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# Physico-chemical Properties of Poly(ethylene glycol)-*block*-polypeptide-*graft*-poly-(ethylene glycol) Film Improved by Poly(propylene glycol)

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Poly(ethylene glycol)-*block*-poly(γ-benzyl L-glutamate)-*graft*-poly(ethylene glycol)/poly(propylene glycol) (PEG-*block*-PBLG-*graft*-PEG/PPG) blend films were prepared by the solution casting method. Surface morphologies of the PEG-*block*-PBLG-*graft*-PEG/PPG blend films were studied by scanning electron microscopy and atomic force microscopy. Mechanical and chemical properties of the polymer blend films were investigated by tensile tests and surface contact angle tests. The results indicated that the introduction of PPG could obviously affect the properties of the polypeptide block-graft copolymer films.

**Keywords: Polypeptide block-graft copolymer, Blend film, Morphology.**

## INTRODUCTION

In the past decade, self-assembly of amphiphilic polypeptide copolymers in selective solvents has received much attention both experimentally and theoretically[1-9]. Due to their amphiphilic characteristics, polypeptide copolymers with hydrophobic and hydrophilic components can self-assemble to form micelles or nanoparticles with a core-shell structure[1,2]. Also, because of the excellent biocompatibility and biodegradability, the polypeptide and its copolymers have received much attention for their potential applications[10-15]. The polypeptides and their copolymers have been investigated widely in the fields of functional biomaterials, protein simulation, polymer carriers for protein conjugates, macromolecular conformational study, catalysis, nanoreactors and drug delivery systems. *etc*.[3-9]. For the polypeptide copolymer films, an important application is for temporary artificial skin substrates in burn therapy[10,16].

Relative to the polypeptide block or graft copolymers, polypeptide copolymers with both block structure and graft structure are expected to possess different properties. The polypeptide block-graft copolymer/synthetic polymer blends have received relatively little attention. As noted, poly(propylene glycol) (PPG) holds better flexibility, weak hydrophilicity and good biocompatibility and biodegradability[17,18], the introduction of PPG chains could improve the properties of the polypeptide block-graft copolymer film and enlarge its research fields. To the best of our knowledge, however, no experimental work has so far been reported on the properties of polypeptide block-graft copolymer/PPG blend films. In the present study, PEG-*block*-PBLG-*graft*-PEG/PPG blend films were prepared by casting the polymer blend solution in dichloroethane. Surface morphologies of the polymer blend films were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Mechanical and chemical properties of the polymer blend films were studied by tensile tests and surface contact angle tests. It was revealed that the introduction of PPG chains could markedly affect the properties of the polypeptide block-graft copolymer 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. Amine-terminated α-methoxy-ω-amino poly(ethylene glycol) (ATPEG, $M_w$ = 5000) and poly(ethylene glycol methylether) (mPEG, $M_w$ = 500) were 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. Dichloroethane and other solvents are of analytical grade and used without further purification.

**Synthesis of polypeptide block-graft copolymer:** PBLG-*block*-PEG copolymer was prepared by a standard *N*-carboxyl-*g*-benzyl-*L*-glutamate anhydride (NCA) method[2,19]. Molecular weight of the PBLG-*block*-PEG copolymer was estimated by NMR method[2]. The molecular weight of PBLG-*block*-PEG used in the study was about 60000. PEG-*block*-

PBLG-*graft*-PEG copolymer was obtained by the ester exchange reaction of PBLG-*block*-PEG with mPEG ($M_w$ = 500) in *1,2*-dichloroethane with *p*-toluenesulfonic acid as a catalyst according to the described method[2,20]. The grafting percentage of PEG-*block*-PBLG-*graft*-PEG was about 8.5 % calculated according to the previous reports[1,20].

**Preparation of polypeptide block-graft copolymer/ PPG blend film:** The 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 58 °C. Also, it is found that, when PPG mole content in polymer blend is over 10 %, the polymer blend can not form an even and continuous film.

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. AFM investigation was carried out on a NanoScope IIIA MultiMode AFM instrument (Digital Instruments Inc., USA) in air at ambient conditions using tapping mode probes with constant amplitude (200 mV). The rotated tapping mode etched silicone probe with a resonance frequency of 250 kHz was used[11]. Tensile tests were carried out with an Instron Model 4468 universal testing machine (Digital Instruments, USA). The crosshead speed was set to 150 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 determinations[11].

## RESULTS AND DISCUSSION

The surface morphologies of PEG-*block*-PBLG-*graft*-PEG/PPG blend films with different PPG mole contents were investigated by SEM technique. Fig. 1 reveals the surface morphologies of the polymer blend films with various PPG mole contents: (a) 0, (b) 5 and (c) 10 %. As it can be seen from Fig. 1, the surface morphologies of the polymer blend films are different. With the increase of the PPG mole content, the surface of the polymer blend film tends to become more coarse and the surface density increases, which is caused by the interaction between the polypeptide block-graft copolymer chains and the PPG segments by entanglement. This phenomenon indicates that the difference of the surface morphologies between the polypeptide block-graft copolymer film and the polymer blend film could be attributed to the introduction of the PPG segments.

**Atomic force microscopic tests:** It is well-known that the AFM height images showed the surface roughness of the polymer film[21-23]. Fig. 2 displays the AFM 2D height images of PEG-block-PBLG-*graft*-PEG/PPG blend film surface with different PPG mole contents: (a) 0, (b) 5 and (c) 10 %. As can be seen from Fig. 2, the surface colors of the polymer blend films present both brighter domains (corresponding to the higher part) and darker domains (corresponding to the lower part)[21-23]. With the in crease of PPG mole contents, the ratio of brighter domains to darker domains is various, suggesting the surface roughness of the polymer blend film is changing with the introduction of the PPG segments[21-23]. This phenomenon shows that the surface roughness difference of the polypeptide block-graft copolymer film and the polymer blend film could also be attributed to the introduction of the PPG segments.

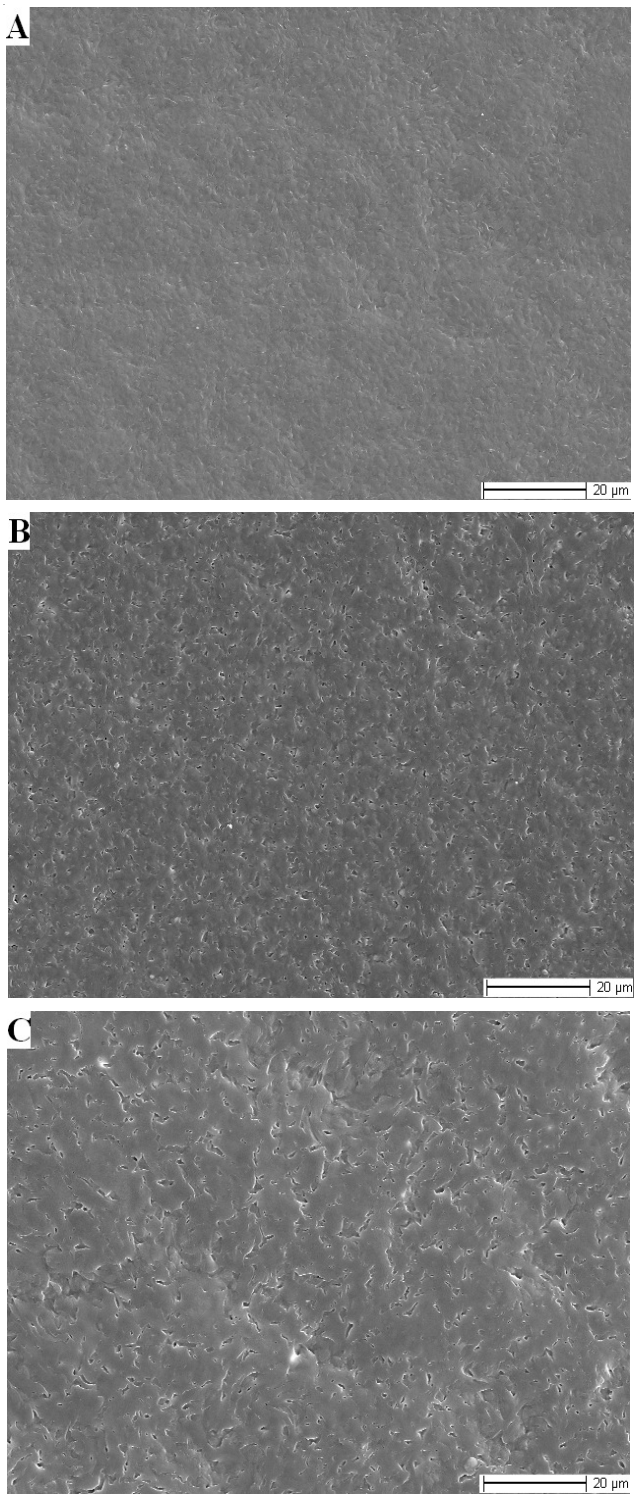


Fig. 1. SEM photographs of the PEG-*block*-PBLG-*graft*-PEG/PPG blend film surface with various PPG mole contents: (a) 0, (b) 5 % and (c) 10 %

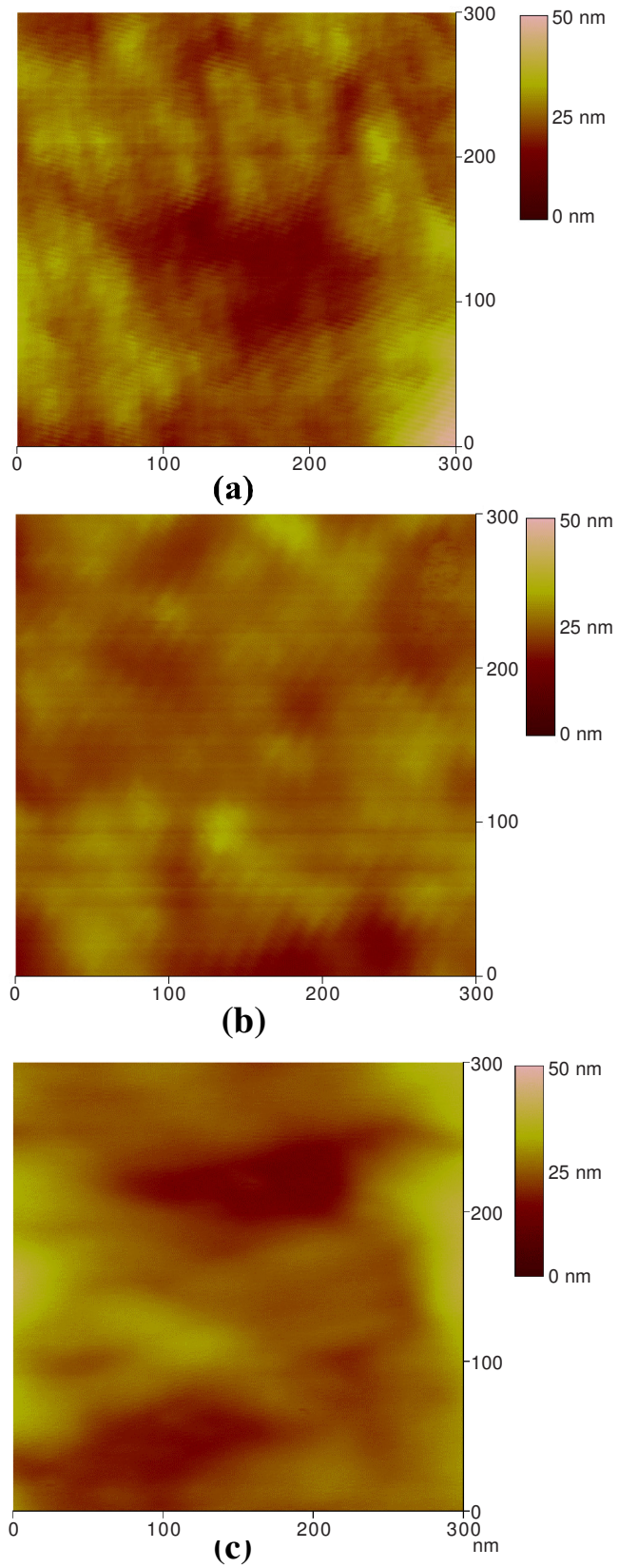


Fig. 2. AFM 2D height images of the PEG-*block*-PBLG-*graft*-PEG/PPG blend film surface with different PPG mole contents: (a) 0, (b) 5 and (c) 10 %

**Tensile tests:** Fig. 3 shows the relationship between the tensile strength of the polymer blend film and the PPG mole contents. As is shown in Fig. 3, the tensile strength of the polymer blend film decreased with the increase of the contents of PPG mole in the polymer blend. As mentioned above, compared with the polypeptide block-graft copolymer, PPG is very flexible, indicating the decrease of the tensile strength of polymer blend film is related with the introduction of the flexible PPG segments. Under permitted PPG mole content, the higher the PPG mole content, the lower the tensile strength of the polymer blend film.

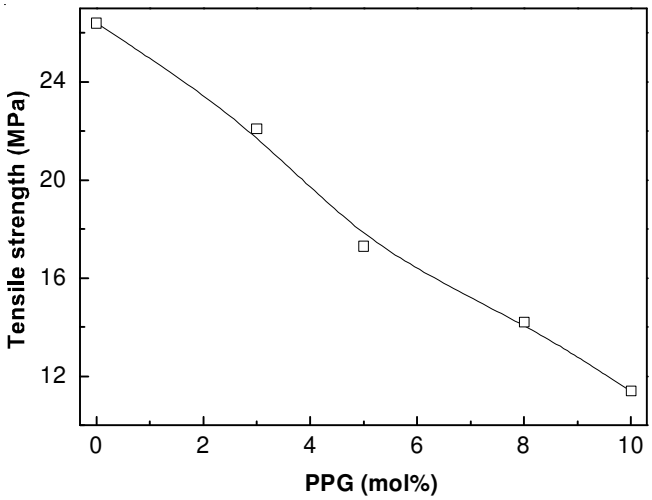


Fig. 3. Relationship between the tensile strength of the polymer blend film and the PPG mole contents

Fig. 4 presents the relationship between the elongation at break of the polymer blend film and the PPG mole contents. As shown in Fig. 4, the elongation at break of the polymer blend film increased with the increase of the PPG mole contents in the polymer blend. As discussed above, the PPG segments are very flexible, suggesting the increase of the elongation at break of the polymer blend film is also concerned with the introduction of the flexible PPG chains.

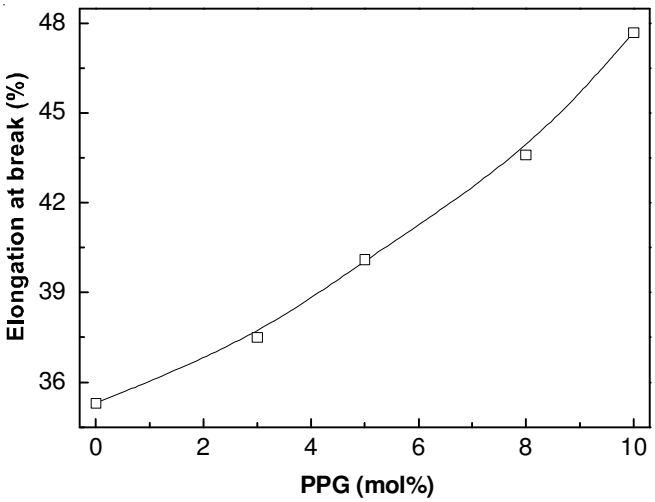


Fig. 4. Relationship between the elongation at break of the polymer blend film and the PPG mole contents

**Surface contact angle tests:** Fig. 5 indicates the relationship between the surface contact angle of the polymer blend film and the PPG mole contents. As seen from Fig. 5, the surface contact angle of the polymer blend film slightly decreased

with increasing contents of the PPG mole in the polymer blend, indicating that the hydrophilicity of the polymer blend film slightly increased. As noted, PBLG segments are hydrophobic and PEG chains hold hydrophilicity, suggesting the polypeptide block-graft copolymer holds a little hydrophilicity. Compared with hydrophobic PBLG segments, PPG chains also hold a little hydrophilicity, indicating the introduction of the PPG chains slightly increased the hydrophilicity of the polypeptide block-graft copolymer film. This phenomenon proves that the decrease of the surface contact angle of the polymer blend film was connected with the introduction of the PPG chains.

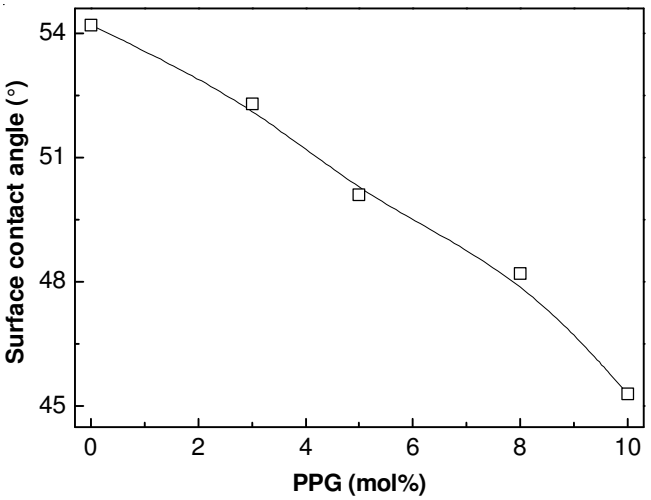


Fig. 5. Relationship between the surface contact angle of the polymer blend film and the PPG mole contents

## Conclusion

A series of PEG-*block*-PBLG-*graft*-PEG/PPG blend films were prepared by casting the polymer blend solution in dichloroethane. Surface morphologies of the polymer blend films were investigated by SEM and AFM. Mechanical and chemical properties of the polymer blend films were studied by tensile tests and surface contact angle tests. SEM photographs proved that the introduction of the PPG chains changed the surface morphologies of the polypeptide block-graft copolymer film. Atomic force microscopic images attested that the introduction of the PPG segments changed the surface roughness of the polypeptide block-graft copolymer film. Tensile tests verified that the introduction of the PPG segments decreased the tensile strength of the polypeptide block-graft copolymer film but promoted its elongation at break. The surface contact angle tests demonstrated that the introduction of the PPG chains slightly increased the hydrophilicity of the polypeptide block-graft copolymer film.

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## REFERENCES

1. D.M. Tang, J.P. Lin, S.L. Lin, S.N. Zhang, T. Chen and X.H. Tian, *Macromol. Rapid Commun*., **25**, 1241 (2004).
2. T. Li, J.P. Lin, T. Chen and S.N. Zhang, *Polymer*, **47**, 4485 (2006).
3. Z. Gao, A. Desjardins and A. Eisenberg, *Macromolecules*, **25**, 1300 (1992).
4. X.F. Zhong, S.K. Varshney and A. Eisenberg, *Macromolecules*, **25**, 7160 (1992).
5. M. Moffitt and A. Eisenberg, *Macromolecules*, **30**, 4363 (1997).
6. G.Q. Zhu, G.C. Li and P. Wang, *Polym.-Plast. Technol. Eng*., **50**, 1470 (2011).
7. G.Q. Zhu, Y.Y. Liu and F.G. Wang, *Int. J. Polym. Mater*., **61**, 737 (2012).
8. G.Q. Zhu, F.G. Wang, Y.Y. Liu and Q.C. Gao, *Fibers Polym*., **11**, 819 (2010).
9. J.P. Lin, G.Q. Zhu, X.M. Zhu, S.L. Lin, T. Nose and W.W. Ding, *Polymer*, **49**, 1132 (2008).
10. K. Jokei, M. Oka, T. Hayashi and Y. Miyachi, *Eur. Polym. J*., **35**, 945 (1999).
11. L.Q. Bai, L.J. Zhu, S.J. Min, L. Liu, Y.R. Cai and J.M. Yao, *Appl. Surf. Sci*., **254**, 2988 (2008).
12. I. Oh, K. Lee, H.-Y. Kwon, Y.-B. Lee, S.-C. Shin, C.-S. Cho and C.-K. Kim, *Int. J. Pharm*., **181**, 107 (1999).
13. G.Q. Zhu, L. Feng and S.N. Zhang, *J. Macromol. Sci. A*, **46**, 694 (2009).
14. N. Higashi, J. Kawahara and M. Niwa, *J. Colloid Interf. Sci*., **288**, 83 (2005).
15. G.Q. Zhu, *Chem. Pap*., **64**, 34 (2010).
16. Y. Miyachi, K. Jokei, M. Oka and T. Hayashi, *Eur. Polym. J*., **35**, 767 (1999).
17. S.M. Cakic, J.V. Stamenkovic, D.M. Djordjevic and I.S. Ristic, *Polym. Degrad. Stab*., **94**, 2015 (2009).
18. M. Liberatore, F. Decker, A. Šurca Vuk, B. Orel and G. Dra•ic, *Sol. Energy Mater. Sol. Cells*, **90**, 434 (2006).
19. G.Q. Zhu, Q.C. Gao, Z.H. Li and F.G. Wang, *Int. J. Polym. Mater*., **60**, 290 (2011).
20. G.Q. Zhu, *J. Macromol. Sci. A*, **46**, 892 (2009).
21. M.Y. Lee, S.H. Kim, H.S. Ganapathy, S.W. Kim and K.T. Lim, *Ultramicroscopy*, **108**, 1210 (2008).
22. M.J. Fasolka, A.M. Mayes and S.N. Magonov, *Ultramicroscopy*, **90**, 21 (2001).
23. S. Yamamoto, Y. Tsujii and T. Fukuda, *Polymer*, **42**, 2007 (2001).