG had better toughness.

3.2. Crystallization and melting behavior

It is reported [14,15] that thermal treatment is responsible for thermal degradation of PHB, and it results in a shift of the highest maximum melting peak (T_{m2}) to a lower temperature in DSC thermograms and a broader endotherms. Ivica et al. [14] investigated PHB/glycerol blends and repeated that glycerol enhanced the thermal degradation of PHB due to its ability to participate in an alcoholysis reaction in the thermal treatment. But further increase in its content resulted in a certain level of recombination of the PHB fragments via condensation reaction with the glycerol moieties, and the degradation of PHB was improved when the content of glycerol was high.

Fig. 4 showed six sequential scanning curves of PHBV according to 2.4 (1). The results indicated that the melting peaks of PHBV notably shifted to lower temperature with broadening of endotherms due to the thermal degradation. Therefore, the second heating scan of samples could be used to describe the thermal degradation and stability of polymers such as PHBV.

Fig. 5 describes the second heating scan of PDLLA/PHBV/PEG blends by DSC, and the parameters of thermal properties obtained from DSC curves are shown in Table 2. The melting curves (curve 1, 2) show that the melting temperature (T_{m2}) of PHBV significantly increased after blending with PDLLA, but it was still lower than that of PHBV obtained from the first heating scan. The melting peak of PHBV/PDLLA was much narrower than that of PHBV, indicating that the addition of PDLLA could improve the thermal stability of PHBV and prohibited thermal degradation to some extent. The addition of PEG had little influence on the position of the melting peak, which

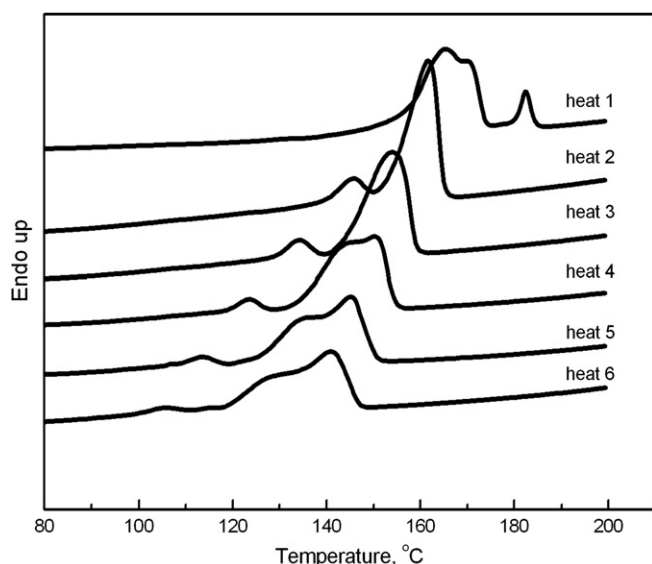


Fig. 4. Six sequential scanning curves of PHBV on DSC.

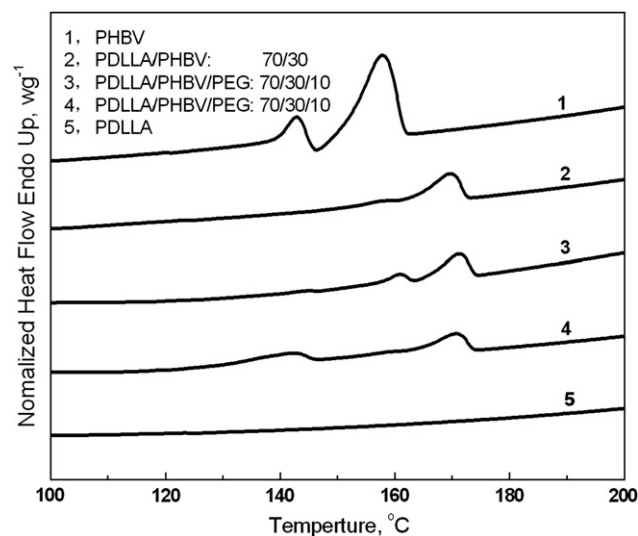


Fig. 5. Second heating scan of PDLLA/PHBV/PEG blends at a heating rate of 10 °C/min by DSC 1, PHBV; 2, PDLLA/PHBV (70/30); 3, PDLLA/PHBV/PEG (70/30/10); 4, PDLLA/PHBV/PEG (70/30/20); 5, PDLLA.

meant PEG did not activate alcoholysis reaction and result in remarkable thermal degradation. It is probably because of the high molecular weight of PEG used in this work and low mol content of alcohol groups, and they were not adequate for an obvious alcoholysis reaction.

In addition, thermal analysis parameters in Table 2 brought more details. Either the crystallinities of PHBV phase or those of blends prominently decreased when PDLLA was added. With increasing PEG content, the crystallinity of PHBV phase increased obviously. PDLLA added blocked the crystallization process of PHBV and changed its crystallization kinetics. On the other hand, PEG could perform as a plasticizer and had a positive influence on the chain mobility of PHBV and better packing of the chains and thus improved the crystallization capacity.

3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) curves are shown in Fig. 6. The thermal weight-losses of PHBV and PDLLA were quite sensitive to temperature with narrow decomposing temperature ranges. Curves 1, 2 and 4 reveal that the thermal stability of PDLLA is higher than that of PHBV, and the thermal decomposing temperature of PDLLA/PHBV blends was between those of PDLLA and PHBV, however, the thermal weight-loss stage of the two components exhibits little distinction. Curve 3 shows the thermal gravimetric analysis result of PEG. PEG started to degrade and lose weight slowly at a quite low temperature of about 200 °C, but the maximum weight-loss rate happened at a much higher temperature. Comparing the curves 4, 5 and 6, the addition of PEG brought out a slight shift of the onset temperature of PDLLA/PHBV blends to

Table 2
Thermal analysis parameters of PDLLA/PHBV/PEG blends

| Formulation: PDLLA/PHBV/PEG | Melting | | | |
|--------------------------------|---------------|--------------------|-----------------|----------------|
| | T_{m2} , °C | ΔH_m , J/g | C_{blend} , % | C_{PHBV} , % |
| 0/100/0 | 157.8 | 20.1 | 53.6 | 53.6 |
| 70/30/0 | 169.8 | 6.7 | 9.9 | 33.1 |
| 70/30/10 | 171.2 | 4.6 | 10.5 | 38.4 |
| 70/30/20 | 170.8 | 14.3 | 13.0 | 51.9 |
| 100/0/0 | – | – | – | – |

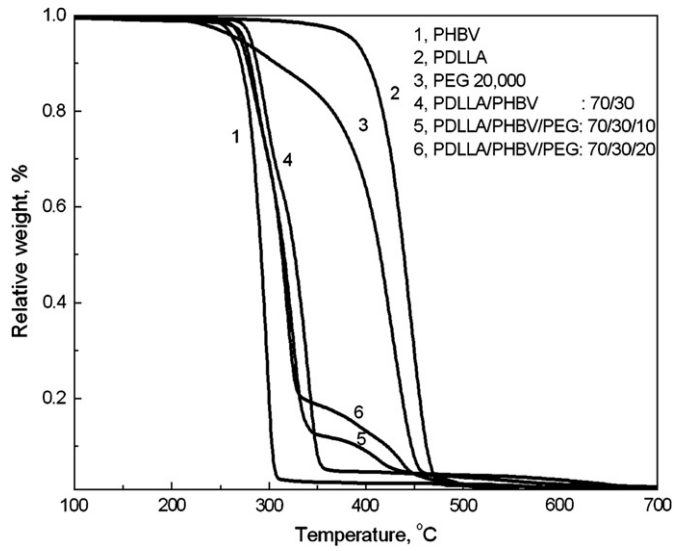


Fig. 6. TGA curves of PDLLA/PHBV/PEG blends.

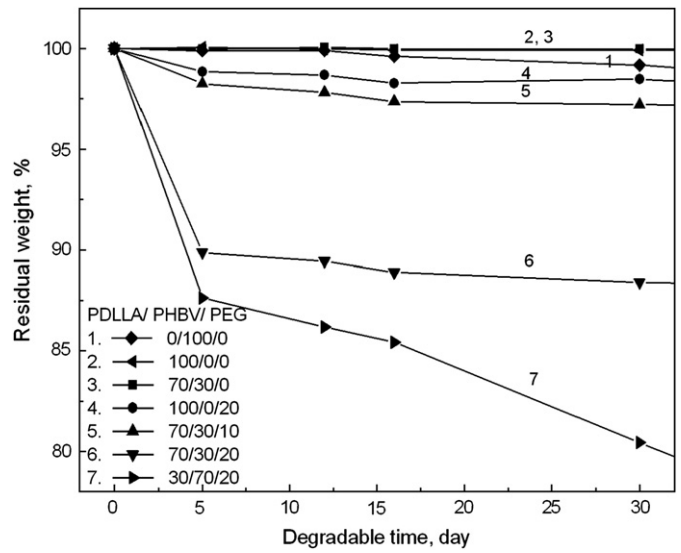


Fig. 7. Weight-loss curves of PDLLA/PHBV/PEG blends.

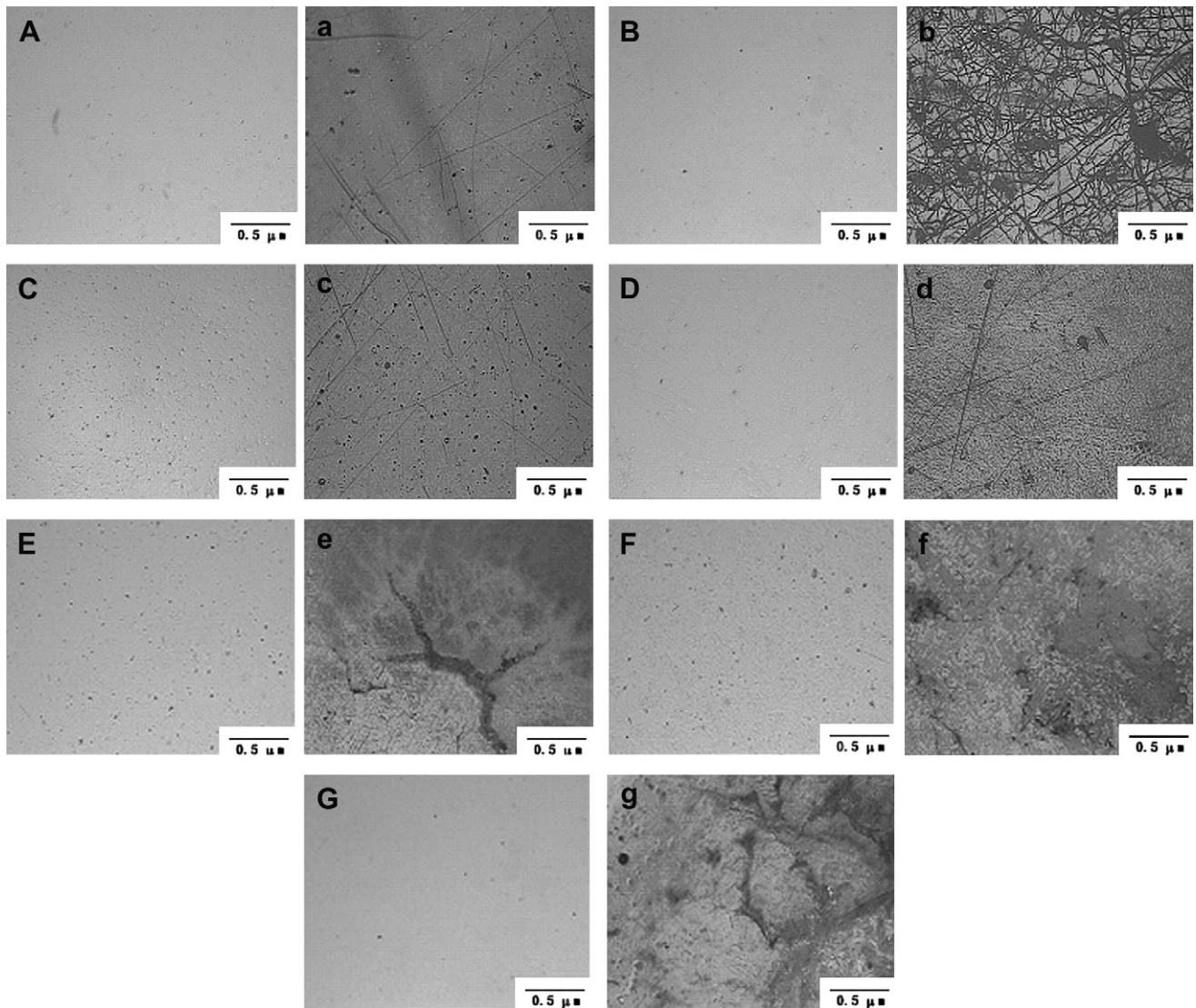


Fig. 8. Photos of the surfaces of the samples before and after (30 days) the environmental degradation test by optical microscopy (A) PDLLA (before); (a) PDLLA (after); (B) PHBV (before); (b) PHBV (after); (C) PDLLA/PHBV (70/30) (before); (c) PDLLA/PHBV (70/30) (after); (D) PDLLA/PHBV/PEG (70/30/10) (before); (d) PDLLA/PHBV/PEG (70/30/10) (after); (E) PDLLA/PHBV/PEG (70/30/20) (before); (e) PDLLA/PHBV/PEG (70/30/20) (after); (F) PDLLA/PHBV/PEG (30/70/20) (before); (f) PDLLA/PHBV/PEG (30/70/20) (after); (G) PDLLA/PEG (100/20) (before); (g) PDLLA/PEG (100/20) (after).

a lower temperature, but the thermal degradation temperature of later thermal weight-loss stage shifted to a higher temperature. This phenomenon was attributed to the natural characteristic of thermal weight-loss of PEG.

3.4. Environmental degradation

The biodegradation of polymers involves distinct mechanisms, depending on the nature of a polymer. Peroxidation followed by bioassimilation of low molar mass products (oxobiodegradation) is typical for carbon chain polymers. But for heterochain polymers, such as poly(L-lactide) (PLA) and poly(hydroxylalkanoates) (PHA), hydrolysis (biotic or abiotic) followed by bioassimilation (hydrodegradation) is the primary pathway involved in the biodegradation [9].

The degradation experiment adopted here made profound sense on environment pollution by using common soil from the garden without any additional bacteria and/or microorganism at room temperature, simulating the real compost environment. The results of environment degradation in 30 days, together with the data for mass loss and optical microscopy findings, are shown in Figs. 7 and 8, respectively. PDLLA, PHBV and PDLLA/PHBV exhibited an extremely low degradation rate in common soil at room temperature, and mass retention was almost 100% in the first month (curves 1–3). As can be seen, PHBV degraded a little faster than PDLLA by comparing curves 1 (PHBV) and 2 (PDLLA). When hydrophilic PEG was added, the degradation rate increased rapidly. The environmental degradation rate grew simultaneously with increasing PEG content (wt%) in the blends, as shown in curves 3, 5 and 6. Because of the hydrophobic nature of PHBV and PDLLA, it was difficult for water to penetrate into the materials. But the excellent water-solubility and hydrophilic characters of PEG in blends could help absorb and keep the water. In the presence of water, both PHBV and PDLLA would carry out hydrolysis reaction, so the linear chains would break down at the ester-bond and finally result in decrease of molecular weight and mass loss. It well agreed with the conclusion and mechanism reported by Li et al. [16]. As the content (wt%) of PEG was the same (PDLLA/PHBV/PEG 70/30/20 in curve 6, 30/70/20 in curve 7), the degradation rate increased isochronously with the increasing PHBV content in the blends. That is because of the better degradation properties of PHBV than that of PDLLA or a synergistic effect existed during the hydrolysis reaction. Therefore, blending materials with different degradation rates could be obtained by adjusting the ratio of PDLLA/PHBV/PEG.

Increasing PEG content also caused morphological change in the surfaces of PDLLA, PHB and blends, shown in Fig. 8. Similar results were also reported by Parra et al. [9], who believed that increasing concentration of plasticizers reduced the interaction between the chains of PHB and PEG in the blends, thereby accelerating biodegradation.

4. Conclusions

The impact strength of the PDLLA/PHBV/PEG blends was 1–4 times than that of the PDLLA/PHBV blends and elongation at break

reached over 200%, which were both attributed to the addition of PEG. The stress–strain behavior and micrograph of the deformed surfaces showed that the addition of PEG evidently improved the toughness of PDLLA/PHBV. The results of DSC and TGA indicated that the blending of PDLLA and PHBV enhanced the thermal stability and thermal degradation temperature of PHBV. PEG with a molecular weight of 20,000 could accelerate the crystallization of PHBV but brought little influence to the thermal stability. The addition of PEG can dramatically increase the degradation rate of PDLLA and PDLLA/PHBV blends in the soil at room temperature.

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