

Properties Study of Poly(*L*-lactic acid) Film Modified by Blending with Flexible Poly(tetramethylene glycol)

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Summary: A series of poly(*L*-lactic acid)/poly(tetramethylene glycol) (PLLA/PTMG) blend films were prepared by casting the polymer blend solution in chloroform. Surface morphologies of the PLLA/PTMG blend films were investigated by scanning electron microscopy (SEM). Thermal, mechanical, and chemical properties of PLLA/PTMG 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 flexible PTMG could markedly modify the properties of the PLLA films.

Key words: Morphology, Properties, PLLA/PTMG blend, Film.

Introduction

Recently, poly(*L*-lactic acid) (PLLA) has attracted much interest in the research of alternative biodegradable polymer [1-10]. As known, PLLA is a linear aliphatic thermoplastic polyester, produced from renewable resources [4]. PLLAs are prepared by ring-opening polymerization of lactides and the lactic acid monomers [5]. Usually, commercial PLAs are copolymers of poly(*L*-lactic acid) (PLLA) and poly(*D,L*-lactic acid) (PDLLA), which are prepared from *L*-lactides and *D,L*-lactides, respectively [1]. To date, PLLA resins have widely been used for biomedical applications such as drug delivery systems [6], surgical sutures [7], and bone fixtures [8] etc. Based on the better biological degradation behavior, PLLA is expected to replace conventional plastics such as PE, PVC, and PET. These materials are practically used as packing materials (e.g., films, membranes) or foaming materials (e.g., containers) [9]. Also, PLLA film is usually used as wound dressing (i.e., artificial skin) [10]. However, the low deformation at break and quite elevated price of PLLA could limit its applications [1].

Up to date, considerable efforts have been made to modify the properties of PLLA in order to compete with the low-cost and flexible commodity polymers. These attempts were carried out via modifying PLLA with biocompatible plasticizers or via blending PLLA with other biopolymers [1]. Various types of chemicals, such as citrate esters, have been tried to plasticize PLLA [11]. Recently, plasticizers such as poly(ethylene glycol) (PEG), glucosemonoesters and partial fatty acid esters were used to promote the flexibility and impact resistance of PLLA [12]. The resulting plasticized PLLA materials gained in deformation and resilience [1].

It is well-known that polymer blending has been an attractive alternative for producing new polymeric materials with tailored properties without having to synthesize completely new materials. Other advantages of polymer blending are versatility, simplicity, and inexpensiveness [13]. Blends of PLLA with various non-biodegradable polymers have been studied [14]. Biodegradable blends of PLLA with other aliphatic polyesters such as poly(ϵ -caprolactone) [15], poly(butylene succinate) [16], and poly(hydroxy butyrate) [17] were also researched.

As noted, PLLA presents poor flexibility [18], while the synthetic PTMG exhibits good flexibility and better biocompatibility [19, 20], the introduction of the PTMG could greatly improve the properties of PLLA film, and further enlarge its application fields. To the best of our knowledge, however, no experimental work has been reported on the properties of PLLA/PTMG blend films so far. In the present work, PLLA/PTMG blend films were prepared by casting the polymer blend solution in chloroform. Surface morphologies of the PLLA/PTMG blend films were investigated by SEM. Thermal, mechanical, and chemical properties of PLLA/PTMG blend films were studied by DSC, TGA, tensile tests, and surface contact angle tests. It was displayed that the introduction of PTMG could exert great effects on the properties of PLLA films.

Results and Discussion

SEM Tests

The surface morphologies of PLLA/PTMG blend films were studied by SEM technique. Fig. 1 shows the surface photographs of PLLA/PTMG

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blend films with various PTMG mole contents: (a) 0%, (b) 3%, and (c) 5%. As it can be seen from Fig. 1, the introduction of PTMG changed the surface morphologies of the polymer blend films. The surface density of the polymer blend film tends to increase with the increase of PTMG mole content in polymer blends. As the flexible PTMG segments and the relatively rigid PLLA chains could exert interaction through entanglement, suggesting that the change of the surface morphologies of the polymer blend films could be attributed to the introduction of the flexible PTMG segments.

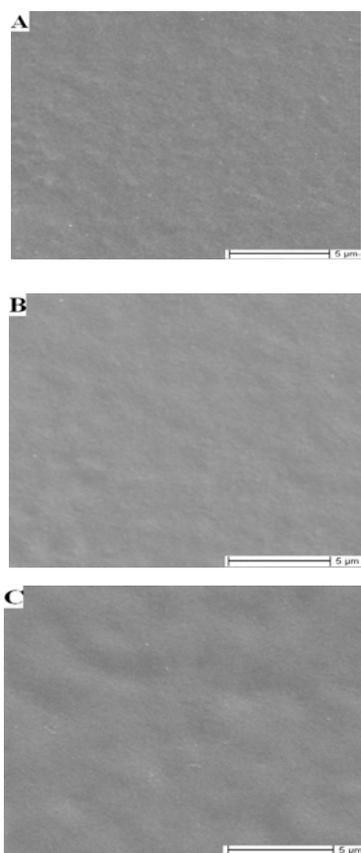


Fig. 1: SEM photographs of PLLA/PTMG blend film surface with different PTMG mole contents: (a) 0%, (b) 3%, and (c) 5% (magnification 5000×).

DSC Tests

Fig. 2 presents the DSC curves of PLLA/PTMG blends with various PTMG mole contents: (a) 0%, (b) 3%, and (c) 5%, the corresponding data are listed in Table-1. As can be seen from Fig. 2 and Table-1, the melting temperature of the PLLA segments in the polymer blends slightly

decreased with the increase of the PTMG mole content. As noted, compared with the PLLA chains, the PTMG segments are very flexible and hold lower melting temperature, the introduction of the PTMG segments could decrease the melting temperature of the PLLA chains in the polymer blends through interaction. This phenomenon indicates that the decrease of the melting temperature of the PLLA chains in the polymer blends could also be attributed to the introduction of the flexible PTMG segments.

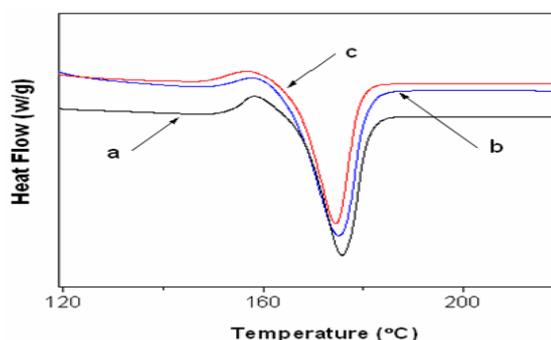


Fig. 2: DSC curves of PLLA/PTMG blends with various PTMG mole contents: (a) 0%, (b) 3%, and (c) 5%.

Table-1: Melting temperature of PLLA segments in polymer blends with various PTMG mole contents

PTMG content (mol %)	Melting temperature (°C)
0	176.8
3	175.3
5	174.2

TG Tests

Fig. 3 displays the DTG curves of PLLA/PTMG blends with various PTMG mole contents: (a) 0%, (b) 3%, and (c) 5%, the corresponding data are listed in Table-2. As is shown in Fig. 3 and Table-2, the maximum decomposition temperature of the PLLA segments in polymer blends decreased with increasing PTMG mole content in the polymer blends. As already noted, the flexible PTMG segments hold lower maximum decomposition temperature, the introduction of the PTMG segments could decrease the maximum decomposition temperature of PLLA chains in the polymer blends through interaction. This situation proves that the decrease of the maximum decomposition temperature of PLLA segments in the polymer blends was connected with the introduction of the flexible PTMG chains.

Table-2: Maximum decomposition temperature of PLLA segments in polymer blends with various PTMG mole contents

PTMG content (mol %)	Maximum decomposition temperature (°C)
0	357.6
3	355.4
5	354.2

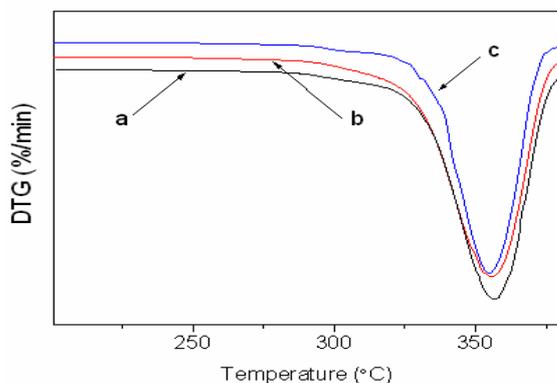


Fig. 3: DTG curves of PLLA/PTMG blends with various PTMG mole contents: (a) 0%, (b) 3%, and (c) 5%.

Tensile Tests

Fig. 4 indicates the relationship between the tensile strength of PLLA/PTMG blend film and PTMG mole content. As shown in Fig. 4, the tensile strength of the PLLA/PTMG blend film decreased with the increase of PTMG mole content. As mentioned above, the synthetic PTMG chains are very flexible; the introduction of the flexible PTMG segments could decrease the tensile strength of the polymer blend film by interacting with PLLA chains. In this blend system, under evaluated PTMG content, the higher the PTMG content, the lower the tensile strength of the polymer blend film.

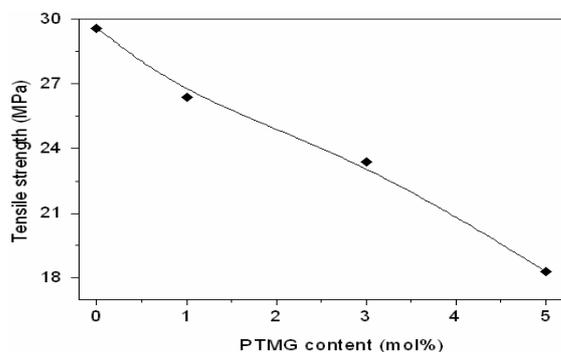


Fig. 4: Relationship between the tensile strength of PLLA/PTMG blend film and PTMG mole content.

Surface Contact Angle Tests

Fig. 5 reveals the relationship between the surface contact angle of PLLA/PTMG blend film and PTMG mole content. As seen from Fig. 5, the surface contact angle of the polymer blend film decreased with the increase of PTMG mole content, indicating that the hydrophilicity of the polymer blend film increased. As known, the PLLA chains are hydrophobic, while the synthetic PTMG segments hold weak hydrophilicity, suggesting that the decrease of the surface contact angle of the polymer blend film was related to the introduction of the PTMG segments with weak hydrophilicity.

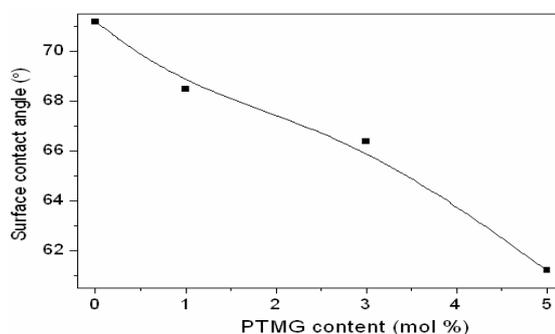


Fig. 5: Relationship between the surface contact angle of PLLA/PTMG blend film and PTMG mole content.

Experimental

Materials

The poly(L-lactic acid) (PLLA) ($M_w=80000$) was purchased from Jinan Daigang Biomaterial Co. Ltd. (China). The poly(tetramethylene glycol) (PTMG) ($M_w=2000$) was purchased from Dongda Chemical Co. Ltd. (China). Chloroform and other solvents are of analytical grade and used without further purification.

Preparation of PLLA/PTMG Blend Film

Polymer blend films were prepared by casting a 30 wt% polymer blend solution in the chloroform onto clean glass plates and drying them under vacuum at 50 °C. Also, it is found that, when PTMG mole content in polymer blend is over 5%, the polymer blend can not form continuous film.

Methods

SEM investigation was carried out using a

scanning electron microscope (Sirin 200, FEI, Holland). Gold was sputtered on the samples in vacuum. Acceleration voltage was 5 kV and photographs of the surface of the polymer blend films were taken. 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 0-250 °C, the heating rate was 15 °C/min. Thermogravimetric analysis (TGA) was carried out on a STA 4490C TG-DTA analyzer (Netzsch, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere over the temperature range of 30-500 °C. Samples of approximately 13 mg were used for the measurements. Tensile tests were carried out with an Instron 4468 machine (Digital Instruments Inc., USA). The crosshead speed was set to 150 mm/min. For each data point, five samples were tested and the average value was taken. The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument Ltd., Finland). 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 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 [21].

Conclusions

A series of PLLA/PTMG blend films with various PTMG mole contents were prepared by casting the polymer blend solution in chloroform. SEM photographs showed that the introduction of PTMG chains changed the surface morphologies of the polymer blend films. DSC tests proved that the melting temperature of the PLLA segments in the polymer blends decreased with increasing PTMG content. TG tests indicated that the maximum decomposition temperature of the PLLA segments in the polymer blends also decreased with the increase of PTMG content. Tensile tests demonstrated that the tensile strength of the polymer blend film decreased with the increase of PTMG content. Surface contact angle measurements verified that the surface contact angle of the polymer blend film decreased with the increase of PTMG content.

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