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Morphology and properties of poly(lactic acid-*co*-glycolic acid) film improved by blending with poly(γ-benzyl L-glutamate)

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Abstract A series of poly(lactic acid-*co*-glycolic acid) (PLGA)/poly(γ-benzyl L-glutamate) (PBLG) blend films were prepared by casting the polymer blend solution in chloroform. Surface morphologies of the PLGA/PBLG blend films were investigated by scanning electron microscopy. Thermal, mechanical, and chemical properties of PLGA/PBLG blend films were studied by differential scanning calorimetry, thermogravimetric analysis, tensile tests, and surface contact angle tests. The results displayed that when PBLG mole content is 4 %, the tensile strength and the maximum decomposition temperature of the polymer blend film are 20.2 MPa and 359 °C, respectively, suggesting that the polymer blend film holds both a better mechanical property and a better thermal property.

Keywords Morphology · Properties · Poly(lactic acid-*co*-glycolic acid) · Polypeptide · Blend · Film

Introduction

Because of the excellent biocompatibility, biodegradability, and nontoxicity, poly(lactic acid-*co*-glycolic acid) (PLGA) has attracted much attention for its potential applications [1–8]. Owing to its unique structure and properties, PLGA has been extensively used in biomedical fields such as absorbable sutures, reconstructive implants, wound healing materials, temporal scaffolds for tissue engineering, and drug release systems [9–17], etc. Also, PLGA films are usually used as artificial skin grafts [1, 2].

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As known, the biodegradable aliphatic polyesters such as PLGA have versatile biodegradation properties because of their molecular weight and chemical compositions [18]. Nevertheless, there have been many attempts to improve the properties of the polymers to make them suitable for specific applications. For example, to prolong the circulation time of PLGA nanoparticles in a blood stream in vivo, PLLA/PEG di-block copolymers were coated onto the surface of PLGA nanoparticles by blending PLLA–PEG di-block copolymers with PLGA during the nanoparticle formulation process [19]. It was postulated that the surface-orientated PEG chains onto the surface of nanoparticles not only suppress the adsorption of serum proteins but also reduce the extent of cell recognition [2]. As noted, protein adsorption onto polymer surfaces could strongly affect the cellular interactions with foreign surfaces [20], induce the macrophage activation followed by immunologic response to foreign materials [21], and control the adhesion behavior of the cells [22].

Usually, PLGA is relatively flexible and holds little hydrophilicity, while the polypeptide such as poly(γ-benzyl L-glutamate) (PBLG) is rigid and hydrophobic [23–26]. The introduction of the polypeptide into PLGA could improve the properties of the PLGA film, and further enlarge its application fields. To the best of our knowledge, however, no experimental work has so far been reported on the studies of the properties of PLGA/PBLG blend films. In the present study, a series of PLGA/PBLG blend films with different PBLG mole content were prepared by casting the polymer blend solution in chloroform. Surface morphologies of PLGA/PBLG blend films were investigated by the scanning electron microscopy (SEM) technique. Thermal, mechanical, and chemical properties of PLGA/PBLG blend films were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile tests, and surface contact angle tests. It was revealed that the introduction of the polypeptide could exert marked effects on the properties of PLGA films.

Experimental

Materials

The PLGA (M_w = 100,000), which was composed by a 70:30 ratio of lactic acid and glycolic acid units, was purchased from Jinan Daigang Biological Technology (China), and used as received. Hexane, tetrahydrofuran, and 1,4-dioxane werre of analytical grade and dried with sodium to remove water before use. Chloroform and other solvents were of analytical grade and used without further purification.

Preparation of PBLG homopolymer

The PBLG homopolymer was synthesized through a standard *N*-carboxyl-γ-benzyl-L-glutamate anhydride method [25, 26]. The molecular weight of PBLG was estimated from the intrinsic viscosity measured in dichloroacetic acid [27]. The molecular weight of PBLG used in the study was about 70,000.

Preparation of PLGA/PBLG blend film

The polymer blend films were prepared by casting a 30 wt% polymer blend solution in chloroform onto clean glass plates and drying them under vacuum at 50 °C. Also, it was found that, when the PBLG homopolymer mole content in polymer blend is over 8 %, the polymer blend cannot form a continuous film.

Characterizations

SEM measurements

SEM investigations were carried out using a scanning electron microscope (Sirin 200; FEI, Netherlands). Gold was sprayed on the polymer blend films in vacuum. The acceleration voltage was 5 kV.

DSC measurements

DSC measurements were made on a DSC Q100 (TA, USA) differential scanning calorimeter; the temperature was calibrated with indium in a nitrogen atmosphere. About 8-mg samples were weighed very accurately. The temperature was controlled within the range of 20–150 °C, the heating rate was 10 °C/min.

TG measurements

TGA was carried out on a STA 4490 C TG-DTA analyzer (Netzsch, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere over the temperature range of 30–550 °C. Samples of approximately 13 mg were used for the measurements.

Tensile tests

Tensile tests were carried out with an Instron Model 4468 universal testing machine (Digital Instruments, USA). The crosshead speed was set to 130 mm/min. For each data point, five samples were tested and the average value was taken.

Surface contact angle tests

A 5-μL drop of pure distilled water was placed on the polymer blend film surface using a syringe with a 22-gauge needle. The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument, Finland). The measurements of each contact angle were performed within 10 s after each drop to ensure that the droplet did not soak into the compact. The surface contact angles were the mean of five determinations [28].

Water-absorption ratio measurements

Water-absorption ratio measurements of the polymer blend films were completed as follows: at room temperature, the sample films were soaked in deionized water for

12 h, and then filter paper was used to wipe off water from the polymer blend film. The water-absorption ratio (%) was calculated according to the formula: Water-absorption ratio (%) = $[(W_2 - W_1)/W_1] \times 100$ %, where W_1 and W_2 are the masses of the polymer blend film before and after being immersed in deionized water, respectively [5, 29, 30].

Results and discussion

Morphology study

The surface morphologies of PLGA/PBLG blend films with different PBLG mole contents were researched by the SEM technique. Figure 1 shows the SEM photographs of the PLGA/PBLG blend film surface with various PBLG mole contents: (a) 0 %, (b) 4 %, and (c) 8 % (magnification ×5,000). As can be seen from Fig. 1, the introduction of PBLG segments changed the surface morphologies of the PLGA films changed from slippy to coarser and a little phase-separation appeared with the increase of the polypeptide content. As noted, with the increase of the polypeptide content in the polymer blends, on the one hand, the PLGA chains and polypeptide segments could exert an interaction by entanglement, while on the other hand, the self-aggregating action could also be exerted between the polypeptide segments. This phenomenon indicates that the change of the surface morphologies of the polymer blend films could be attributed to the introduction of the polypeptide segments.

Thermal properties

Figure 2 presents the DSC curves of the PLGA/PBLG blends with various PBLG mole contents: (a) 0 %, (b) 4 %, and (c) 8 %; the corresponding data are listed in Table 1. As seen from Fig. 2 and Table 1, the glass transition temperature of the PLGA segments in the polymer blends slightly increased with the increase of the PBLG mole content in the polymer blends. As known, compared with PLGA segments, the polypeptide chains are relatively rigid and hold a higher glass transition temperature, and the introduction of the polypeptide segments could slightly promote the glass transition temperature of the PLGA chains in the polymer blends. This phenomenon reveals that the increase of the glass transition temperature of the PLGA segments in the polymer blends could also be attributed to the introduction of the polypeptide segments.

Figure 3 displays the DTG curves of PLGA/PBLG blends with various PBLG mole contents: (a) 0 %, (b) 4 %, and (c) 8 %. As shown in Fig. 3, the maximum decomposition temperature of the PLGA segments in the polymer blends slightly increased with the increase of PBLG mole content. As mentioned above, the PLGA segments and the rigid polypeptide chains could exert interactions by entanglement, indicating that the increase of the maximum decomposition temperature of the PLGA segments in the polymer blends was connected with the introduction of the rigid polypeptide chains.

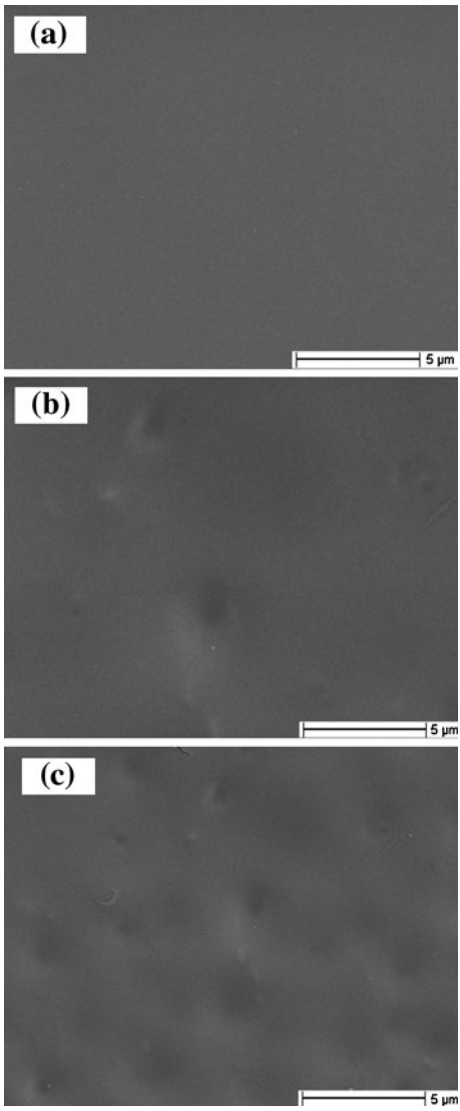

Fig. 1 SEM photographs of PLGA/PBLG blend film surface with different PBLG mole contents: **a** 0 %, **b** 4 %, and **c** 8 % (magnification ×5,000)

Mechanical properties

Figure 4 represents the relationship between the tensile strength of the PLGA/PBLG blend film and the PBLG mole content. As shown in Fig. 4, the tensile strength of the PLGA/PBLG blend film increased with the increase of the PBLG mole content. As discussed above, relative to the PLGA chains, the polypeptide segments are rigid, and the introduction of the polypeptide segments could promote the tensile strength of the PLGA films. This phenomenon indicates that the increase of the tensile strength of the polymer blend film was also connected with the introduction of the rigid polypeptide segments.

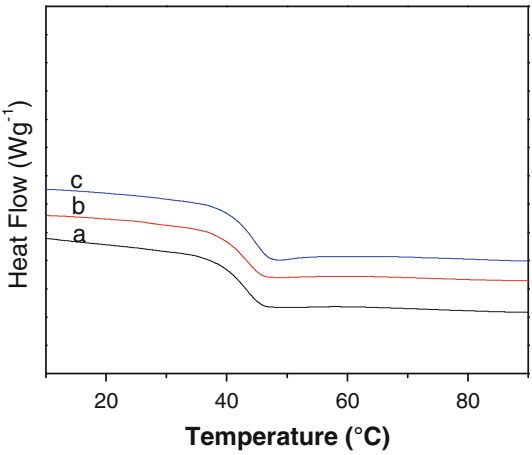

Fig. 2 DSC curves of PLGA/PBLG blends with various PBLG mole contents: (*a*) 0 %, (*b*) 4 %, and (*c*) 8 %

Table 1 The glass transition temperature of PLGA segments in the polymer blends with different PBLG mole content

PBLG (mol %)	Glass transition temperature (°C)
0	43.5
4	44.6
8	45.8

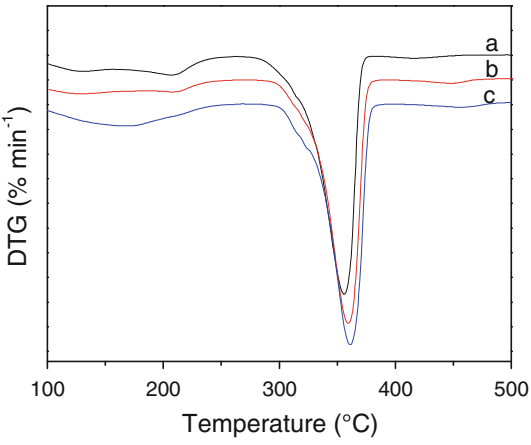

Fig. 3 DTG curves of PLGA/PBLG blends with various PBLG mole contents: (*a*) 0 %, (*b*) 4 %, and (*c*) 8 %

Water-resistant properties

Figure 5 indicates the relationship between the surface contact angle of the PLGA/PBLG blend film and the PBLG mole content. As can be seen from Fig. 5, the surface contact angle of the PLGA/PBLG blend film increased with the increase of PBLG mole content in the polymer blends, suggesting that the hydrophobicity of the

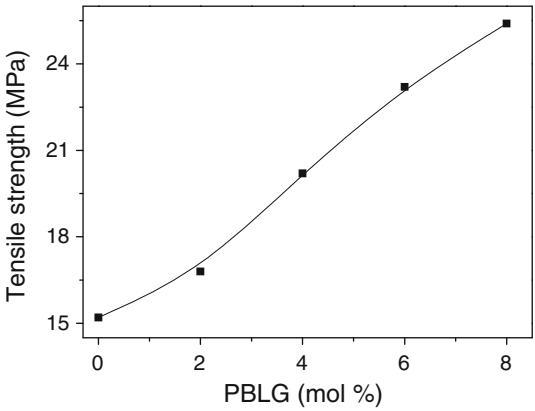

Fig. 4 Relationship between the tensile strength of the PLGA/PBLG blend film and the PBLG mole content

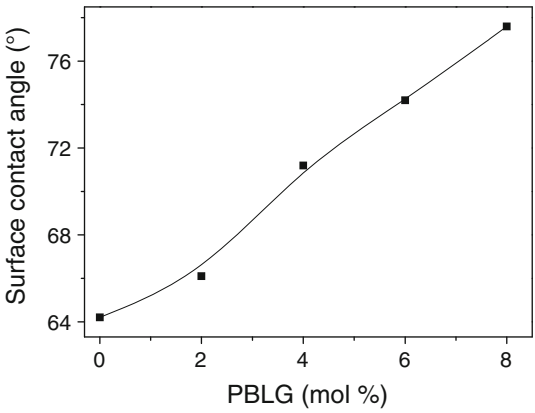

Fig. 5 Relationship between the surface contact angle of PLGA/PBLG blend film and PBLG mole content

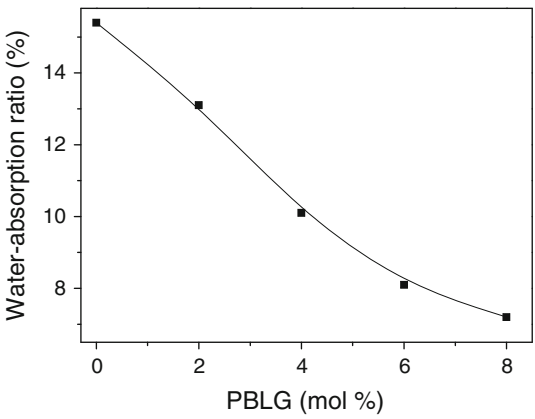

Fig. 6 Relationship between water-absorption ratio of the PLGA/PBLG blend film and the PBLG mole content

polymer blend film increased. As noted, PLGA chains hold a little hydrophilicity, while the PBLG segments are hydrophobic, and the introduction of the polypeptide segments could upgrade the hydrophobicity of the PLGA film. This phenomenon

demonstrates that the increase of the surface contact angle of the polymer blend film was connected with the introduction of the polypeptide segments.

Figure 6 exhibits the relationship between the water-absorption ratio of the PLGA/PBLG blend film and the PBLG mole content. As seen from Fig. 6, the water-absorption ratio of the polymer blend film decreased with the increase of the PBLG mole content. As discussed above, the polypeptide segments are hydrophobic, and the introduction of the polypeptide chains could promote the hydrophobicity of the PLGA film with a little hydrophilicity, suggesting that the water-absorption ratio of the polymer blend film was also linked to the introduction of the polypeptide chains.

Conclusions

A series of PLGA/PBLG blend films with various PBLG mole contents were prepared by casting the polymer blend solution in chloroform. SEM, DSC, TGA, tensile tests, and surface contact angle tests were used to investigate the surface morphologies and the properties of the polymer blend films. SEM photographs showed that the introduction of PBLG chains changed the surface morphologies of the PLGA films. DSC measurements demonstrated that the introduction of PBLG segments increased the glass transition temperature of the PLGA segments in the polymer blends. TG measurements verified that the introduction of PBLG increased the maximum decomposition temperature of the PLGA segments in polymer blends. The tensile tests indicated that the tensile strength of the polymer blend film increased with increasing the PBLG content. Both the surface contact angle tests and the water-absorption ratio tests proved that the introduction of PBLG segments promoted the hydrophobicity of the polymer blend films.

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