

Study on Properties of Polypeptide Mixture Film Modified *via* Blending with Polyurethane

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A series of poly(γ -benzyl *L*-glutamate) (PBLG) and poly(γ -benzyl *L*-glutamate)-*block*-poly(ethylene glycol) (PBLG-*block*-PEG) mixture films (mole ratio is 1:1) modified by polyurethane were prepared by casting the polymer blend solution in *N,N*-dimethylformamide. Surface morphologies of the polymer blend films were investigated by scanning electron microscopy. Mechanical and chemical properties of the polymer blend films were investigated by tensile tests and surface contact angle tests. It was displayed that the introduction of polyurethane could markedly affect the properties of the polymer blend films.

Keywords: Polypeptide mixture, Polyurethane, Blend film, Morphology.

INTRODUCTION

In the past decade, the polypeptides and their copolymers have received much interest for their potential applications owing to their outstanding biodegradability and biocompatibility¹⁻¹⁰. The synthetic polypeptides and their copolymers have been investigated widely in the fields of functional biomaterials, protein simulation, polymer carriers for protein, macromolecular conformational research, catalysis, nano-reactors and drug delivery systems, *etc.*¹¹⁻¹⁵. As noted, for polypeptide copolymer films, an important application is for temporary artificial skin substrates in burn therapy^{9,10}.

As known, polypeptide is rigid and hydrophobic, while the synthetic polyurethane in the study is flexible and hydrophilic¹⁶, the introduction of polyurethane chains could greatly modify the properties of the polypeptide mixture film and further enlarge its application fields. However, to the best of our knowledge, no experimental work has so far been reported on the properties of poly(γ -benzyl *L*-glutamate) (PBLG) and poly(γ -benzyl *L*-glutamate)-*block*-poly(ethylene glycol) (PBLG-*block*-PEG) mixture (mole ratio is 1:1) films modified by polyurethane. In the present work, a series of PBLG and PBLG-*block*-PEG mixture/polyurethane blend films were prepared by casting the polymer blend solution in DMF. Surface morphologies of the polymer blend films were investigated by SEM technique. Mechanical and chemical properties of the polymer blend films were researched using tensile tests and surface contact angle tests. It was revealed that the introduction of polyurethane into the polypeptide mixture could

exert marked effects on the properties of the polypeptide mixture films.

EXPERIMENTAL

Poly(propylene glycol) (PPG) ($M_w = 2000$) was purchased from Zibo Dongda Chemical Industrial Co. Ltd. (China) and dried under vacuum to remove water before use. Dimethylol propionic acid (DMPA), 2,4-toluene diisocyanate (TDI), dibutyltin dilaurate (DBTL), butanediol (BDO) and dimethylformamide (DMF) are of analytical grade and used without purification. Amine-terminated α -methoxy- ω -amino poly(ethylene glycol) (AT-PEG, $M_w = 5000$) was purchased from Sigma Inc. (USA) and used without further purification. Hexane, tetrahydrofuran (THF) and 1,4-dioxane are of analytical grade and dried with sodium to remove water before use.

Synthesis of PBLG and PBLG-*block*-PEG: The PBLG sample was prepared by a standard *N*-carboxyl- γ -benzyl-*L*-glutamate anhydride (NCA) method¹⁻³. Molecular weight of PBLG was estimated from the intrinsic viscosity measured in dichloroacetic acid (DCA)¹⁷. The molecular weight of PBLG used in the study was about 70000. PBLG-*block*-PEG copolymer was prepared by a standard *N*-carboxyl- γ -benzyl-*L*-glutamate anhydride (NCA) method^{1,18}. Briefly, PBLG-*block*-PEG copolymer was obtained by the ring-opening polymerization of γ -BLG NCA initiated by AT-PEG ($M_w = 5000$) in 1,4-dioxane at room temperature. The reaction mixture was poured into a large volume of anhydrous methanol. The precipitated product was dried under vacuum and then purified twice by repeated precipitation from a chloroform solution into a large volume

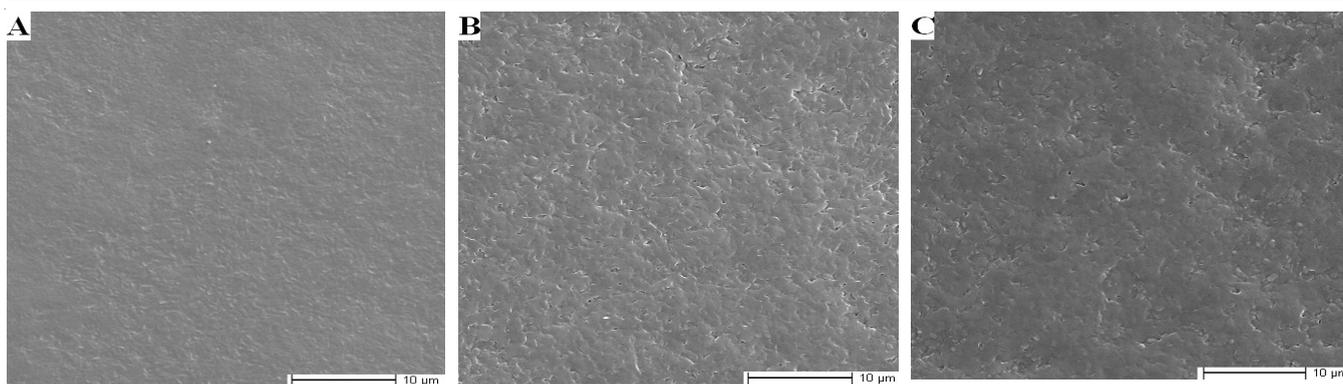


Fig. 1. SEM photographs of the polymer blend film surface with various polyurethane mole content: (a) 0 (b) 8 and (c) 15 %

of anhydrous methanol. The molecular weight of PBLG-*block*-PEG copolymer was estimated by NMR measurements¹. The molecular weight of PBLG-*block*-PEG used in the study was about 65000.

Preparation of polyurethane polymer: Polyurethane polymer based on 2,4-toluene diisocyanate, poly(propylene glycol), dimethylol propionic acid and butanediol were prepared with butanediol as chain extender, dimethylformamide as solvent and dibutyltin dilaurate as initiator^{19,20}. The molecular weight of polyurethane polymer in the study is about 20000.

Preparation of polypeptide mixture/polyurethane blend film: The polymer blend films were prepared by casting a 30 wt % polymer blend solution in DMF onto clean glass plates and drying them under vacuum at 60 °C. It is also found that, when polyurethane mole content in polymer blend is over 15 %, the polymer blend can not form continuous film.

Test method: SEM investigation was carried out using a scanning electron microscope (Sirin 200, FEI, Holland). Gold was sprayed on the polymer blend films in vacuum. Acceleration voltage was 10 kV. Tensile tests were carried out with an Instron Model 4468 universal testing machine (Digital Instruments, USA). The crosshead speed was set to 160 mm/min. For each data point, five samples were tested and the average value was taken. 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 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 determinations²¹. 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 12 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 polymer blend films before and after being immersed in distilled water, respectively²²⁻²⁴.

RESULTS AND DISCUSSION

The surface morphologies of the polymer blend films with different polyurethane content were studied by SEM. Fig. 1 exhibits the surface morphologies of the polymer blend films

with various polyurethane mole content: (a) 0, (b) 8 and (c) 15 %. As it can be seen from Fig. 1, the surface morphologies of the polymer blend films changed with the introduction of polyurethane chains. The surface morphologies of the polymer blend films became coarse and the surface density markedly increased, which is caused by the interaction between the polypeptide chains and the flexible polyurethane segments through entanglement. This phenomenon reveals that the change of the surface morphologies of the polymer blend films could be attributed to the introduction of the polyurethane segments.

Tensile tests: Fig. 2 displays the relationship between the tensile strength of the polymer blend film and the polyurethane mole content. Fig. 2 showed that the tensile strength of the polymer blend film decreased with the increase of the polyurethane mole content in the polymer blend. As known, the polypeptide segments are relatively rigid, while the synthetic polyurethane chains are flexible, suggesting that the decrease of the tensile strength of the polymer blend film is related with the introduction of the flexible polyurethane segments. Under evaluated polyurethane content, the higher the polyurethane content, the lower the tensile strength of the polymer blend film.

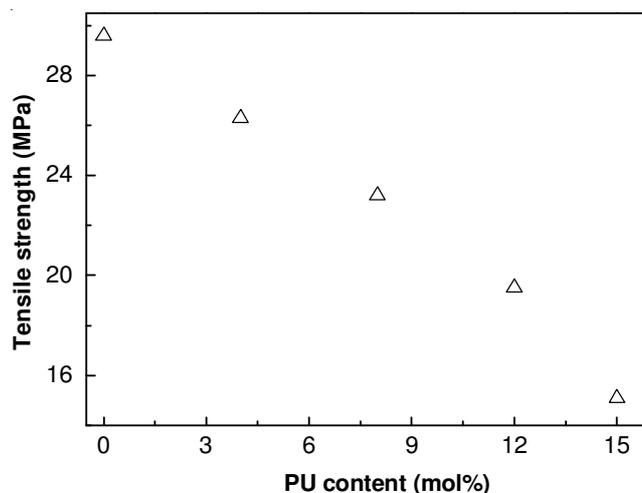


Fig. 2. Relationship between the tensile strength of the polymer blend film and the polyurethane (PU) mole content

Surface contact angle tests: Fig. 3 presents the relationship between the surface contact angle of the polymer blend

film and the polyurethane mole content. As is shown in Fig. 3, the surface contact angle of the polymer blend film decreased with increasing the polyurethane mole content in the polymer blend, indicating that the hydrophilicity of the polymer blend film increased. As known, the PBLG chains are hydrophobic, the PBLG-*block*-PEG segments hold a little hydrophilicity, while the synthetic polyurethane chains with carboxy groups hold good hydrophilicity, indicating that the decrease of the surface contact angle of the polymer blend film could also be attributed to the introduction of the hydrophilic polyurethane chains.

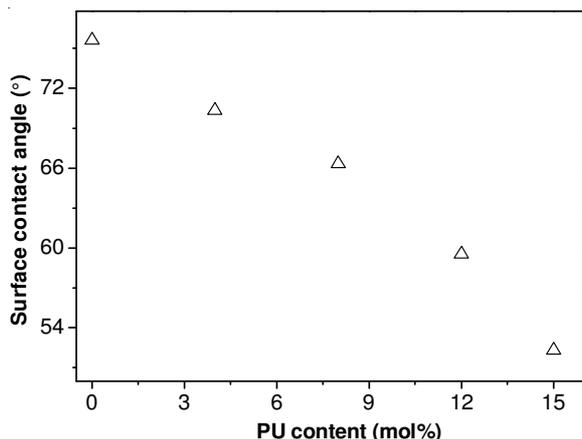


Fig. 3. Relationship between the surface contact angle of the polymer blend film and the polyurethane (PU) mole content

Water-absorption ratio tests: Fig. 4 indicates the relationship between the water-absorption ratio of the polymer blend film and the polyurethane mole content. As shown in Fig. 4, the water-absorption ratio of the polymer blend film increased with the increase of the polyurethane mole content in the polymer blend, suggesting that the hydrophilicity of the polymer blend film increased. As mentioned above, compared with the polypeptide chains, the synthetic polyurethane segments hold better hydrophilicity, the introduction of the polyurethane segments could promote the hydrophilicity of the polymer blend film. This phenomenon shows that the increase of the water-absorption ratio of the polymer blend film was related with the introduction of the hydrophilic polyurethane chains.

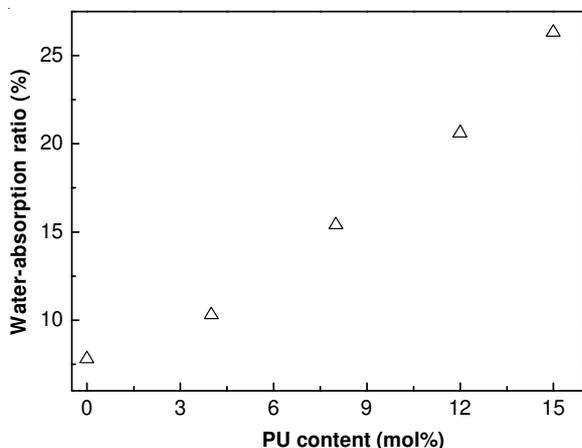


Fig. 4. Relationship between the water-absorption ratio of the polymer blend film and the polyurethane (PU) mole content

Conclusion

A series of polypeptide mixture/polyurethane blend films were prepared by casting the polymer blend solution in DMF. Surface morphologies of the polymer blend films were investigated by SEM. Mechanical and chemical properties of the polymer blend films were studied using tensile tests and surface contact angle tests. SEM photographs proved that the introduction of polyurethane changed the surface morphologies of the polymer blend films. Tensile tests verified that the introduction of polyurethane decreased the tensile strength of the polymer blend film. Both the surface contact angle tests and the water-absorption ratio tests demonstrated that the introduction of the polyurethane chains increased the hydrophilicity of the polymer blend films.

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