

## Properties of Rigid Poly( $\gamma$ -benzyl *L*-glutamate) Film Improved by Flexible Poly(styrene-*block*-butadiene-*block*-styrene)

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A series of rigid poly( $\gamma$ -benzyl *L*-glutamate) (PBLG)/poly(styrene-*block*-butadiene-*block*-styrene) (SBS) blend films with different PBLG/SBS mole ratios were prepared by the solution casting method. Surface morphologies of PBLG/SBS blend films were investigated by scanning electron microscopy. Thermal, mechanical and chemical properties of PBLG/SBS blend films were studied by differential scanning calorimetry, tensile tests and contact angle tests. The results revealed that the introduction of SBS segments could markedly affect the morphology and the properties of poly( $\gamma$ -benzyl *L*-glutamate) films.

**Keywords:** Morphology, Properties, PBLG/SBS blend, Improved, Film.

### INTRODUCTION

Because of the excellent biocompatibility and biodegradability, polypeptides and their copolymers have attracted much attention for their potential applications<sup>1-8</sup>. Due to their unique structures and properties, polypeptides and their copolymers have been studied widely in the fields of functional biomaterials, protein simulation, macromolecular conformational study, catalysis, nanoreactors and drug delivery systems<sup>9-12</sup>. For polypeptide films, an important application is for temporary artificial skin substrates in burn therapy<sup>1,4</sup>.

As noted, polymer blending has been a most useful method for improving or modifying the physicochemical properties of polymer materials<sup>13</sup>. An important property of the polymer blend is the miscibility of its ingredients, as it affects the morphology, the permeability, the degradation and the mechanical properties<sup>13,14</sup>. A lot of studies regarding the 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<sup>15-17</sup>.

Compared with pure polypeptide copolymers, rigid polypeptide/flexible polymer blends have received relatively little attention. To the best of our knowledge, no experimental work has been reported on the properties of PBLG/SBS blend film so far. As known, poly( $\gamma$ -benzyl *L*-glutamate) is a rigid polymer, while SBS (mole ratio of butadiene to styrene is 3:1) is a flexible polymer, it is expected that the introduction of SBS into PBLG could improve the properties of PBLG film.

In the present work, PBLG/SBS blend films were prepared by the solution casting method. The morphologies of the PBLG/SBS blend films were investigated by scanning electron microscopy. Thermal, mechanical and chemical properties of PBLG/SBS blend films were studied by differential scanning calorimetry, tensile tests and contact angle tests.

### EXPERIMENTAL

Poly(styrene-*block*-butadiene-*block*-styrene) ( $M_w = 70000$ ) was purchased from Shandong Shituo Chemical Co. Ltd. (China). Hexane, tetrahydrofuran (THF) and 1,4-dioxane are of analytical grade and dried with sodium to remove water before use. Dichloroethane and other solvents are of analytical grade and used without further purification.

**Synthesis of polypeptide homopolymer:** Poly( $\gamma$ -benzyl *L*-glutamate) homopolymer was synthesized by a standard *N*-carboxyl- $\gamma$ -benzyl-*L*-glutamate anhydride (NCA) method<sup>2,3</sup>. Briefly, PBLG was obtained by the ring-opening polymerization of  $\gamma$ -BLG NCA initiated by triethylamine in 1,4-dioxane at room temperature for 72 h. The reaction mixture was poured into a large volume of anhydrous ethanol. The precipitated product was dried under vacuum and then purified twice by repeated precipitation from a chloroform solution into a large volume of anhydrous methanol. The molecular weight of PBLG was estimated from the intrinsic viscosity measured in dichloroacetic acid<sup>18</sup>. The molecular weight of PBLG used in the study was about 110000.

**Preparation of PBLG/SBS blend film:** Polymer blend films were prepared by casting a 30 wt % polymer blend solution

in dichloroethane onto clean glass plates and drying them under vacuum at 60 °C. It is also found that when SBS mole content in polymer blend is over 8 %, the polymer blend can not form continuous film.

**Measurements:** Scanning electron microscopy investigation was carried out using a scanning electron microscope (Sirin 200, FEI, Holland). Gold was sputtered on the samples in vacuum. Acceleration voltage was 10 kV and photographs of the surface of the polymer blend films were taken. Differential scanning calorimetry measurements were made on a differential scanning calorimetry Q100 (TA, USA) differential scanning calorimeter, the temperature calibrated with indium in nitrogen atmosphere. About 8 mg sample was weighted very accurately. The temperature was controlled within the range of 50–380 °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 100 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<sup>5</sup>. Water-absorption ratio measurements of the polymer blend films were carried out as follows: at room temperature, the sample films were soaked in distilled water for 24 h and then filter paper was used to wipe off water from the blend film surface. The water-absorption ratio (%) was calculated according to the formula: Water-absorption ratio (%) =  $[(m_2 - m_1) / m_1] \times 100$  %, where  $m_1$  and  $m_2$  are the masses of the blend film before and after being immersed in distilled water, respectively<sup>7,19</sup>.

## RESULTS AND DISCUSSION

**Scanning electron microscopy tests:** The surface morphologies of PBLG/SBS blend films were studied by scanning electron microscopy technique. Fig. 1 presents the SEM photographs of PBLG/SBS blend film surface with various SBS mole contents: (a) 0 and (b) 8 % (magnification 3000 ×). As can be seen from Fig. 1, the surface morphology of PBLG homopolymer film shows a coarse surface with some thin gaps; while the surface of the polymer blend film takes on some little aggregates (caused by the self-aggregating action of SBS segments) and the thin gaps disappear (caused by the interaction between PBLG chains and SBS segments). This phenomenon proves that the surface morphology change of the polypeptide film could be attributed to the introduction of SBS segments.

**Differential scanning calorimetry analysis:** Fig. 2 indicates the differential scanning calorimetry curves of PBLG/SBS blend with various SBS mole contents: (a) 0, (b) 4 % and (c) 8 %. Through comparing curves a, b and c, it is found that the melting temperature of PBLG segments in the polymer blend slightly decreases with the increase of the SBS mole content. As mentioned above, PBLG is rigid polymer with higher melting temperature, while SBS is flexible polymer

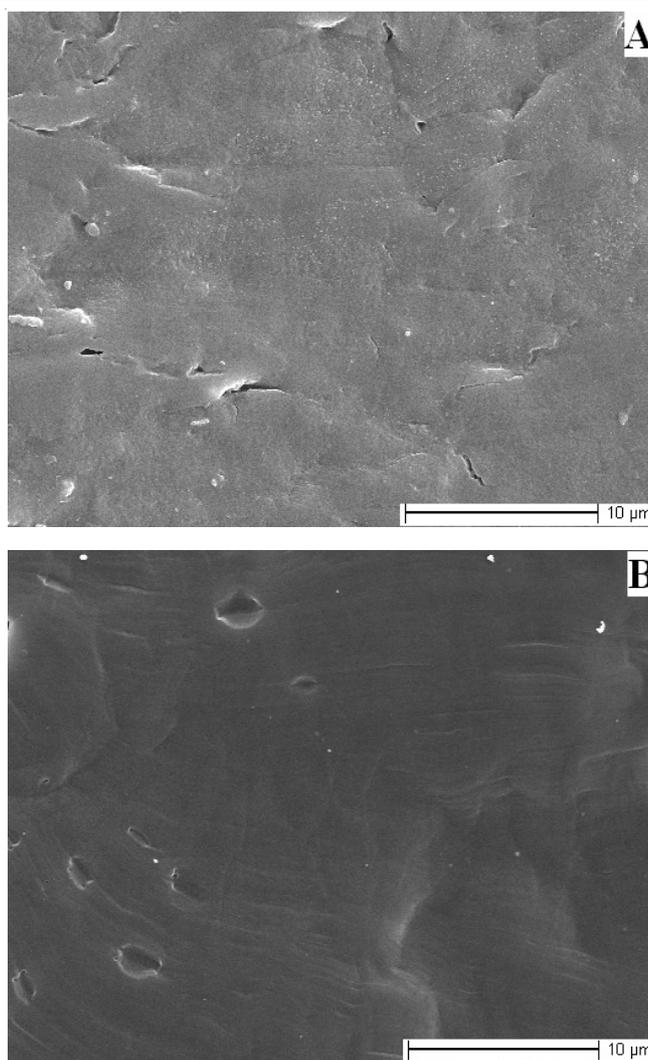


Fig. 1. SEM photographs of PBLG/SBS blend film surface with various SBS mole contents: (a) 0 and (b) 8 % (magnification 3000 ×)

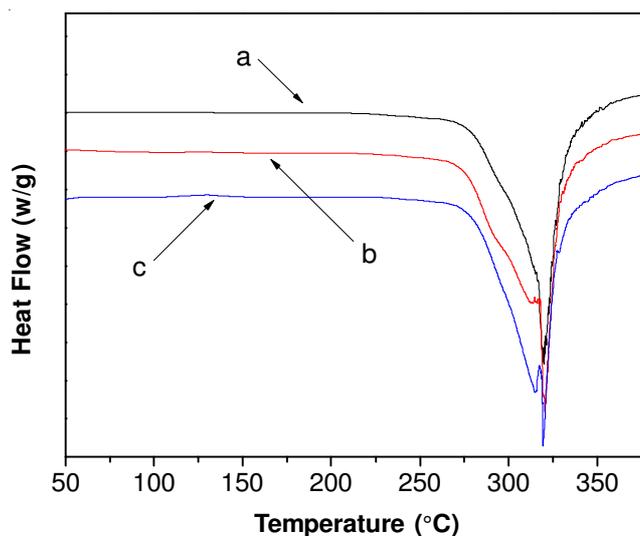


Fig. 2. DSC curves of PBLG/SBS blend with various SBS mole contents: (a) 0, (b) 4 % and (c) 8 %

with relatively lower melting temperature. The interaction between the PBLG segments and the SBS chains through entanglement could affect the melting temperature of PBLG

segments in polymer blend. This phenomenon demonstrates that the decrease of the melting temperature of PBLG segments in polymer blend was connected with the introduction of SBS chains.

**Tensile tests:** Fig. 3 presents the relationship between the tensile strength of PBLG/SBS blend film and the SBS mole contents. As shown in Fig. 3, the tensile strength of PBLG/SBS blend film decreases with the increase of the SBS mole content in polymer blend. As discussed above, the rigid PBLG segments and the soft SBS chains could exert interaction through entanglement, suggesting the decrease of the tensile strength of polymer blend film was related with the introduction of the soft SBS chains. Under permitted SBS content, the higher the SBS content, the lower the tensile strength of the polymer blend film.

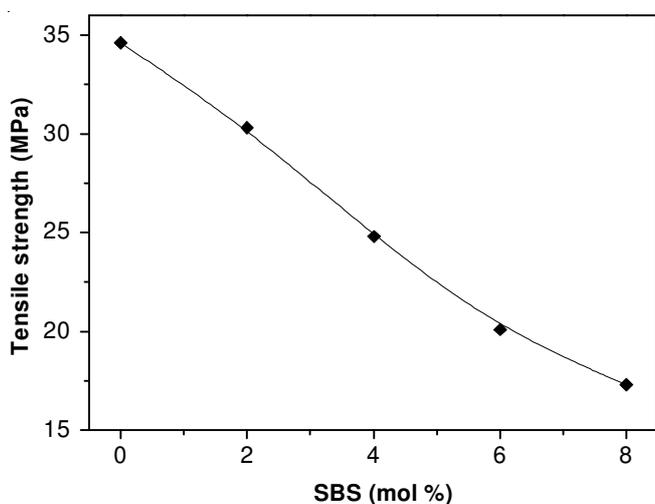


Fig. 3. Relationship between the tensile strength of PBLG/SBS blend film and the SBS mole contents

**Surface contact angle tests:** Fig. 4 shows the relationship between the surface contact angle of PBLG/SBS blend film and the SBS mole contents. As is shown in Fig. 4, the

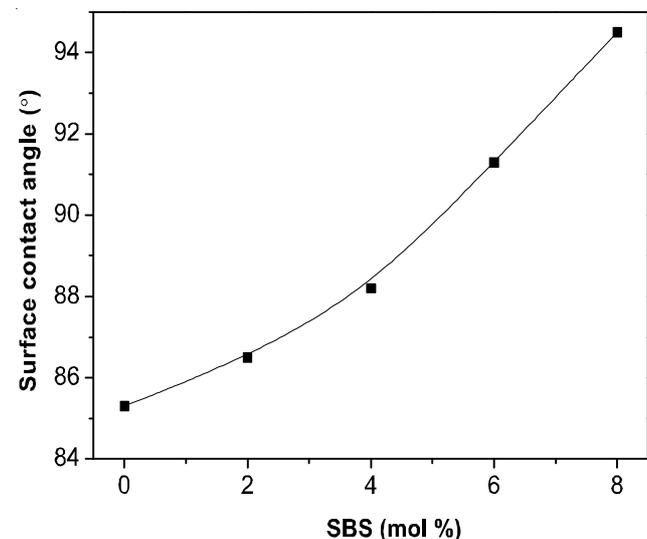


Fig. 4. Relationship between the surface contact angle of PBLG/SBS blend film and the SBS mole contents

surface contact angle of the polymer blend film slightly increased with the increase of SBS contents in the polymer blend, suggesting that the hydrophobicity of the polymer blend film relatively increased. As described by Xu *et al.*<sup>19</sup>, there are some thin gaps between the PBLG segments with  $\alpha$ -helix structure, indicating the hydrophobic PBLG film could absorb appropriate water. The entanglement between hydrophobic PBLG segments and the hydrophobic SBS chains could markedly reduce thin gaps. This phenomenon attests that the increase of the surface contact angle of the polymer blend film was concerned with the introduction of the SBS chains.

**Water-absorption ratio tests:** Fig. 5 indicates the relationship between the water-absorption ratio of PBLG/SBS blend film and the SBS mole contents. As shown in Fig. 5, the water-absorption ratio of the polymer blend film slightly decreased with the increase of the SBS mole content. As discussed above, the entanglement of PBLG segments and the SBS chains could markedly reduce the thin gaps of PBLG film, suggesting the decrease of the water-absorption ratio of the polymer blend film was related to the introduction of the SBS chains.

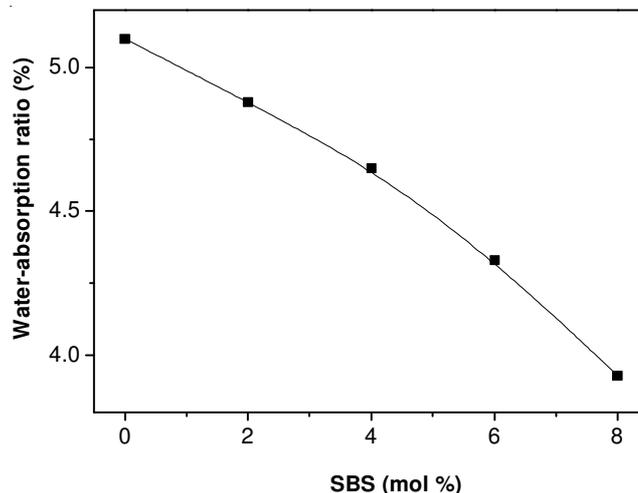


Fig. 5. Relationship between the water-absorption ratio of PBLG/SBS blend film and the SBS mole contents

## Conclusion

PBLG/SBS blend films were prepared by casting the polymer blend solution in dichloroethane. SEM photographs confirm that the introduction of SBS chains changed the surface morphology of the PBLG film. The differential scanning calorimetry data demonstrated that the melting temperature of PBLG segments in the polymer blend decreased with the increase of SBS mole content. Tensile tests verified that the decrease of the tensile strength of the polymer blend film could be attributed to the introduction of soft SBS segments. Both surface contact angle tests and water-absorption ratio tests proved that the introduction of SBS chains slightly increased the hydrophobicity of the PBLG film.

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