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Physicochemical Properties of Poly(lactic acid-co-glycolic acid) Film Modified via Blending with Poly(butyl acrylate-co-methyl methacrylate)

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Abstract: A series of poly(lactic acid-co-glycolic acid) (PLGA)/poly(butyl acrylate-co-methyl methacrylate) (P(BA-co-MMA)) blend films with different P(BA-co-MMA) mole contents were prepared by casting the polymer blend solution in chloroform. Surface morphologies of the PLGA/P(BA-co-MMA) blend films were studied by scanning electron microscopy (SEM). Thermal, mechanical, and chemical properties of PLGA/P(BA-co-MMA) blend films were investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), tensile tests, and surface contact angle tests. The introduction of P(BA-co-MMA) could modify the properties of PLGA films.

Keywords: *Modification, PLGA/P(BA-co-MMA) blend, film.*

Introduction

It is well-known that polymer blending has been a widely used way for improving or modifying the physicochemical properties of polymer materials^[1,2]. An important property of a polymer blend is the miscibility of its ingredients, as it could affect the mechanical properties, morphology, permeability, and degradation^[1,2]. Many researches regarding to miscibility in multi-component polymer systems have been reported. Among them, the polymer blends between biopolymers and synthetic polymers are of particular significance as they could be used as biomedical and biodegradable materials^[3-5].

Based on the outstanding biodegradability, biocompatibility, and nontoxicity, poly(lactic acid-co-glycolic acid) (PLGA) has received much attention for its potential applications^[6-12]. Because of its unique structure and properties, poly(lactic acid-co-glycolic acid) has been widely used in the biomedical fields such as absorbable sutures, reconstructive implants, wound healing materials, temporal scaffolds for tissue engineering, and drug release systems^[13-23], etc. Also, PLGA films are usually used as artificial skin grafts^[8,9].

The biodegradable aliphatic polyesters such as PLGA have versatile biodegradation properties because of their molecular weight and chemical compositions^[24]. Nevertheless, there have been lots of 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 nanoparticle formulation process^[25]. 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^[9]. As known, protein adsorption onto polymer surfaces

could strongly affect the cellular interactions with foreign surface^[26], induce the macrophage activation followed by immunologic response to foreign materials^[27] and control the adhesion behavior of the cells^[28].

For PLGA film, different mole ratios of LA to GA could change its properties; the increase of GA content could promote the hydrophilicity of the film but decrease its tensile strength. Usually, the polymer blending is used to modify the properties of the PLGA films. Relative to the PLGA (e.g., mole ratio of LA to GA is 60:40), the synthetic P(BA-co-MMA) (mole ratio of BA to MMA is 1:3) holds relatively higher hardness^[29,30]. The introduction of the P(BA-co-MMA) could modify the properties of PLGA film, and further enlarge its research fields. However, to the best of our knowledge, no experimental work has so far been reported on the studies of the physicochemical properties of PLGA/P(BA-co-MMA) blend films. In the present work, a series of PLGA/P(BA-co-MMA) blend films with different P(BA-co-MMA) mole content were prepared by casting the polymer blend solution in chloroform. Surface morphologies of PLGA/P(BA-co-MMA) blend films were investigated by SEM technique. Thermal, mechanical, and chemical properties of PLGA/P(BA-co-MMA) blend films were studied by DSC, TGA, tensile tests, and surface contact angle tests. It was found that the introduction of the P(BA-co-MMA) could exert marked effects on the properties of PLGA films.

Experimental

Materials

Poly(lactic acid-co-glycolic acid) ($M_w=90000$), which was composed by a 60:40 ratio of lactic acid and glycolic acid units, was purchased from Jinan Daigang Biological Technology Co., Ltd. (China), and used as

received. Poly(butyl acrylate-co-methyl methacrylate) ($M_w=50000$, mole ratio of BA to MMA is 1:3) was purchased from Shandong Shituo Chemical Co. Ltd. (China). Chloroform and other solvents were of analytical grade and used without further purification.

Preparation of PLGA/P(BA-co-MMA) 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 is found that, when P(BA-co-MMA) mole content in polymer blend is over 12%, the polymer blend can not form continuous film.

Scanning Electron Microscopy (SEM)

The morphologies of PLGA/P(BA-co-MMA) blend films were observed using a scanning electron microscope (Sirin 200, FEI, Holland). Gold was sputtered on the samples in vacuum. Acceleration voltage was 5 kV.

Differential Scanning Calorimetry (DSC)

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 20-160 °C, the heating rate was 15 °C/min. The DSC thermograms were obtained from a second heating procedure in order to observe the glass transition temperature^[9].

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (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 12 mg were used for the measurements.

Tensile tests

Tensile tests were carried out with an Instron 4468 machine (USA). The crosshead speed was set to 100 mm/min. For each data point, five samples were tested and the average value was taken.

Surface contact angle tests

The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument Ltd., Finland). A 5 microlitre drop of pure distilled water was placed on the polymer blend film surface using a syringe with a 22-gauge needle. 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^[31].

Water-resistant pressure (mm) measurements

The water-resistant pressure (mm) measurements of PLGA/P(BA-co-MMA) blend films were carried out according to a conventional method. The sample films

were made in round shape with a diameter of 30 mm. The sample films were used to seal the mouth of a long round tube with graduation in millimeters (tube diameter: 10 mm). After the tube mouth was sealed with the film, it was upset, and deionized water was added into the long round tube drop by drop. As soon as the deionized water permeated through the film, the height of water column was written down^[32].

Results and Discussion

SEM analysis

Figure 1 presents the surface photographs of PLGA/P(BA-co-MMA) blend films with various P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%. As it can be seen from Figure 1, the introduction of P(BA-co-MMA) changed the surface morphologies of the PLGA films. The surface morphologies of PLGA films become rougher and appear a little phase-separation phenomenon with the introduction of the P(BA-co-MMA) segments. As known, with the increase of the P(BA-co-MMA) segments content in polymer blends, on the one hand, PLGA chains and P(BA-co-MMA) segments could interact by entanglement; on the other hand, the self-aggregation action could exert between the P(BA-co-MMA) segments.

DSC analysis

Figure 2 displays the DSC curves of PLGA/P(BA-co-MMA) blends with various P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%, the corresponding data are listed in Table 1. As seen from Figure 2 and Table 1, the glass transition temperature of the PLGA segments in the polymer blends slightly increased with the increase of P(BA-co-MMA) mole content. Compared with the PLGA chains (mole ratio of LA to GA is 60:40), the P(BA-co-MMA) segments (mole ratio of BA to MMA is 1:3) are more rigid. The introduction of the rigid P(BA-co-MMA) segments could increase the glass transition temperature of PLGA segments in the polymer blends by interaction between PLGA chains and P(BA-co-MMA) segments.

TGA analysis

Figure 3 shows the TG curves of PLGA/P(BA-co-MMA) blends with different P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%. From Figure 3, it can be seen that the thermograms of the polymer blends decrease with the increasing temperature especially in the range of 100-200 °C corresponding to the evaporation of water, and of 200-400 °C corresponding to the decomposition of the polymer blends. Also seen from Figure 3, the initial decomposition temperature of the PLGA segments in the polymer blends slightly increased with increasing the P(BA-co-MMA) mole content. As discussed above, the PLGA chains and the rigid P(BA-co-MMA) segments could interact by entanglement.

Figure 4 exhibits the DTG curves of PLGA/P(BA-co-MMA) blends with different P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%. The

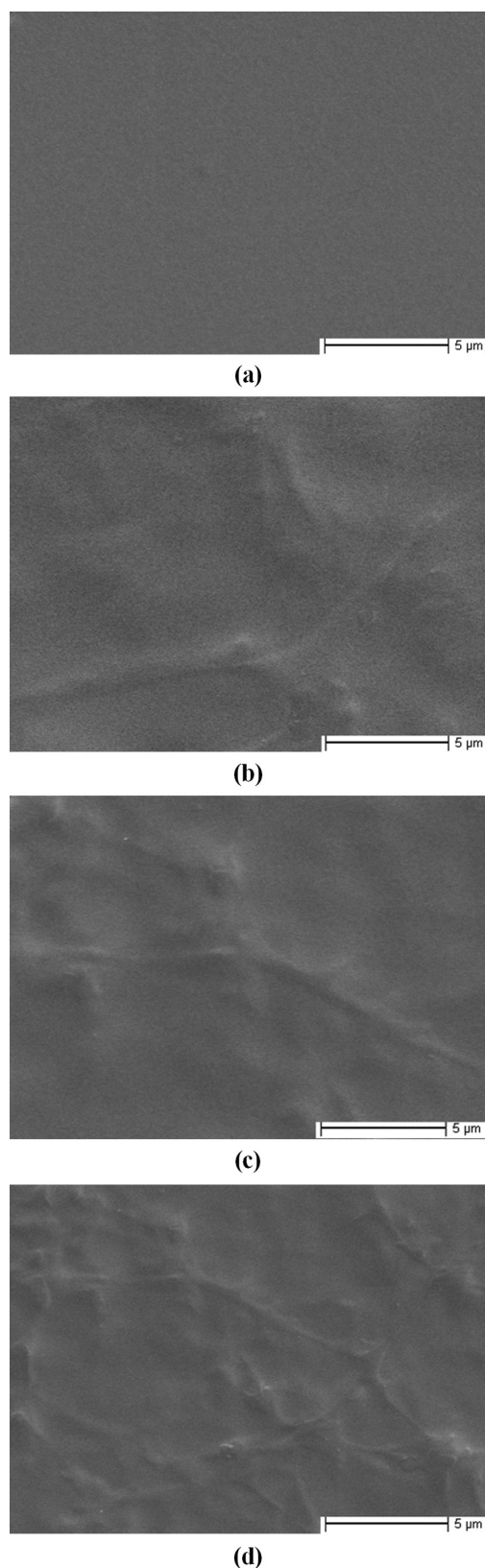


Figure 1. SEM photographs of PLGA/P(BA-co-MMA) blend film surface with various P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%.

corresponding data are listed in Table 2. As shown in Figure 4 and Table 2, the maximum decomposition temperature of the PLGA segments in the polymer blends slightly increased with the increase of P(BA-co-MMA) mole content.

Tensile tests

Figure 5 indicates the relationship between the tensile strength of PLGA/P(BA-co-MMA) blend film and P(BA-co-MMA) mole content. As seen from Figure 5, the tensile strength of the polymer blend film increased

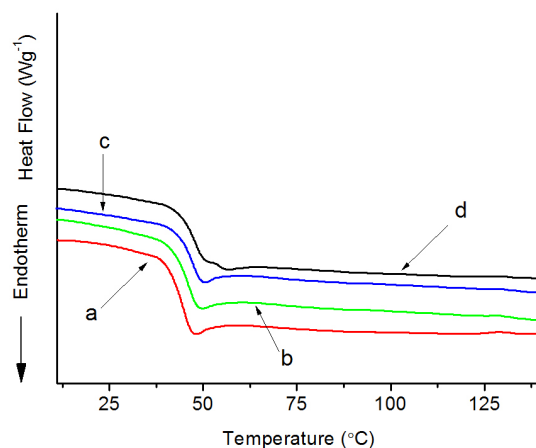


Figure 2. DSC curves of PLGA/P(BA-co-MMA) blends with various P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%.

Table 1. The glass transition temperature of PLGA segments in the polymer blends with different P(BA-co-MMA) mole contents.

P(BA-co-MMA) (mol %)	Glass transition temperature (°C) ^a
0	43.4 ± 0.868
4	44.9 ± 0.898
8	45.8 ± 0.916
12	46.6 ± 0.932

^aTen experiments were tested.

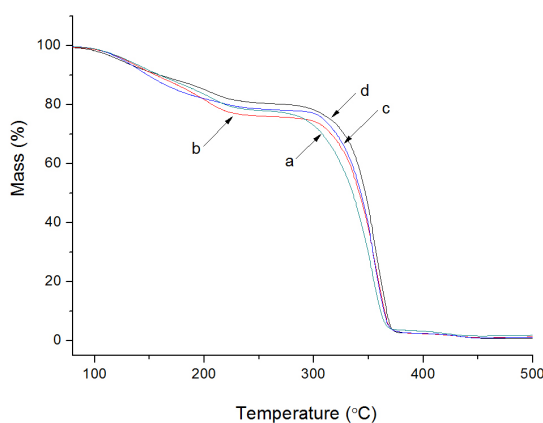


Figure 3. TG curves of PLGA/P(BA-co-MMA) blends with different P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%.

with the increase of P(BA-co-MMA) mole content in the polymer blend film. As already noted, compared with PLGA chains used in the study, P(BA-co-MMA) segments are relatively rigid and the introduction of P(BA-co-MMA) segments could promote the tensile strength of the polymer blend film by interaction between PLGA chains and P(BA-co-MMA) segments.

Surface contact angle tests

Figure 6 reveals the relationship between the surface contact angle of PLGA/P(BA-co-MMA) blend film and

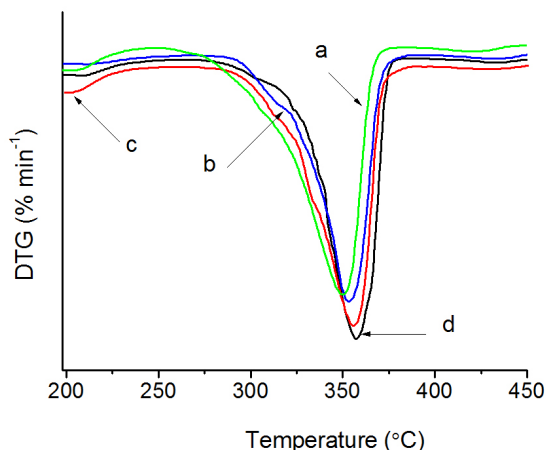


Figure 4. DTG curves of PLGA/P(BA-co-MMA) blends with different P(BA-co-MMA) mole contents: (a) 0%, (b) 4%, (c) 8%, and (d) 12%.

Table 2. The maximum decomposition temperature of PLGA segments in the polymer blends with different P(BA-co-MMA) mole contents.

P(BA-co-MMA) (mol %)	Maximum decomposition temperature (°C) ^a
0	352.6 ± 0.987
4	354.3 ± 0.992
8	355.9 ± 0.996
12	357.8 ± 1.001

^aTen experiments were tested.

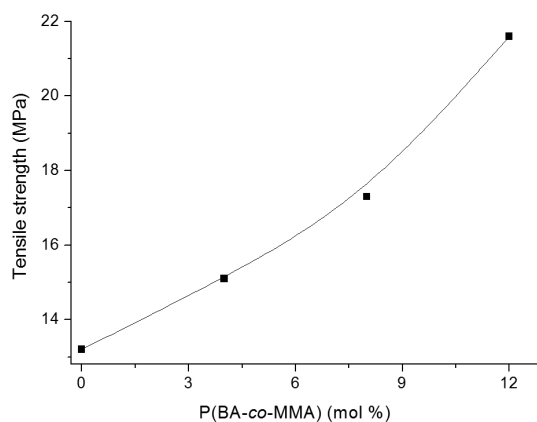


Figure 5. Relationship between the tensile strength of PLGA/P(BA-co-MMA) blend film and P(BA-co-MMA) mole content.

P(BA-co-MMA) mole content. As shown in Figure 6, the surface contact angle of the polymer blend film increased with the increase of P(BA-co-MMA) mole content in the polymer blend film, suggesting that the hydrophilicity of the polymer blend film decreased. As known, PLGA segments hold a little hydrophilicity, while the P(BA-co-MMA) chains are hydrophobic, the introduction of P(BA-co-MMA) segments could decrease the hydrophilicity of the polymer blend film.

Water-resistant pressure (mm) measurements

Figure 7 represents the relationship between the water-resistant pressure of PLGA/P(BA-co-MMA) blend film and P(BA-co-MMA) mole content. As shown in Figure 7, the water-resistant pressure of PLGA/P(BA-co-MMA) blend film increased with the increase of P(BA-co-MMA) content in the polymer blend film. As already discussed above, PLGA chains hold a little hydrophilicity, while the P(BA-co-MMA) segments hold hydrophobicity, indicating that the increase of the water-resistant pressure of the polymer blend film was connected with the introduction of the hydrophobic P(BA-co-MMA) segments.

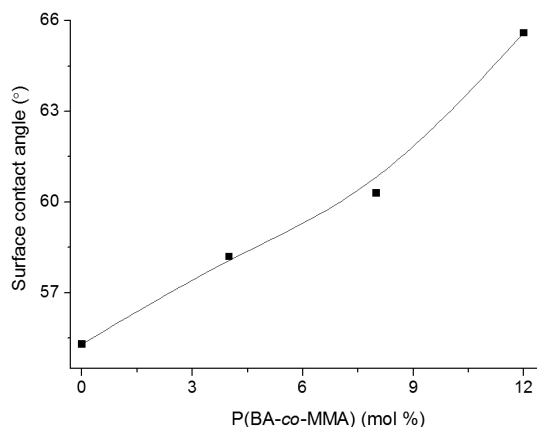


Figure 6. Relationship between the surface contact angle of PLGA/P(BA-co-MMA) blend film and P(BA-co-MMA) mole content.

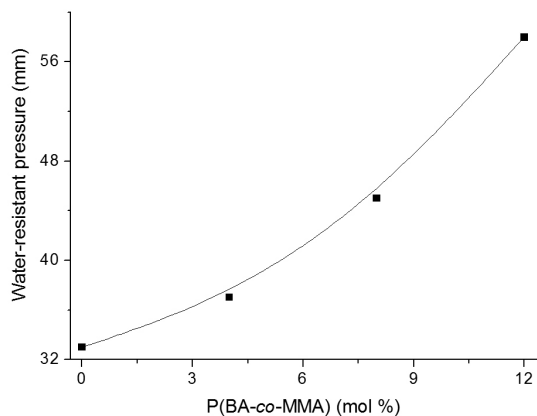


Figure 7. Relationship between the water-resistant pressure of PLGA/P(BA-co-MMA) blend film and P(BA-co-MMA) mole content.

Conclusions

A series of PLGA/P(BA-co-MMA) blend films with various P(BA-co-MMA) mole contents were prepared by casting the polymer blend solutions in chloroform. SEM photographs showed that the introduction of P(BA-co-MMA) changed the surface morphologies of the PLGA films. DSC measurements indicated that the introduction of P(BA-co-MMA) increased the glass transition temperature of the PLGA segments in the polymer blends. TG measurements demonstrated that the introduction of P(BA-co-MMA) increased both the initial decomposition temperature and the maximum decomposition temperature of the PLGA segments in the polymer blends. Tensile tests verified that the tensile strength of the polymer blend film increased with the increase of P(BA-co-MMA) content. Both the surface contact angle tests and the water-resistant pressure tests proved that the introduction of P(BA-co-MMA) segments promoted the hydrophobicity of the polymer blend film.

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