Surface characterization and platelet adhesion studies of aliphatic polyurethanes grafted by fluorocarbon oligomers: effect of fluorocarbon chain length and carboxylic acid group

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The surfaces of aliphatic polyurethane films, which were synthesized by 1,6 hexamethylene diisocyanate, poly(tetramethylene glycol) and 1,4 butanediol, were modified by grafting different chain length of fluorocarbon oligomers. The fluorocarbon oligomers on polyurethane surfaces were terminated with trifluorocarbon or carboxylic acid functionality. The alkyl groups were also grafted onto polyurethane surfaces for comparison. The surface characterization and platelet-contacting property were studied using electron spectroscopy for chemical analysis (ESCA), static contact angle analysis and *in vitro* platelet adhesion experiments. The effects of fluorocarbon oligomers and their terminal functionalities are discussed. The ESCA results demonstrate the fluorocarbon enrichment at the outmost layer in fluorocarbon oligomer grafted polyurethanes. The fluorocarbon content at the surface increases with increasing the chain length of fluorocarbon oligomers. The fluorocarbon oligomer grafted polyurethanes exhibit highly hydrophobic surfaces, while alkyl groups grafted polyurethanes show relatively hydrophobic surfaces compared with the untreated polyurethane. The *in vitro* platelet adhesion experiments indicated that the fluorocarbon oligomer and carboxylic acid functionality significantly reduced the number and the degree of activation of the adherent platelets.

1. Introduction

Polyurethanes have been used for various blood-contacting applications because of their excellent blood compatibility and physical properties [1]. To date, most of the commercial biomedical-grade polyurethanes like Biomer® and Pellethane® are composed of 4,4′-methylene diphenyl diisocyanate (MDI) moiety and belong to aromatic polyurethanes, which might be decomposed to 4,4′-diamino diphenylmethane (MDA); a toxic, carcinogenic, and mutagenic substance [2]. However, aliphatic polyurethanes were shown not to degrade to form carcinogenic by-products, such as MDA [2].

Commercially available biomedical-grade polyurethane still seems not quite appropriate for use in high demanding blood-contacting applications such as small diameter vascular grafts and the artificial heart. Rapid thrombus formation was noticed on the small diameter catheters (i.e. ID < 5 or 7 mm). Numerous techniques have been used to improve blood compatibility of polyurethanes, including bulk [3–7] or surface [8–12] modification. The surface modification has many advantages in application. It modifies only the surface characteristics without changing the bulk properties of the substrates.

Fluorocarbon chains have exhibited many interesting properties, including low interfacial free energy, good water and oil repellent. They were also found to be relatively blood compatible. Some researchers introduced fluorocarbon chains into polyurethanes by surface or bulk modification for biomedical applications. Bulk modification can be attainted by the incorporation of fluorocarbon chains into polyurethanes via fluoro-containing diisocyanate, chain extender, or soft segment. Kashiwagi *et al.* [13] synthesized polyurethanes containing fluoroalkyl groups in the side chains of hard segments and showed that the *in vitro* thrombus formation was reduced as fluoroalkyl content increased. Tonelli *et al.* [14] showed that fluorinated polyurethanes with different fluorine content were not thrombogenic, and not cytotoxic. Takakura *et al.* [15] synthesized a series of fluorinated poly(urethane-urea)s via fluorine-

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containing diisocyanate, polyether and chain extender to produce high performance antithrombus elastomers. Surface immobilization or derivation of fluorocarbon chains has been attempted by various approaches. For instances, Kim *et al*. [16, 17] modified polyurethane surface by grafting of perfluoroalkyl chains and reported an enhanced blood compatibility of perfluoroalkyl chains grafted polyurethane. Ukpabi *et al*. [18] used different perfluoroalkyl agents to modify the surfaces of polyurethane membranes intended for use in surgical gowns. Santerre *et al*. [19, 20] mixed fluorine-containing polyurethanes, as surface-modifying macromolecules, with base polyurethanes to alter the surface chemistry of the base polyurethanes, thereby altering their biostability and/or biocompatibility.

On the other hand, many investigators [4–6] have incorporated the negatively charged groups into polyurethanes for improvement of blood compatibility. In our previous studies [21, 22], the incorporation of ionic groups into polyurethanes, especially for the carboxylate groups, significantly reduced platelet deposition and activation. However, the ionic polyurethanes exhibited high water uptake, which would result in a large loss of tensile properties [23]. Thereby, the introduction of ionic groups onto the surfaces of polyurethanes by surface modification would be given much attention.

To date, most investigators have focused on improving the biocompatibility of polyurethanes derived from aromatic diisocyanate. However, only a few investigators have studied how to improve aliphatic polyurethanes. In this study, the surfaces of aliphatic polyurethane films were modified by grafting of different chain length of fluorocarbon oligomers. The alkyl groups were also grafted onto polyurethane surfaces for comparison. The fluorocarbon oligomers or alkyl groups terminated with dicarboxylic acid groups were grafted onto polyurethane surfaces to evaluate the effect of carboxylic acid groups. Surface characterization using electron spectroscopy for chemical analysis and static contact angle analysis was performed. *In vitro* platelet adhesion experiments were conducted to evaluate the preliminary blood compatibility of these aliphatic polyurethanes.

2. Materials and methods

2.1. Materials

A hydroxyl-terminated polytetramethyl oxide of molecular weight 1000 (PTMO; Aldrich) was dehydrated under vacuum at 60 °C for 48 h before use. Hexamethylene diisocyanate (HDI; Aldrich) and stannous octoate (Sigma) were used as received. 1,4-butanediol (BD; Jassen) was vacuum distilled and then dried over 4 Å molecular sieves. Dimethylacetamide (DMAc; Tedia) and toluene (Tedia) were dehydrated over calcium hydride (Lancaster) for two days and then stripped. Anhydrous ether (Tedia) and acetone (Tedia) was dried over 4 Å molecular sieves. Heptadecafluorononanoic acid (HDFNAC; Acros), perfluorotetradecanoic acid (PFTDAC; Lancaster), perfluorosebacic acid (PFSAC; Acros), nonanoic acid (NAC; Acros), and sebacic acid (SAC; Acros) were dehydrated under vacuum at 40 °C for 24 h before use.

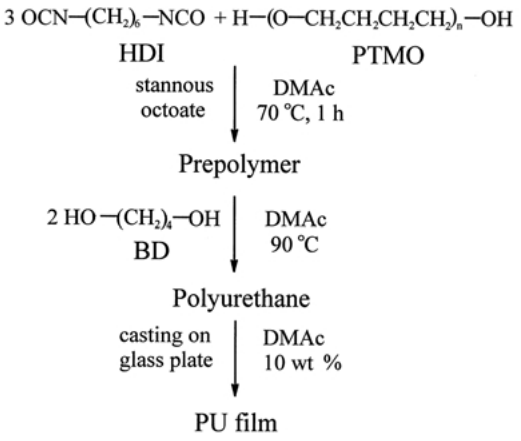


Figure 1 Synthetic scheme for the preparation of polyurethane film.

2.2. Preparation of polyurethane film

Polyurethane based on HDI, PTMO and BD was synthesized in a 3/1/2 molar ratio using a standard two-step solution polymerization in DMAc described in Fig. 1. It was carried out as follows. HDI was dissolved in DMAc in a four-neck flask under a nitrogen atmosphere and PTMO/DMAc solution containing 0.5 wt % stannous octoate as catalyst was added dropwise at 60 °C. After PTMO solution was added, the temperature was raised to 70 °C and kept there for 1 h. In the second step, BD/DMAc solution was added drop by drop and reacted at 90 °C. The total solid content was 15 wt/vol %. Reaction completion was monitored by the absence of free NCO group absorption at 2270 cm^{-1} by Fourier transfer infrared spectra. Polyurethanes obtained were precipitated in deionized water, washed thoroughly with methanol, and then dried in a vacuum oven at 60 °C for one week.

Polyurethane film was prepared by casting from 10 wt % DMAc solution onto glass plate, drying at 60 °C for 48 h, followed by further drying in a vacuum oven at 60 °C for 72 h to remove any residual solvent. The dimensions of polyurethane film are 2 cm × 6 cm × 0.3 mm.

Elemental analysis: Calculated C 61.68, H 9.92, N 4.99%; found C 61.64, H 9.91, N 5.08%. Gel permeation chromatography in dimethylforamide shows that the number-average molecular weight and polydispersity is 8.5×10^4 and 2.53, respectively. The molecular weight is based on the polystyrene standards, and thus it is estimated.

2.3. Surface modification polyurethane film

The surface modifications were carried out following literature procedure [16–18]. The synthetic scheme for the surface modification of polyurethane films was described in Fig. 2. Polyurethane film was kept in 120 ml toluene followed by the addition of 8 g HDI, 0.5 g stannous octoate and 30 ml toluene. After reacting at 40 °C for 1 h under a nitrogen atmosphere, the film was washed with toluene (3 × 20 ml) and then anhydrous ether (3 × 20 ml) to produce PU-HDI. Subsequently, PU-HDI film was immersed in 40 ml toluene followed by the addition of 40 ml acetone, 0.5 g stannous octoate and

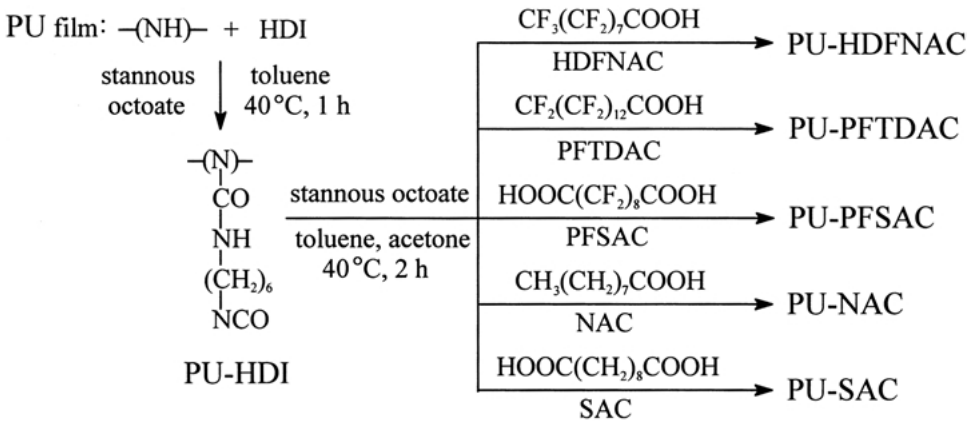


Figure 2 Synthetic scheme for the surface modification of polyurethane films.

1×10^{-3} HDFNAC, PFTDAC, PFSAC, NAC, or SAC. After reacting at 40 °C for 2 h under a nitrogen atmosphere, the film was washed with toluene (3×20 ml) and then acetone (3×20 ml) to obtain PU-X, in which X represents the kind of oligomer used. The PU-X film was washed with deionized water over night and then dried in a vacuum oven at 60 °C for 24 h.

2.4. Surface characterization

Electron spectroscopy for chemical analysis (ESCA) measurements were obtained on a VG Escalab 210 instrument using monochromatic MgK_{α} radiation. The angle between the sample surface and the photoelectron detector was 45°, which corresponded to an effective sampling depth of around 50 Å. Survey scans (0–1000 eV binding energy range) were used to identify the surface elemental compositions of polyurethane film. High-resolution scans (10 eV wide) of C1s were obtained to provide the chemical bonding details of carbon. The C1s of hydrocarbon was taken at 285.0 eV as an internal reference. Deconvolution of C1s was performed by using the Gaussian peak shapes.

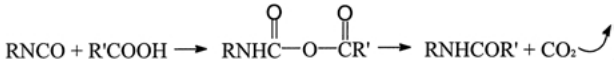
The surface hydrophilicity was determined by the static contact angle measurement performed on a Face CA-A device. A drop of deionized water was introduced onto the sample surface by a microliter syringe. Ten different points of each film were performed to calculate the mean static contact angle and its standard deviation.

2.5. Platelet adhesion experiments

Human platelet concentrate obtained from Taiwan Blood Donation Center was used to assess the blood compatibility of various polyurethane films. Human platelet concentrate was prepared by Taiwan Blood Donation Center as follows. Human blood (250 ml) was collected from a healthy donor, and 35 ml of citrate phosphate dextrose adenine solution (CPD-A1), in which citric acid (3.27 g), sodium hydrogenphosphate (2.22 g), di-sodium citrate (26.3 g), adenine (0.275 g), and dextrose (29 g) were dissolved in distilled water (1000 ml), was added as anticoagulant. The solution was centrifuged at 2350 rpm for 6 min and 4300 rpm for 6 min to obtain human platelet concentrate. The platelet concentration of human platelet concentrate was about 8.0×10^8 platelets/ml. Polyurethane films were cut into 5 mm × 5 mm square samples, suck onto aluminum plate, and equilibrated in the Hepes-Tyrodes buffer solution (pH 7.3) at 4 °C for 24 h. After removing the buffer solution, the samples were immersed in human platelet concentrate and incubated at 37 °C at 5% CO_2 atmosphere for 1 h to carry out platelet adhesion experiments. At the end of incubation, the samples were rinsed with Hepes-Tyrodes buffer solution with gentle shake several times to wash out the nonattached platelets. The adhered platelets were then fixed with 2 vol% glutaraldehyde (Fisher) in a Hepes solution at room temperature. After 1 h, the samples were flushed with deionized water several times to remove glutaraldehyde solution. The samples were then immersed in liquid nitrogen for 1 min, and subsequently dehydrated by freeze-drying them for 16 h under vacuum at −3 °C. The dried samples were immediately sputter-coated with gold for further scanning electron microscopy (SEM) examination. The morphology of adhered platelets was determined with a Hitachi S-2500 SEM operating at an accelerating voltage of 25 kV. The number of adhered platelets per 7200 μm^2 was also counted by SEM. More than 10 different sites were randomly chosen and averaged. Five measurements of the same sample were repeated with human platelet concentrate obtained from different donors to calculate the mean platelet density on the surface and its standard deviation. Statistical analysis comparing the platelet deposition between materials was performed using Student's *t*-test.

3. Results and discussion

In this study, polyurethane film surface was treated with excess HDI to introduce free isocyanate groups onto a polyurethane surface by allophanate reaction of urethane NH groups with isocyanate moiety [24]. Further, these pendent isocyanate groups could be utilized to graft fluorocarbon oligomers or alkyl groups onto polyurethane surface. In the presence of a suitable catalyst, the free diisocyanate moiety can react with an carboxylic acid group of modifier to form anhydride compound which will further decompose into amide and carbon dioxide at normal temperature [25], as expressed in the following reaction scheme,



For the reaction of the difunctional modifier (PFSAC and SAC) with PU-HDI, both functional groups might be reacted to form crosslinking or one of the difunctional groups was reacted to give one free function group. However, the material obtained remained soluble in DMAc indicating that either no or every little crosslinking occurred.

3.1. Electron spectroscopy for chemical analysis

Since blood directly contacts with the material surface, the surface chemical compositions of material is very important for its blood compatibility. In this study, polyurethane films were rinsed with deionized water and then dried in a vacuum oven at 60 °C for 24 h before ESCA analysis to avoid dust pollution. Table I shows ESCA results for the surface atomic percentage of the polyurethane films studied. Due to the reaction of isocyanate group with water to yield amine group during the rinse process, the surface of PU-HDI has the obviously higher nitrogen content and lower oxygen content than PU. As expected, the presence of fluorine atoms for fluorocarbon oligomers grafted polyurethane surfaces is observed. Furthermore, PU-PFDTAC, PU-HDFNAC and PU-PFSAC have high fluorine content at the surfaces. This result indicates that the surfaces of fluorocarbon oligomer grafted films are considerably covered with fluorocarbon chains. Moreover, PU-PFDTAC has higher fluorine content at the surface than PU-HDFNAC and PU-PFSAC, indicating that the fluoro content at the surface increases with increasing the chain length of fluorocarbon oligomers.

Fig. 3 shows high-resolution C1s spectra for various polyurethane film surfaces. Table II lists the results of the deconvolution of C1s. The C1s spectra of PU and PU-HDI were resolved into three subpeaks centered around 285, 286.5, and 289 eV, representing unsubstituted hydrocarbon (C–C and C–H), ethereal carbon (C–O), and carbonyl carbon (C=O), respectively. The surface of PU-HDI has a higher fraction of C=O and C–C, and a lower fraction of C–O than PU. C–O mainly originates from the PTMO soft segment. Therefore, the surface C–O content decreases after HDI was grafted onto polyurethane surface. The higher C=O is attributed to the allophanate reaction of urethane NH groups with isocyanate moiety. These results confirm the grafting of HDI onto polyurethane surface.

For PU-HDFNAC and PU-PFTDAC, there are further two subpeaks in addition to C–C, C–O, and C=O. These two subspeaks are attributed to the carbon bonded to two fluorine atoms (CF_2; 291.9 eV) and three fluorine atoms (CF_3; 294.1 eV). In the case of PU-PFSAC, the terminal group of fluorocarbon oligomer is COOH instead of CF_3, which results in only CF_2 present on the surface. As shown in Table II, after the grafting of fluorocarbon oligomers onto PU-HDI, the C–C and C–O content drastically decrease, especially where the decrement is extended with increasing the chain length of fluorocarbon oligomers, i.e. PU-PFTDAC. In addition, PU-PFDTAC has more CF_2 present at the surface than PU-HDFNAC and PU-PFSAC. This indicates that the fluorocarbon content at the surface increases with increasing the chain length of fluorocarbon oligomers. Moreover, PU-PFSAC has the obviously higher C–O content and slightly higher C=O content than PU-HDFNAC and PU-PFTDAC, indicating one of the difunctional groups, COOH, present on the PU-PFSAC surface.

As shown in Fig. 3 and Table II, after the introduction of alkyl groups onto PU-HDI surface to yield PU-NAC and PU-SAC, the relative content ascribed to the hydrocarbon increases and C–O content decreases. Especially for PU-NAC, the C–O fraction completely disappeared. This indicates that the surfaces of PU-NAC and PU-SAC are covered with alkyl groups. In addition, the existence of C–O groups for PU-SAC compared with PU-NAC confirms COOH group present on PU-SAC surface.

3.2. Contact angle analysis

The surface hydrophilicity of material is another important factor for its blood compatibility. Table III lists the static contact angle values of various polyurethane film surfaces. The smaller the contact angle is, the more hydrophilic the film surface. Obviously, the surface hydrophilicity of polyurethane films is closely related to the surface chemical compositions. Therefore, fluorocarbon oligomers grafted polyurethanes have the most hydrophobic surfaces, while alky groups grafted polyurethanes have relatively hydrophobic surfaces compared with PU. Since PU-HDI terminated with more hydrophilic groups (i.e. NH_2), PU-HDI is slightly hydrophilic than PU. As expected, among all the fluorocarbon oligomers grafted surfaces, polyurethane terminated with longer fluorocarbon chains, PU-PFTDAC, has the highest contact angle (110.4°), PU-

TABLE I Surface atomic percentage of various polyurethane films

Material	C1s (At %)	O1s (At %)	N1s (At %)	F1s (At %)	Si2p (At %)
PU	68.0	23.7	4.1		4.2
PU-HDI	68.2	14.7	15.5		1.6
PU-HDFNAC	40.0	17.1	2.6	38.2	2.1
PU-PFTDAC	30.3	14.7	1.5	51.3	2.2
PU-PFSAC	41.4	16.3	3.6	36.1	2.6
PU-NAC	75.6	14.6	5.6		4.2
PU-SAC	71.8	21.0	4.1		3.1

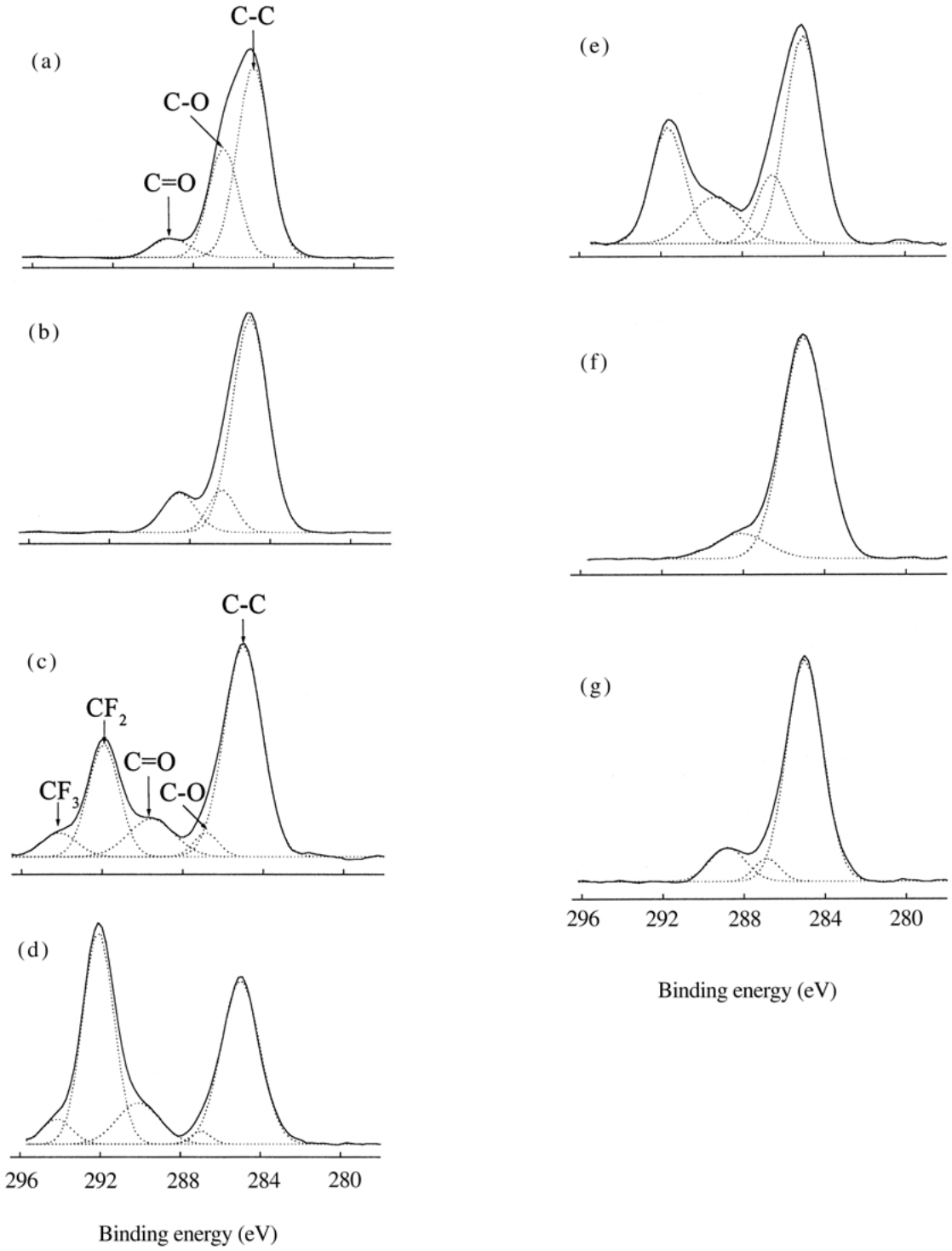


Figure 3 ESCA C1s high-resolution spectra of various polyurethane film surfaces: (a) PU; (b) PU-HDI; (c) PU-HDFNAC; (d) PU-PFTDAC; (e) PU-PFSAC; (f) PU-NAC; (g) PU-SAC.

TABLE II Peak area percentage of the C1s spectra of various polyurethane film surfaces

Material	C–C (%)	C–O (%)	C=O (%)	CF_2 (%)	CF_3 (%)
PU	61.2	32.0	6.8		
PU-HDI	75.8	11.2	13.0		
PU-HDFNAC	54.9	3.9	11.7	23.9	5.6
PU-PFTDAC	40.2	1.6	11.2	42.2	4.8
PU-PFSAC	47.3	13.5	14.1	25.1	
PU-NAC	88.0		12.0		
PU-SAC	82.0	5.8	12.2		

TABLE III Static contact angle values of various polyurethane film surfaces

Material	Contact angle ± s.d.
PU	75.5 ± 2.5
PU-HDI	70.9 ± 4.6
PU-HDFNAC	107.2 ± 3.5
PU-PFTDAC	110.4 ± 2.9
PU-PFSAC	102.6 ± 3.6
PU-NAC	85.3 ± 1.4
PU-SAC	80.9 ± 1.8

HDFNAC has the next (107.2°), and hydrophilic COOH terminated polyurethane, PU-PFSAC, has the smallest contact angle (102.6°). However, there is no marked difference in contact angles among the fluorocarbon oligomers grafted surfaces, irrespectively of fluoroalkyl chain length or type of terminal functionalities. This might be ascribed to the highly hydrophobic fluorocarbon chains enrichment at the outmost layer in fluorocarbon oligomer grafted polyurethanes, as indicated in the above ESCA analysis. For alkyl groups grafted surfaces, hydrophilic COOH terminated polyurethane, PU-SAC, has slightly smaller contact angle (80.9°) than hydrophobic CH_3 terminated polyurethane, PU-NAC (85.3°).

3.3. *In vitro* platelet adhesion studies

Platelet adhesion and activation, which may lead to thrombus formation, will occur as blood makes contact with the material surfaces. In this study, *in vitro* platelet adhesion experiments were used to evaluate the preliminary blood compatibility of various polyurethane films. Fig. 4 shows scanning electron micrographs of various polyurethane film surfaces after 60 min of human platelet concentrate exposure. The number of adhered platelets on various polyurethane film surfaces is indicated in Table IV.

On PU and PU-HDI surfaces, many of the adhered platelets were partially activated or fully spread. Moreover, some platelets aggregated to form thrombi on these surfaces. It seems that there was no obvious differences in platelet adhesion between these two films. Because it is impossible to accurately count the number

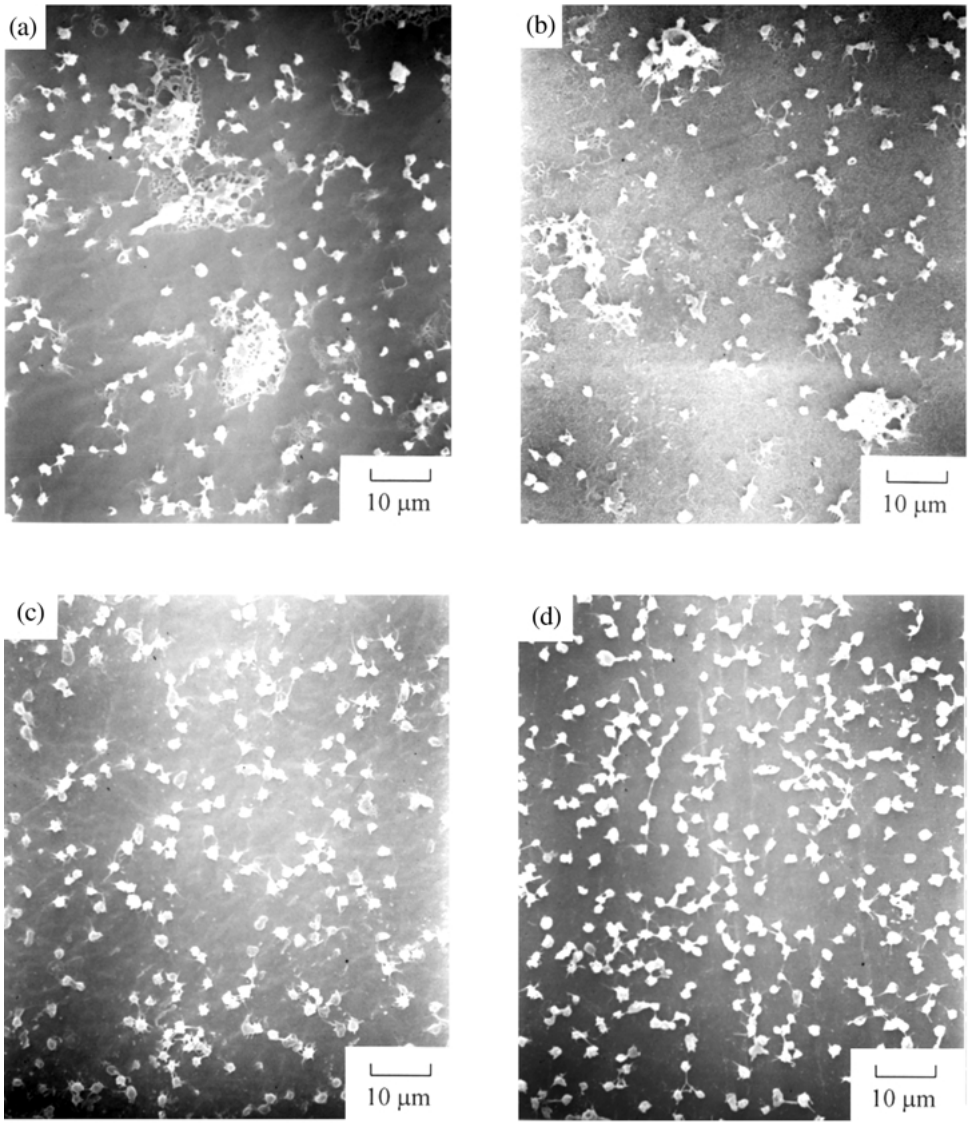


Figure 4 SEM photographs after 60 min of platelet adhesion for (a) PU; (b) PU-HDI; (c) PU-HDFNAC; (d) PU-PFTDAC; (e) PU-PFSAC; (f) PU-NAC; (g) PU-SAC.

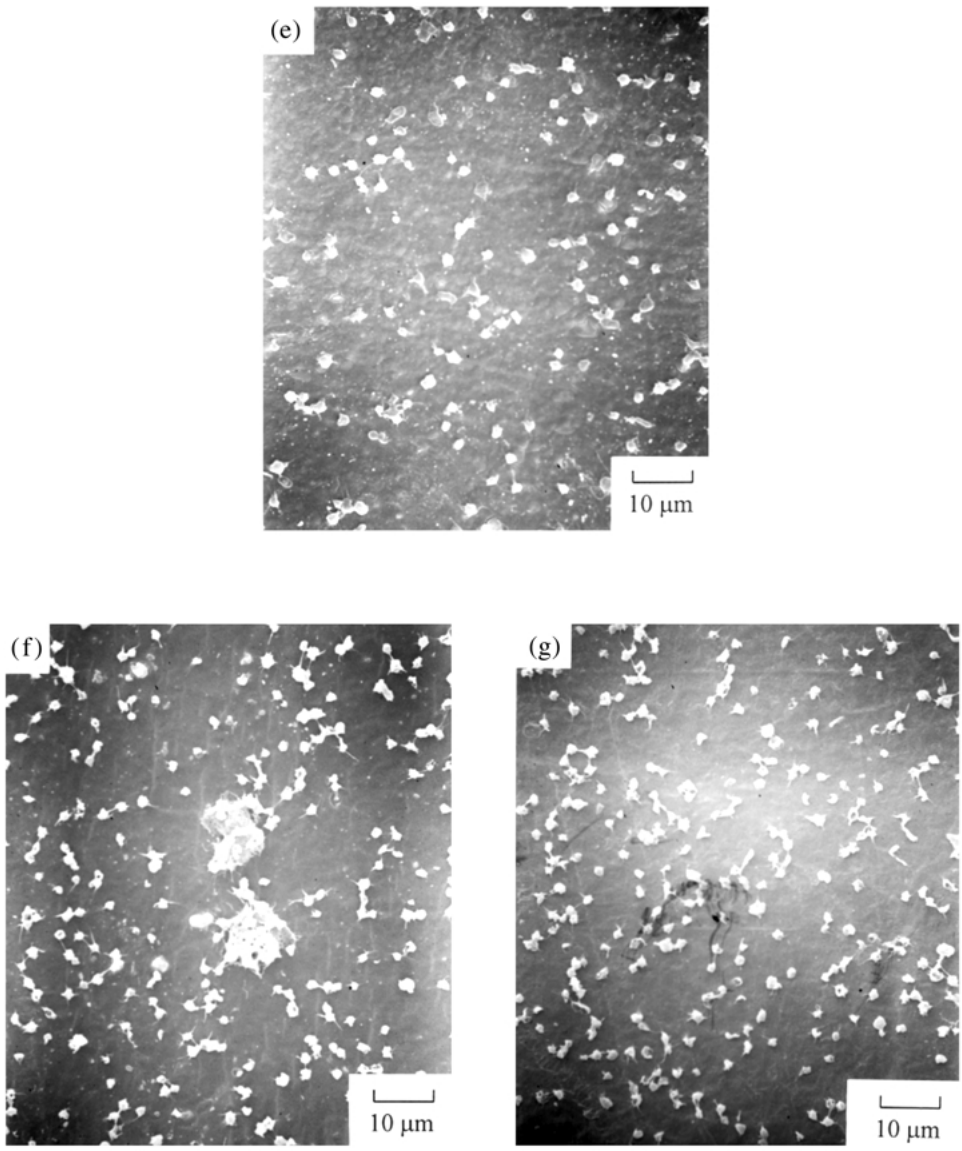


Figure 4 (Continued)

of platelets in the thrombi, the number of adhered platelets on these surfaces was not counted.

As shown in Fig. 4, fluorocarbon oligomers grafted polyurethanes are less thrombogenic than PU and PU-HDI. All adherent platelets on PU-HDFNAC, PU-PFTDAC and PU-PFSAC surfaces exhibited pseudopodial formation but without any aggregation to form thrombi. This result is consistent with the blood compatibility evaluations by Kim *et al*. [16], in which polyurethane surface was modified by grafting of perfluoroalkyl chains. They have noticed that perfluoroalkyl chains grafted polyurethane exhibited less adhesion and shape change of platelets than untreated polyurethane due to the unique effect of grafted perfluoroalkyl chains. Kashiwagi *et al*. [13] showed that the introduction of fluoroalkyl groups into polyurethanes significantly reduced the number of adhered platelets.

TABLE IV Number of adhered platelets on various polyurethane film surfaces

Material	No. of adhered platelets (per 1000 μm^2)
PU-HDFNAC	39.8 ± 3.6
PU-PFTDAC	41.5 ± 4.7
PU-PFSAC	25.2 ± 4.3
PU-SAC	43.9 ± 4.1

The platelet adherent density on fluorocarbon oligomers grafted polyurethane surfaces increased in the following order:

PU-PFSAC (25.2 ± 4.3 platelets/1000 μm^2) $<$
PU-HDFNAC (39.8 ± 3.6 platelets/1000 μm^2) $\approx$
PU-PFTDAC (41.5 ± 4.7 platelets/1000 μm^2).

PU-HDFNAC showed a similar platelet adherent density to PU-PFTDAC, irrespectively of fluorocarbon content at the surface. This indicates that the introduction of fluorocarbon chains onto polyurethane surface can effectively reduce the number and the degree of activation of the adherent platelets, however, the increase of fluorocarbon content at the surface does not further enhance the effect. In contrast, a lower number of adhered platelets on the PU-PFSAC surface than on PU-HDFNAC and PU-PFTDAC surfaces was noticed ($P < 0.005$). Moreover, most of the adherent platelets on PU-PFSAC surface retained discoid shape with short

pseudopods, while further pseudopod extension was observed on PU-HDFNAC and PU-PFTDAC surfaces. These results might be ascribed to the COOH group on the PU-PFSAC surface, which reduced the degree of platelet adhesion and platelet activation on the polyurethane surface. A number of investigators [26–29] incorporated the carboxylic acid or carboxylate groups into polymers to improve their blood compatibility. Lee *et al*. [29] found that carboxylic acid-containing polyethylene showed a low amount of platelet adhesion, probably due to the negative-charge character of carboxylic acid groups. In our previous studies [21, 22], the incorporation of carboxylate groups into polyurethanes significantly reduced platelet deposition and activation for *in vitro* platelet adhesion experiments, in which the carboxylate groups played a decisive role in platelet adhesion due to electrostatic interaction between the carboxylate groups and platelet membrane.

For the alky groups grafted polyurethanes, PU-NAC surface showed a similar platelets deposition profile to PU and PU-HDI. Some of the adhered platelets were activated, spread and aggregated to form three dimension thrombi on PU-NAC surface. In contrast, for the alky groups grafted polyurethane surface with COOH terminal functionality, PU-SAC, the adhered platelets did not aggregated to form thrombi. Henceforth, carboxylic acid functionality could improve the platelet compatibility of polyurethane film. Compared the platelet adherent density of PU-SAC $(43.9 \pm 4.1 \text{ platelets}/1000\,\mu\text{m}^2)$ with that of PU-HDFNAC and PU-PFTDAC, there is no difference in platelet adhesion density among these surfaces. This indicates that both fluorocarbon oligomer and carboxylic acid functionality have a similar effect on improving the platelet reactivity of polyurethanes. Furthermore, PU-PFSAC has an obviously lower platelet adherent density than PU-SAC ($P < 0.005$). The surface of PU-PFSAC contains both fluorocarbon oligomer and carboxylic acid functionality. Therefore, fluorocarbon oligomer and carboxylic acid functionality might have a synergistic effect to reduce the number and the degree of activation of the adherent platelets.

4. Conclusions

In this study, fluorocarbon oligomers were grafted onto aliphatic polyurethanes to improve their blood compatibility. ESCA analysis has shown that the surfaces of fluorocarbon oligomers grafted polyurethanes are considerably covered with fluorocarbon chains. Moreover, the amount of fluorocarbon chains at the surface increases with increasing the chain length of fluorocarbon oligomers. In addition, ESCA analysis has demonstrated that the surfaces of alkyl groups grafted polyurethanes are covered with alkyl groups.

Contact angle analysis reveals that the surface hydrophilicity increases in the following order: fluorocarbon oligomers grafted polyurethanes < alky groups grafted polyurethanes < untreated polyurethane. Furthermore, carboxylic acid-containing polyurethane surfaces are slightly hydrophilic than the non-carboxylic acid-containing counterparts.

In vitro platelet test has exhibited fluorocarbon oligomers can improve the platelet compatibility of polyurethanes. However, the increase of length of fluorocarbon oligomers, i.e. the increase of fluorocarbon content at the surface, does not further improve platelet compatibility. In contrast, carboxylic acid functionality terminated polyurethanes can further reduce the number and the degree of activation of the adherent platelets on the fluorocarbon oligomers grafted polyurethanes. Hence, carboxylic acid functionality and fluorocarbon oligomers might have a synergistic effect on improvement of the platelet compatibility of the aliphatic polyurethanes.

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