

Modification of Poly(lactic acid-co-glycolic acid) Film *via* Blending with Polyacrylonitrile

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A series of poly(lactic acid-co-glycolic acid) (PLGA)/polyacrylonitrile blend films with different polyacrylonitrile mole content were prepared by casting the polymer blend solution in dimethyl sulfoxide. Surface morphologies of the PLGA/PAN blend films were studied by scanning electron microscopy. Thermal, mechanical, and chemical properties of PLGA/PAN blend films were investigated by differential scanning calorimeter, tensile tests and surface contact angle tests. It was displayed that the introduction of polyacrylonitrile could greatly modify the properties of PLGA films.

Keywords: Poly(lactic acid-co-glycolic acid), Polyacrylonitrile, Blend film, Modification.

INTRODUCTION

Because of the outstanding biodegradability, biocompatibility and non-toxicity, poly(lactic acid-co-glycolic acid) (PLGA) has attracted much attention for its potential applications¹⁻⁸. Based on its unique structure and properties, poly(lactic acid-co-glycolic acid) has been widely used in biomedical fields such as absorbable sutures, reconstructive implants, wound healing materials, temporal scaffolds for tissue engineering and drug release systems⁹⁻¹⁶, etc. Also, PLGA films are usually used as artificial skin grafts^{2,3}.

The biodegradable aliphatic polyesters such as PLGA have versatile biodegradation properties because of their molecular weight and chemical compositions¹⁷. Nevertheless, there have been a lot of attempts to modify 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 process¹⁸. It was postulated that the surface orientated PEG chains onto the surface of nanoparticles not only suppress the adsorption of serum proteins but also decrease the extent of cell recognition³. As known, protein adsorption onto polymer surfaces could markedly affect the cellular interactions with foreign surface¹⁹, induce the macrophage activation followed by immunologic response to foreign materials²⁰ and control the adhesion behaviour of the cells²¹.

As known, polyacrylonitrile (PAN) holds good mechanical property²²⁻²⁶, compared with PLGA (mole ratio of lactic acid

to glycolic acid is 70:30), PAN holds higher hardness; the introduction of PAN could modify the properties of PLGA film and further enlarge its application fields. However, to the best of our knowledge, no experimental work has so far been reported on the studies of the properties of PLGA/PAN blend films. In the present work, a series of PLGA/PAN blend films with different PAN mole content were prepared by casting the polymer blend solution in dimethyl sulfoxide. Surface morphologies of PLGA/PAN blend films were investigated by SEM technique. Thermal, mechanical and chemical properties of PLGA/PAN blend films were studied by DSC, tensile tests and surface contact angle tests. It was revealed that the introduction of the PAN could exert marked effects on the properties of PLGA films.

EXPERIMENTAL

Poly(lactic acid-co-glycolic acid) ($M_w = 90000$), which was composed by a 70:30 ratio of lactic acid and glycolic acid units, was purchased from Jinan Daigang Biological Technology Co., Ltd. (China) and used as received. Polyacrylonitrile ($M_w = 60000$) was purchased from Qilu Petrochemical Fiber Plant (China). Dimethyl sulfoxide (DMSO) was of analytical grade and used without further purification.

Preparation of PLGA/PAN blend film: The polymer blend films were prepared by casting a 35 wt % polymer blend solution in DMSO onto clean glass plates and drying them under vacuum at 60 °C. It is also found that, when PAN mole content in polymer blend is over 10 %, the polymer blend can not form a continuous film.

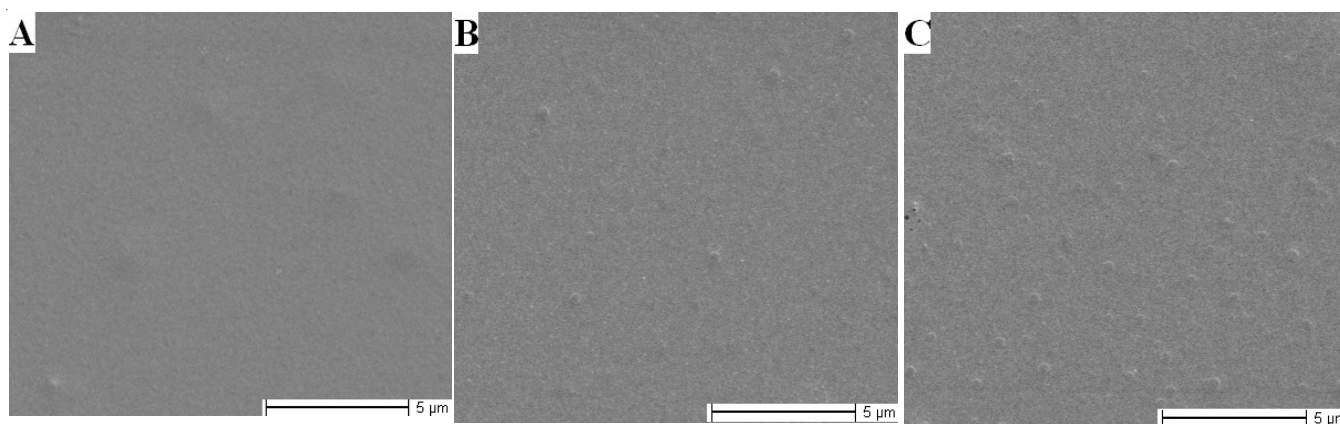


Fig. 1. SEM photographs of PLGA/PAN blend film surface with various PAN mole content: (a) 0 (b) 5% and (c) 10 %

Test method: Scanning electron microscopic 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 calibrated with indium in nitrogen atmosphere. About 7 mg sample was weighted very accurately. The temperature was controlled within the range between 0 and 200 °C, the heating rate was 10 °C/min. Tensile tests were carried out with an Instron 4468 machine (Digital Instruments Inc., USA). The crosshead speed was set to 130 mm/min. For each data point, five samples were tested and the average value was taken. A 5 μ L 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 Ltd., 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 determinations²⁷.

RESULTS AND DISCUSSION

The morphologies of PLGA/PAN blend film surface were studied by SEM technique. Fig. 1 shows the surface morphologies of PLGA/PAN blend films with various PAN mole content: (a) 0, (b) 5 and (c) 10 %. As it can be seen from Fig. 1, the introduction of PAN changed the surface morphologies of the polymer blend films. The surface morphologies of PLGA films become more rougher and appear a little phase-separation with the introduction of the PAN. As known, with the increase of the PAN content in the polymer blend, on the one hand, PLGA chains and PAN segments could interact by entanglement; on the other hand, the self-aggregating action could exert between the PAN segments. This phenomenon indicates that the change of the surface morphologies of PLGA films could be attributed to the introduction of PAN segments.

DSC analysis: Fig. 2 indicates the DSC curves of PLGA/PAN blends with different PAN mole content: (a) 0 (b) 5 and (c) 10 %, 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 PAN mole content in the polymer blends.

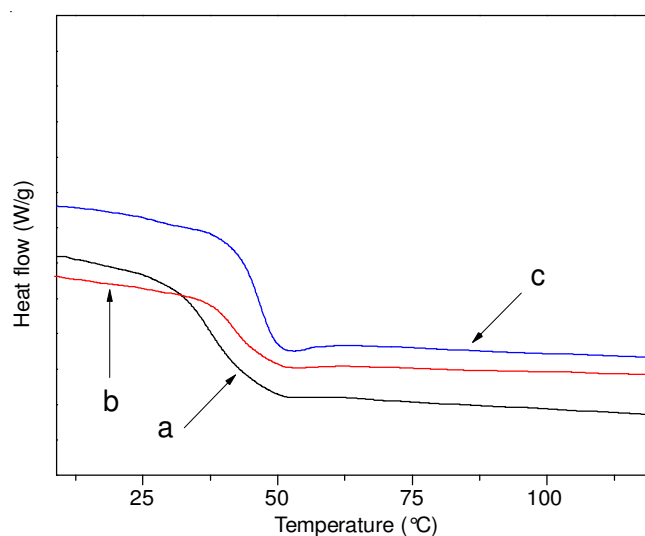


Fig. 2. DSC curves of PLGA/PAN blends with various PAN mole content: (a) 0 (b) 5 and (c) 10 %

TABLE-1
GLASS TRANSITION TEMPERATURE OF PLGA SEGMENTS IN POLYMER BLENDS WITH VARIOUS PAN MOLE CONTENT

PAN content (mol %)	Glass transition temperature (°C)
0	45.1
5	47.2
10	48.5

As mentioned above, compared with PLGA (70:30) chains, PAN segments hold higher glass transition temperature, the introduction of the PAN segments could promote the glass transition temperature of PLGA segments in the polymer blends through entanglement. This phenomenon proves that the increase of the glass transition temperature of PLGA segments in the polymer blends could also be attributed to the introduction of PAN segments.

Tensile tests: Fig. 3 presents the relationship between the tensile strength of PLGA/PAN blend film and the PAN mole content. As is shown in Fig. 3, the tensile strength of the polymer blend film increased with the increase of PAN mole content. As discussed above, the PLGA segments and the rigid PAN chains could interact by entanglement and the interaction could promote the tensile strength of the polymer blend film, suggesting that the increase of the tensile strength of the

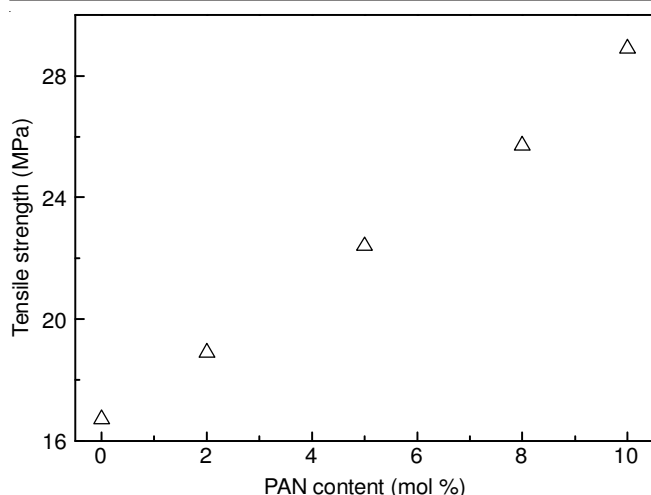


Fig. 3. Relationship between the tensile strength of PLGA/PAN blend film and PAN mole content

polymer blend film was connected with the introduction of the PAN segments. In this blend system, under evaluated PAN content, the higher the content of the PAN, the higher the tensile strength of the polymer blend film.

Surface contact angle tests: Fig. 4 displays the relationship between the surface contact angle of PLGA/PAN blend film and PAN mole content. As shown in Fig. 4, the surface contact angle of the polymer blend film increased with the increase of PAN mole content, suggesting that the hydrophobicity of the polymer blend film increased. As noted, PLGA chains hold a little hydrophilicity, while PAN segments are hydrophobic, the introduction of PAN segments could promote the hydrophobicity of the polymer blend film. This phenomenon reveals that the increase of the surface contact angle of the polymer blend film was concerned with the introduction of PAN segments.

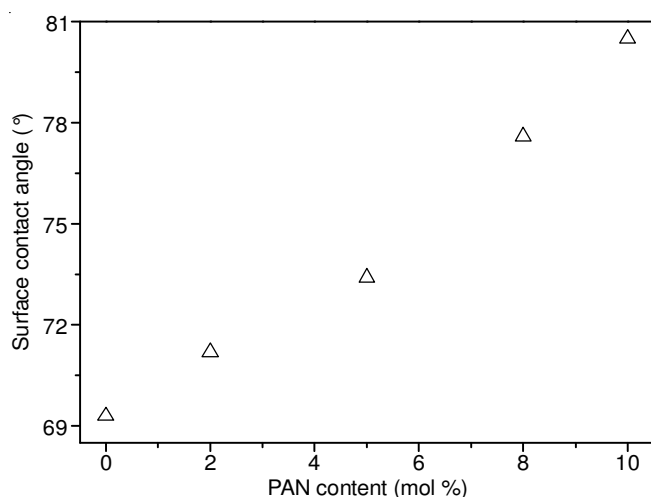


Fig. 4. Relationship between the surface contact angle of PLGA/PAN blend film and PAN mole content

Conclusion

A series of PLGA/PAN blend films with various PAN mole content were prepared by casting the polymer blend solution

in DMSO. SEM, DSC, tensile tests and surface contact angle tests were used to investigate the morphologies and the properties of the polymer blend films. SEM photographs indicated that the introduction of PAN changed the surface morphologies of the PLGA films. DSC measurements proved that the introduction of PAN increased the glass transition temperature of the PLGA segments in the polymer blends. The tensile tests demonstrated that the tensile strength of the polymer blend film increased with the increase of PAN content. The surface contact angle tests showed that the introduction of PAN segments decreased the hydrophilicity of the polymer blend films.

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