Surface and Bulk Properties of Poly(ether urethane)s/Fluorinated Phosphatidylcholine Polyurethanes Blends

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ABSTRACT: As a part of long-term project aimed at biomembrane mimicking polyurethanes (PU) with excellent biocompatibility and good mechanical properties, in this work, we report the surface and bulk properties of two series blends of fluorinated phosphatidylcholine polyurethanes (FPCPU) with poly(ether urethane)s (PEU). The blend films were prepared by solution mixing, and the surface and bulk properties were investigated by contact angle measurement, XPS, DSC, and Instron. Our results demonstrated that the surface with high percentage of phosphorus, fluorine, and nitrogen content could be achieved by blending FPCPU with PEU, because of the migration of FPCPU to the surface, resulting in a decreased water contact angle and increased hystersis. The blend films showed a reversible rearrangement of surface structure according to the change of environment from dry state to hydrated state. DSC result suggested that FPCPU could be phase miscible with PEU well in a broad composition region (as the content of FPCPU is less than 50 wt %). The blends showed an increased tensile strength and elongation at break compared with FPCPU, and increased modulus compared with PEU. Combined with the improved mechanical properties and much reduced price, together with the excellent blood compatibility, it can be expected these materials may play important roles in future medical application. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 548–553, 2008

Key words: fluorinated phosphatidylcholine polyurethanes; polyurethanes; blends; surface properties

INTRODUCTION

Segmented polyurethanes (PU) with two-phase structure have been used to fabricate biomedical devices for the last two decades because of their favorable tensile and fatigue properties as well as their thromboresistance.[1,2] The applications include vascular prosthesis, catheters, heart valves, cardiac assist devices, and the total artificial heart. The widely spread biomedical application of this class of polymers have resulted in extensive research activities in this field.[3] *In vivo* application demands polymers with better biocompatible and mechanical properties. These properties in the surface region of the polymers are even more important since the surface chemistry between blood/body tissues and the implanted medical devices plays a significant role in the usefulness of the devices. The use of surface modification methods can greatly improve the blood/tissue compatibility and resistance to the degradation of the implanted devices and, therefore, can extend the lifetime of the devices and reduce the cost of implantation. Many attempts concerned with the surface modification of PU have been reported.[4–9]

Recently, much effort has been concentrated on molecular design and synthesis of even more biocompatible PU containing phospholipid functionality, and particularly to those with the phosphatidylcholine (PC) group, which is a major component of the cellular membrane of the phospholipid bilayer. Up to now, various polymeric materials containing the PC group were synthesized and the biocompatibility and blood compatibility of these polymers were carefully evaluated.[10–16] It was showed excellent nonthrombogenicity even when the PC polymers came in contact with whole human blood in the absence of anticoagulants.[10,11,13,15,17]

As an alternative to synthesize new PC-containing polymers with good mechanical properties and cheaper price, polymer blends is a more effective technique to modify PU, and offer the opportunity to further investigate the surface properties of the blend film containing PC group. Anderson and coworkers carried out the blending of polymeric materials having a ternary amino group into PU and evaluated protein adsorption and cell adhesion on the

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modified materials.[18–20] Both protein adsorption and cell adhesion on the polyurethane surface could be reduced by the addition of polymeric materials having a ternary amino group. Furthermore, a series of 2-methacryloyloxyethyl phosphorylcholine (MPC) and PU blends were reported.[21–25] The blood compatibility of the PU/MPC polymer blend with attention to platelet adhesion and protein adsorption was superior compared with that of the original PU.

In our previous work, a novel chain extender with long fluorinated side chain PC and a series of fluorinated phosphatidylcholine polyurethanes (FPCPU) attached to the hard block were designed and synthesized.[26] The long side chain fluorinated alkyl group has low surface free energy so that the PC polar group can be very easily transferred to the surface or subsurfaces of PU. And an overturn and rearrangement of the fluorinated PC side groups with PC polar head groups located on the outermost surface area could provide biomembrane mimicry under hot water condition.[27] Our previous study also showed that the fluorinated phosphorylcholine polyurethanes (FPCPU) had good mechanical properties superior to that of phospholipid PU reported in literature, and could effectively suppress protein adsorption even at a low content of PC in the bulk. However, it should be noted that the tensile properties of the FPCPU are lower than that of normal PU. Especially, the tensile strength of series fluorinated phosphatidylcholine poly(ether urethane)s (FPCPEU) is decreased to only 20% of normal poly(ether urethane)s (PEU).[28,29] Also the price of FPCPU is much higher than that of normal PEU.

In this study, two series of FPCPU blends were prepared by mixing fluorinated phosphatidylcholine poly(carbonate urethane)s (FPCPCU) with PEU, or FPCPEU with PEU to obtain biomembrane mimicking PU with excellent biocompatibility and biostability on one hand, and good mechanical properties and cheap price on the other hand, by using as less FPCPU as possible. The polymer blend membranes were prepared with solution blending method. X-ray photoelectron spectroscopy (XPS), contact angle measurements (CA), DSC measurements, mechanical testing was carried out for evaluation of the surface structure and mechanical properties of the series of polymer blends prepared. The biocompatibility will be reported elsewhere.

EXPERIMENTAL

Materials

Fluorinated phosphatidylcholine poly(carbonate urethane)s (FPCPCU) and fluorinated phosphatidylcholine poly(ether urethane)s (FPCPEU) were synthesized in our laboratory by the method reported pre-
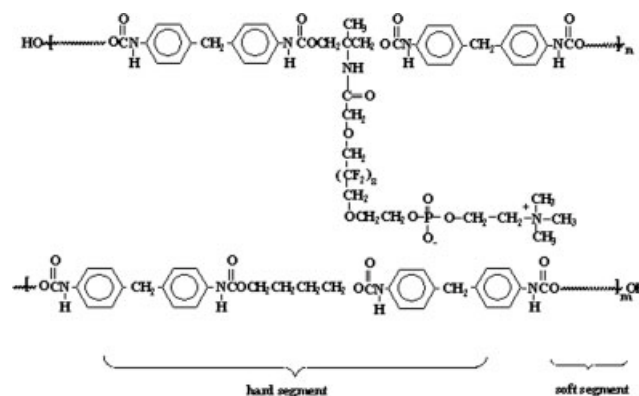

Figure 1 The schematic structure of fluorinated phosphatidylcholine polyurethanes, $n = 1, 2, 3, \ldots$, $m = 0, 1, 2, 3, \ldots$. Soft segment is PTMO or PHPCD.

viously.[26] The extender with long fluorinated side chain PC used took 50% of the total chain extender. The schematic structure of FPCPU is shown in Figure 1. Poly(ether urethane)s (PEU) was synthesized with methylenebis(phenyleneisocyanate) (MDI), poly-tetramethyleneoxide (PTMO), and 1,4-butandiol (BDO) (moral ratio 2 : 1 : 1) using two-step bulk polymerization.[30] The number-average-molecular weight (M_n) (GPC) of PEU, FPCPCU, and FPCPEU are 5.85×10^4, 1.8125×10^4, and $1.19\ 71 \times 10^4$, respectively. N,N-dimethylacetamide (DMAc) was dried over CaH_2 for 2 days at room temperature and distilled under vacuum, and stored over 4 Å molecular sieves. Other reagents and solvents were commercial extra-pure reagent grade and used without further purification.

Sample preparation

Two series mixture of PEU/FPCPEU blends and PEU/FPCPCU blends were prepared in 5% (w/v) DMAc solution. The content of FPCPEU or FPCPCU in the blends is 10, 25, 40, and 50 wt %, and labeled as 10FPCPEU, 25FPCPEU, 40FPCPEU, and 50FPCPEU, or 10FPCPCU, 25FPCPCU, 40FPCPCU, and 50FPCPCU, respectively. The sample films were prepared by casting the solution onto clean hydrophilic glass plates, and then put the plates into an oven at 50°C for 24 h, then under vacuum at 50°C for 48 h, 80 °C for 2 h. These specimens were used for XPS, water contact angle, and Instron measurements.

Contact angle measurement

Contact angles were measured with an Eyma contact angle goniometer. Air-facing side of the membranes were analyzed, stationary, advancing, and receding contact angles were measured by using of distill-deionized water at room temperature, and the

results in the study are the mean values of six replicates.

X-ray photoelectron spectroscopy

XPS was carried out on an XSAM-800 electron spectrometer. The spectrometer was equipped with a Mg Kα achromatic X-ray source (20 KV, 10 mA) and two take-off angles of 30° and 90° were used with X-ray source. The take-off angle represents the depth having been detected as 30° that is near the surface (50 Å) and 90° that is 10 nm away from the surface. Air-facing side of the membranes was analyzed.

DSC measurement

The DSC heating data were collected at 10°C/min from −100 to 100°C by TA instrument 2910 thermal analyzer. During the measurement, dried N_2 gas was purged at a constant flow rate. The temperature reading and calorific measurement were calibrated by using standard indium.

Mechanical testing

Mechanical testing was carried out with an Instron 4302 Model Universal Testing machine at 23°C (73 F) and relative humidity of 50%.The blend films were cut into dumbbell of 5 cm in length and 1 cm in width; the narrow section was 2 cm × 0.5 cm in area and about 0.25 mm in thickness. The results reported are the mean values of five replicates.

RESULTS AND DISCUSSION

Water contact angles analysis

The surface microheterogeneity sensitivity of contact angle measurement is about 0.5–1.0 nm on polymer surface.[31] To study the surface property of two series of FPCPU and PEU blends, the measurement of water contact angle was carried out. The results are summarized in Table I.

From the contact angle measurement, it is seen that all advancing and receding contact angle of the blends are decreased compared with that of pure PEU. For example, the advancing and receding contact angles are decreased from 71.5° and 58.5° for PEU to 58.8°, 28.5° for 50FPCPCU, respectively. Moreover, the trend of decrease for PEU/FPCPCU blends is more apparent than that for PEU/FPCPEU blends.

Usually, a decreased water contact angle indicates an increased hydrophilicity.[32] Thus, this result suggests that the polymer blends are more hydrophilic than that of PEU. But the increased hystersis indicates a possible rearrangement of surface structure

TABLE I
Contact Angles Results

| Sample | Water | | |
	θ_a	θ_r	$\Delta\theta$
PEU	71.5 ± 1.5	58.5 ± 1.5	13.0 ± 3.0
10FPCPEU	67.7 ± 1.3	41.8 ± 1.5	25.9 ± 3.2
25FPCPEU	66.3 ± 1.9	38.8 ± 1.8	27.5 ± 3.7
40FPCPEU	63.5 ± 1.3	36.7 ± 1.3	26.8 ± 2.6
50FPCPEU	62.3 ± 0.8	34.2 ± 0.9	28.1 ± 1.7
FPCPEU	70.0 ± 1.9	33.6 ± 1.1	36.4 ± 3.0
10FPCPCU	69 ± 1.7	53.5 ± 3.8	15.5 ± 5.5
25FPCPCU	66.2 ± 0.8	47.6 ± 1.8	18.6 ± 2.6
40FPCPCU	60.2 ± 1.1	30.7 ± 2.0	29.5 ± 3.1
50FPCPCU	58.8 ± 1.0	28.5 ± 1.7	30.3 ± 2.7
FPCPCU	66.0 ± 1.3	26.3 ± 1.2	19.9 ± 3.2

Advancing θ_a and receding θ_r angles with corresponding hysteresis $\Delta\theta = \theta_a - \theta_r$ values.

as a rule.[32] In this article, we will show the rearrangement and reversible surface change for these polymer blends. The change of surface structure was investigated by water contact measurement in each case after dried in vacuum or treated in hot water. In the air (vacuum)-equilibrated state, lower surface free energy components (hydrophobic fluorinated alkyl groups) are enriched at the air-solid interface, whereas in the water-equilibrated state, higher surface free energy components (hydrophilic PC polar head groups) are enriched at the water-solid interface. So the surface change from hydrophobic in dry state to hydrophilic in hydrated state is a reversible process. To prove the fact, the films of 40FPCPCU blends and 40 FPCPEU blends were chosen for this experiment. A film of 40 FPCPCU blends was first dried in vacuum at 50°C for 12 h, and then the water contact angle was measured. One observes an increased hydrophobic surface with a contact angle of 71.8°. Then the same film of 40 FPCPCU blends was treated in distill-deionized hot water at 80°C for 1 h. After dried quickly at room temperature by using nitrogen (N_2), the water contact angle was measured. Expectedly, in this case a hydrophilic surface is observed with a contact angle of 50°. The same method was used to treat the films of 40FPCPEU blends, and the similar result was obtained, as listed in Table II.

In our previous study,[29] the mechanism of fluorinated PC groups with environmental responsiveness have been verified by ATR-IR and XPS techniques. The novel segmented poly(carbonate urethane)s containing both hydrophobic fluorinated alkyl group and hydrophilic PC polar head groups on the side chain(FPCPCU in this article) showed smart surface behavior. The contact angle measurement, XPS, together with ATR-IR investigation indeed indicated a reversible overturn of the PC groups with the movement of the hydrophobic fluorinated alkyl groups

TABLE II
The Stationary Contact Angles for 40FPCPU in Different Environment

Sample	Dry state (°)	Hydrated state (°)
40FPCPCU	71.8 ± 2.2	50 ± 3.0
40FPCPEU	69.1 ± 1.9	54.5 ± 3.5

TABLE III
Atomic Percentage of Phosphorus, Fluorine, and Nitrogen at the Depth of About 5 and 10 nm on the Blend Film Surfaces

	P_{2p} (%)		F_{1s} (%)		N_{1s} (%)	
	Take-off angle		Take-off angle		Take-off angle	
Sample	30°	90°	30°	90°	30°	90°
PEU	0.0	0.0	0.0	0.0	0.0	1.0
10FPCPEU	0.0	0.0	3.7	2.7	0.0	2.6
25FPCPEU	0.0	0.0	7.9	5.7	1.2	2.7
40FPCPEU	0.0	0.2	9.9	9.0	2.0	2.6
50FPCPEU	0.0	0.0	6.9	5.9	2.0	3.7
FPCPEU	1.2	0.5	10.3	9.3	2.3	3.0
10FPCPCU	0.0	0.0	7.9	4.4	2.9	3.0
25FPCPCU	0.4	0.7	17.8	13.2	2.9	3.8
40FPCPCU	1.3	0.7	22.7	16.0	2.6	3.1
50FPCPCU	0.8	1.0	19.0	15.4	2.2	3.2
FPCPCU	1.2	0.9	16.1	14.5	24.2	2.4

when the samples were treated in dry air or water. In this study, the contact angle analysis shows a similar phenomenon for these polymer blends, a hydrophobic surface with a contact angle of 71.8° in dry state and a hydrophilic surface with a contact angle of 50° in hydrated state for 40FPCPCU blends compared to the contact angle of 77.7° and 57.5° reported by Tan et al,[29] and all these experiments were repeated several times. Therefore, we presume that the surface change of these polymer blends could also be reversible with the changed environment. Although there may exist another possibility that the surface change is due to temperature difference as treated in vacuum at 50°C and in hot water at 80°C. To rule out this possibility, the same experiment was repeated by using conventional PEU. No change of water contact angle was observed, indicating that the treated temperature in our study will not give rise to an obvious difference in change of surface structure.

XPS analysis

If the fluorinated PC groups were really condensed at the surface of blend films, one should detect the change of elements of phosphorus (P_{2p}) and fluorine (F_{1s}) and nitrogen (N_{1s}) by the XPS experiment. The atomic percentage of P_{2p}, F_{1s}, and N_{1s} at the depth of 5 nm (take-off angle 30°) and 10 nm (take-off angle 90°) away from surface of the two series blend films are listed in Table III. And the amount of elemental phosphorus and fluorine at surface represents the amount of PC polar group and fluorinated side chain that migrate to the surface respectively. In addition, the elemental nitrogen was not detected at the depth of 5 nm (take-off angle 30°) on the surface of PEU as the same as our previous study results (Table III).[30] Since the hard segments of PEU are usually in their glassy state, the soft segments have higher mobility and can easily migrate to the surface region, as suggested in literature.[33,34]

From the Figure 2, it could be clearly observed that the atomic percentage of fluorine element on the surface of PEU/FPCPEU blends increase with increasing content of FPCPEU, and the fluorine content on the surface of 40FPCPEU blends is the highest, nearly equal to that of FPCPEU among the fluorine content on the surfaces of PEU/FPCPEU blend films. Phosphorus is not detected on the surface of

series of PEU/FPCPEU blends by XPS except the 40FPCPEU blend membrane probably because of low rate of migration of fluorinated PC chains to the surface in this blend system. Or this is due to the possible down position of hydrophilic PC group during XPS experiment. On the other hand, compared with the pure FPCPEU, the atomic percentage of fluorine and phosphorus element on the surface is decreased for the blend films with all the composition studied. This result is expected and can be understood because of the dilute effect, as FPCPEU is blended with PEU.

For the PEU/FPCPCU blend system (Table III and Fig. 2), the similar trend is observed that the atomic percentage of fluorine, phosphorus, and nitrogen element on the surface is increased with increasing con-
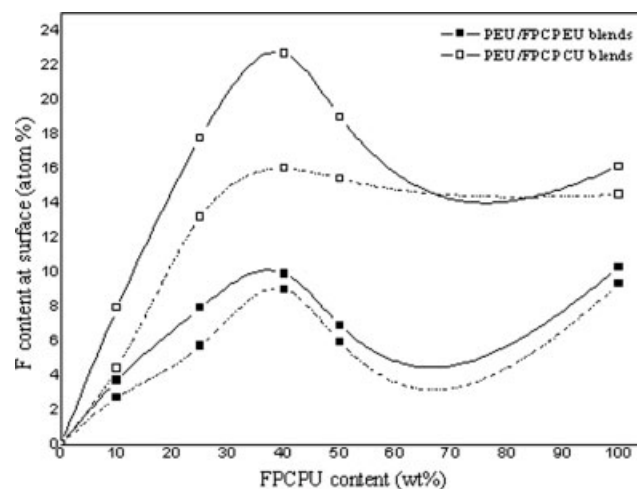

Figure 2 The XPS results of fluorine content (at %) at the surface of blend films depend on the FPCPU content. Take-off angle 30° (solid line) and take-off angle 90° (dash dot line).
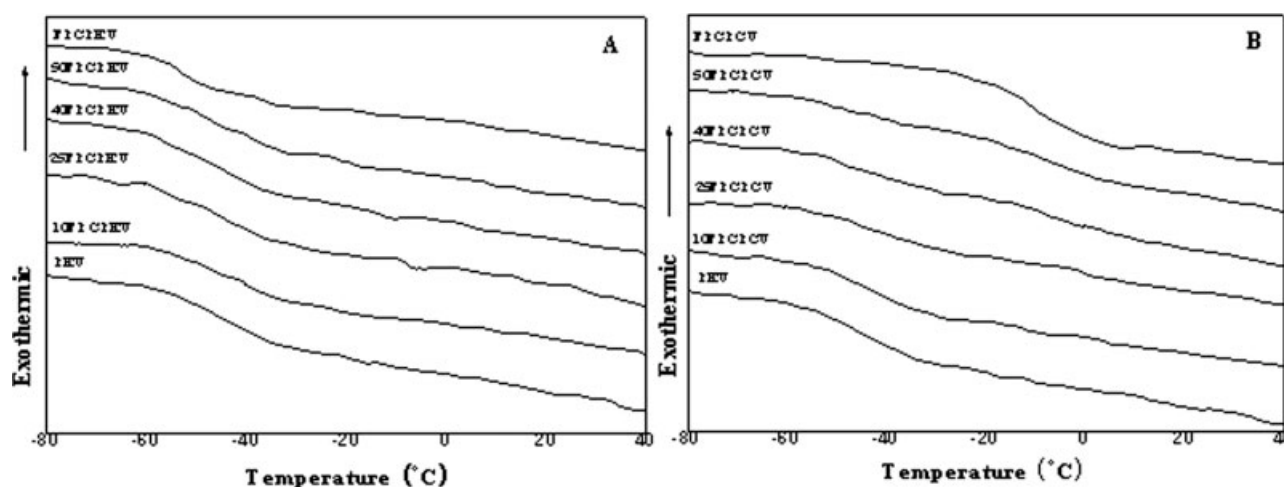
Figure 3 DSC curves of fluorinated phosphatidylcholine polyurethanes and poly(etherurethane)s. (A) poly(ether urethane)s series, (B) poly(carbonate urethane)s series.

tent of FPCPCU. It is interesting to see that the atomic percentage of phosphorus, fluorine, and nitrogen element on the blend films surface is even higher that for pure FPCPCU as FPCPCU content is more than 25 wt %. For example, the atomic percentage of phosphorus, fluorine, and nitrogen element on the surface at the depth of 5 nm (take-off angle 30°) for 40 FPCPCU is 1.3%, 22.7.0%, and 2.6%, respectively, compared with 1.2%, 16.1%, and 2.2% for the pure FPCPCU.

DSC analysis

The DSC curves of two series blend of FPCPU with PEU blends compared with that of PEU and two sets of pure FPCPU are shown in Figure 3, and the glass transition temperatures of the polymer blends are listed in Table IV.

TABLE IV
Glass Transition Temperature of Poly(ether urethane)s and Fluorinated Phosphatidylcholine Polyurethanes Blends

Sample	$T_{g(\text{soft seg})}$ (°C)	$T_{(\text{onset})}$ (°C)	$T_{(\text{terminal})}$ (°C)	ΔT^b (°C)
PEU	−44.77	−54.99	−34.55	20.44
10FPCPEU	−45.43	−54.54	−34.67	19.87
25FPCPEU	−46.20	−56.93	−35.44	21.49
40FPCPEU	−47.89	−56.82	−38.95	17.87
50FPCPEU	−47.44	−55.95	−38.93	17.02
FPCPEU	−52.20	−62	−42	20
10FPCPCU	−44.02	−55.77	−32.19	23.58
25FPCPCU	−41.49	−52.60	−30.71	21.89
40FPCPCU	−43.16	−54.58	−35.50	19.08
50FPCPCU	−47.73	−52.64	0.11	52.77
	−7.52			
FPCPCU	−9.40	−16.79	5.49	22.28

$\Delta T^b = T(\text{terminal}) - T(\text{onset})$.

For PEU/FPCPEU blends, the T_g and the width of glass transition are found to decrease slightly with an increase in FPCPEU content [Table IV, Fig. 3(A)]. The result indicates that FPCPEU and PEU are most likely miscible because of the similar structure of the backbone. Whereas, the change trend of glass transition temperature for PEU/FPCPCU blends is complicated. It is shown that T_gs and the width of T_g of the blends are almost the same as that of PEU with increasing content of FPCPCU till to 40 wt % [Table IV, Fig. 3(B)]. This result suggests that the FPCPCU could be miscible with PEU till to 40 wt % of FPCPCU. However, two T_gs (−47.74°C, −7.52°C) are observed from the DSC curve of 50FPCPCU, which correspond to the T_g of PEU and FPCPCU, respectively. Also a much wider glass transition region is seen for this blend. Since the width of glass transition temperature could also reflect the phase heterogeneity,[35] the existence of two T_gs and enlarged glass transition temperature region for 50FPCPCU may suggest phase separated structure in this blend. The change of T_g of PEU should be treated with care due to the fact that DSC analytical methods often brought to controversial or inconclusive results because of the lack of reliable models to determine accurate glass transition temperatures. Therefore, more work is needed to further confirm it using other methods, such as DMA, and this is under going in our group.

Mechanical properties analysis

Finally, let's look at mechanical properties of these blends. The tensile properties of 40FPCPEU and 40FPCPCU were measured to evaluate the bulk property change of PEU by adding the FPCPEU or FPCPCU, and the results are listed in Table V.

TABLE V
Mechanical Properties of the Poly(ether urethane)s and Fluorinated Phosphatidylcholine Polyurethanes Blends

Sample	Ultimate tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PEU	30.7 ± 2.8	16.7 ± 2.8	1051.9 ± 106.7
40FPCPEU	16.5 ± 1.2	21.7 ± 5.2	868.4 ± 29.6
FPCPEU	8.3 ± 0.5	26.9 ± 9.0	152.7 ± 9.3
40FPCPCU	24.1 ± 1.6	30.6 ± 6.7	521.7 ± 67.0
FPCPCU	22.8 ± 4.1	35.5 ± 0.9	387.8 ± 45.1

It is noted that the tensile strength of polymer blends is lower than that of normal PEU. However, the tensile strength of 40FPCPEU blends is doubled compared with that of pure FPCPEU. The modulus of the two polymer blends is also larger than that of PEU. A decreased elongation is seen for both blends compared with PEU. However, compared the FPCPEU, a largely improved elongation is achieved. For example, the elongation at break of 40FPCPEU blend membrane (868.4%) is about 5 times higher than that of FPCPEU (152.7%). The enhanced tensile properties for polymer blends could be understood because of the phase mixed structure in the blends.

CONCLUSION

In this study, we examined the surface and bulk properties of PEU/FPCPU blends by the contact angle and XPS, DSC, and tensile testing measurements. It has been demonstrated that fluorinated PC units were enriched on the surface by blending FPCPU with PEU. These blends also showed smart surface behavior because of the alternating change of up and down between hydrophobic fluorinated group and hydrophilic PC group with the change of environment from dry state to hydrated state. DSC result suggested that the FPCPEU blends were miscible well with PEU because of the similar backbone structure, and the FPCPCU blends also could be miscible with PEU as the content of FPCPCU is less than 50 wt %. The blends (40FPCPCU and 40FPCPEU) showed an increased tensile strength and elongation at break compared with FPCPU, and increased modulus compared with PEU. Because of the largely enriched fluorinated PC units on the surface, particularly for PEU/FPCPCU blends films, a biomembrane mimicking PU with excellent biocompatibilities and biostability could be expected (this has been proven by the measurement of blood compatibility, and will be reported elsewhere). Our result indicates that blending of PEU with FPCPU is simple yet effective way to prepare PU with good mechanical properties, excellent blood compatibility and cheap price.

References

1. Lelah, M. D.; Cooper, S. L. Polyurethanes in Medicine; CRC: Boca Raton, FL, 1986; p 23.
2. Andrade, J. D., Ed. Surface and Interfacial Aspects of Biomedical Polymers; Plenum: New York, 1988.
3. Wirpsza, Z. Polyurethanes, Chemistry, Technology, and Applications; Chichester: New York, 1993.
4. Pitt, W. G.; Grasel, T. G.; Cooper, S. L. Biomaterials 1988, 9, 36.
5. Park, K. D.; Okano, T.; Nojiri, C.; Kim, S. W. J Biomed Mater Res 1988, 22, 977.
6. Okkema, A. Z.; Yu, X. H.; Cooper, S. L. Biomaterials 1990, 12, 3.
7. Han, D. K.; Jeong, S. Y.; Kim, Y. H.; Min, B. G.; Cho, H. I. J Biomed Mater Res 1991, 25, 561.
8. Nojiri, C.; Okano, T.; Jacobs, H. A.; Park, K. D.; Mohammad, F.; Olsen, D. B.; Kim, S. W. J Biomed Mater Res 1990, 24, 1151.
9. Nojiri, C.; Park, K. D.; Okano, T.; Kim, S. W. Trans Am Soc Artif Intern Organs 1989, 35, 357.
10. Ishihara, K.; Ueda, T.; Nakabayashi, N. Polym J 1990, 23, 355.
11. Ueda, T.; Oshida, H.; Kurita, K.; Ishihara, K.; Nakabayashi, N. Polym J 1992, 24, 1259.
12. Kojima, M.; Ishihara, K.; Watanabe, A.; Nakabayashi, N. Biomaterials 1991, 12, 121.
13. Ishihara, K.; Aragaki, R.; Ueda, T.; Watanabe, A.; Nakabayashi, N. J Biomed Mater Res 1990, 24, 1069.
14. Xi, T.; Wenhua, T.; Xuehui, L.; Lejun, Z.; Ishihara, K. Biomaterials 1992, 13, 357.
15. Ishihara, K.; Tsuji, T.; Kurosaki, T.; Nakabayashi, N. J Biomed Mater Res 1994, 28, 225.
16. Ishihara, K.; Hanyuda, H.; Nakabayashi, N. Biomaterials 1995, 16, 873.
17. Ishihara, K.; Oshida, H.; Ueda, T.; Endo, Y.; Watanabe, A.; Nakabayashi, N. J Biomed Mater Res 1992, 26, 1543.
18. Brunstedt, M. R.; Ziats, N. P.; Schubert, M.; Hiltner, A.; Anderson, J. M. J Biomed Mater Res 1993, 27, 255.
19. Brunstedt, M. R.; Ziats, N. P.; Robertson, S. P.; Hiltner, A.; Anderson, J. M.; London, G. A.; Payet, C. R. J Biomed Mater Res 1993, 27, 367.
20. Brunstedt, M. R.; Ziats, N. P.; Robertson, S. P.; Stack, S.; Rose-Caprara, V.; Hiltner, A.; Anderson, J. M. J Biomed Mater Res 1993, 27, 499.
21. Yoneyama, T.; Ishihara, K.; Nakabayashi, N.; Ito, M.; Mishima, Y. J Biomed Mater Res 1998, 43, 15.
22. Ishihara, K.; Tanaka, S.; Furukawa, N.; Kurita, K.; Nakabayashi, N. J Biomed Mater Res 1996, 32, 391.
23. Yoneyama, T.; Sugihara, K.; Ishihara, K.; Iwasaki, Y.; Nakabayashi, N. Biomaterials 2002, 23, 1455.
24. Iwasaki, Y.; Aiba, Y.; Morimoto, N.; Nakabayashi, N.; Iwasaki, Y. J Biomed Mater Res 2000, 52, 701.
25. Morimoto, N.; Watanabe, A.; Iwasaki, Y.; Akiyoshi, K.; Ishihara, K.; Biomaterials 2004, 25, 5353.
26. Tan, H.; Li, J. H.; Luo, J. B.; Xie, X. Y.; Zhong, Y. P.; Fu, Q. Eur Polym J 2005, 41, 1893.
27. Sun, T. L.; Tan, H.; Han, D.; Fu, Q.; Jiang, L. Small 2005, 1, 959.
28. Tan, H.; Li, J. H.; Guo, M.; Du, R. N.; Xie, X. Y.; Zhong, Y. P.; Fu, Q. Polymer 2005, 46, 7230.
29. Tan, H.; Sun, T. L.; Li, J. H.; Guo, M.; Xie, X. Y.; Zhong, Y. P.; Fu, Q.; Jiang, L. Macromol Rapid Commun 2005, 26, 1418.
30. Tan, H.; Xie, X. Y.; Li, J. H.; Zhong, Y. P.; Fu, Q. Polymer 2004, 45, 1495.
31. Tingey, K. G.; Andrade, J. D. Langmuir 1991, 7, 2471.
32. Hiemenz, P. C.; Rajagopalan, R. Principles of Colloid and Surface Chemistry, 3rd ed. Mercel Dekker: New York, 1997.
33. Yoon, S. C.; Ratner, B. D. Macromolecules 1988, 21, 2392.
34. Yoon, S. C.; Ratner, B. D. Macromolecules 1988, 21, 2401.
35. Turi, E. A. Thermal Characterization of Polymeric Materials; Academic Press: San Diego, 1981; p 132