The Surface Modification of Medical Polyurethane to Improve the Hydrophilicity and Lubricity: The Effect of Pretreatment

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Received 20 May 2009; accepted 25 September 2009
DOI 10.1002/app.31499
Published online 23 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The medical polyurethane (PU) film was grafted with poly(acrylic acid) (PAA) to improve the hydrophilic and lubricious properties. The influences of pretreatment by ozone or potassium peroxydisulfate on themorphologies of PU films and grafting results were systematically investigated. The grafted PU films were characterized using attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM) and gel permeation chromatography (GPC). The hydrophilic and lubricious properties were evaluated by water contact angle and friction coefficient, respectively. The results showed that PAA could be grafted firmly on PU activated by both ozone and potassium peroxydisulfate, and the PAA-grafted PU showed good hydrophilic and lubricious performance. More importantly, the PAA-grafted PU films with the pretreatment of ozone were better in surface roughness, hydrophilicty and lubricity, compared to those with the pretreatment of potassium peroxydisulfate. Hence, surface ozonation could be a better choice for the pretreatment of medical polymer. J Appl Polym Sci 116: 1284–1290, 2010

Key words: modification; polyurethane; surface; hydrophilicity; friction coefficient

INTRODUCTION

Surface modification plays an important role in medical materials because the designed surface of biomaterials is able to control the interaction between a living system and an implanted materials.[1,2] Surface properties of polymeric biomaterials determine their biocompatibility.[3,4] For example, high hydrophilicity and good lubricity are the essential characters for catheter and other medical devices used in blood vessels, body conduits, and guide wire. In general, enhancing surface hydrophilicity is an efficient way to improve biocompatibility and antibacterial property; therefore surface property is one of the most important parameters in the design of biomaterials or implant devices.[5] Moreover, the good lubricity could reduce the damage to blood vessels and tissues due to reduce frictional force during inserting or removing of the device, and make a patient more comfortable.[6]

There are various approaches that were adopted to modify biomaterial surfaces to improve the hydrophlicity and lubricity, such as chemical modification,[7,8] ozone induced grafting technology,[9,10] self-assembled monolayers,[11] plasma deposition,[12] gamma radiation, and ultraviolet (UV) light. Some methods, such as plasma and UV light etc., would introduce specific functional groups which cannot be attained by conventional method, but also lead to complex reaction and uncontrolled surface chemistry. Other methods, such as self-assembly technology, generally need high demand for serious reaction condition and substrate. Comprehensively considering all the points, ozone oxidation could not only introduce uniform peroxides, but also process the inner wall of medical catheter with a small-diameter.

Among the polymers materials, polyurethanes (PU) are often chosen because of their biocompatibility and unique chemistry and processing which

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: NSFC, 60725101.
Contract grant sponsor: National Basic Research Program of China; contract grant numbers: 2006CB933206, 2006CB705602.
Contract grant sponsor: Jiangsu Planned Projects for Postdoctoral Research Funds; contract grant number: 0701027B.
Contract grant sponsor: SuZhou Dushu Lake Higher Education Town.

make them ideal for numerous medical applications, especially for those which require good blood-compatibility and excellent mechanical strength, such as vascular devices, medical coating.[13] Furthermore, PU are the most versatile construction materials that can be formulated for medical devices. However, the hemocompatibility and lubricity of PU need to be improved for more clinically applicable blood-compatible surfaces because of its hydrophobic surface.[4,14]

In this article, PU was chemically modified by acrylic acid (AA), one kind of hydrophilic vinyl monomers, through surface graft polymerization. Surface hydroxyl groups or peroxides groups are essential to the modification which could be introduced by chemical modification of potassium peroxydisulfate or ozonation. In the process, surface functional groups, surface topography, structure, and molecular weight distribution were monitored, and the effect of pretreatment on hydrophilicity and lubricity were also explored.

EXPERIMENTS

Materials

PU (Pellethane) was obtained from Dow Chemical Company, Shanghai, China. Tetrahydrofuran, potassium peroxydisulfate, ammonium cerium (IV) nitrate, nitric acid (AR, SCRC, China) were used as received. Acrylic acid (AR, SCRC, China) were used after vacuum distillation.

The pretreatment of PU films

The PU was extracted with methanol for 24 h to remove low molecular weight component. PU films were prepared by casting thin films from 10% tetrahydrofuran (THF) solutions onto round glass dishes. Solvent was removed by drying at room temperature for at least 1 week followed by 24 h drying under vacuum. The formed films were ~0.05 mm thick and were quite smooth. To get the surface hydroxyl group, PU films were dipping in a 10% (w/v) aqueous solution of potassium peroxydisulfate at 80°C for 4 h. After the reaction, films were rinsed in hot water (exchang water every one hour) for 5 h. And then films were dried in vacuum. The PU film after pretreatment of potassium peroxydisulfate was denoted as PU1. Alternatively, the peroxides groups were introduced by ozone oxidation. Ozone was generated with dried oxygen by passing through an ozone generator (Sankang Ozone, China). Both surfaces of PU films were exposed to ozone stream and to be oxidized. The oxygen flow rate is 300 L h^{-1}, and the operation condition was set at 0.2 A for 45 min. The concentration of ozone was about 20 mg L^{-1}. After the ozonization, it was degassed by purging O_2 to remove zone adsorbed in the specimen. The PU film after pretreatment of ozone was denoted as PU2.

Surface grafting of PU films

After pretreatment, poly(acrylic acid) (PAA) films were grafted by the graft polymerization of monomers AA onto PU films. The polymerization was initiated using ceric ion. The activated films were immersed immediately into a 10 wt % aqueous solutions of AA containing 0.4 M HNO_3 solution and 0.02 *M* ceric ion. The reaction was carried out at 50°C for 4 h with stirring under nitrogen atmosphere.

The grafted PU films were rinsed with hot water (80°C, exchange water every 1 hour) for at least 24 h to remove the homopolymer, subsequently were dried in vacuum at 60°C for 24 h.

Characterization

Gel permeation chromatography (GPC) was carried out in THF (flow rate of 1 mL/min.) on a HLC802UR GPC instrument with G4000H8 + G2000H8 columns. The temperature was maintained at 40°C. And molecular weight of the sample polymer was calibrated with standard poly(2-vinylpyridine) samples of ten different molecular weights ranging from 1.3×10^3 to 3.0×10^6.

Surface functional groups were measured by attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR) spectra on a FTIR spectrophotometer from Nicolet 6700, coupled with omni-ATR accessory. Thirty-two scans were collected with a resolution of 4 cm^{-1}.

Surface morphology and structures of PU and modified PU flims were characterized by SEM (LEO, 1530VP, Germany) and AFM.

A Digital Instruments (Veeco) atomic force microscope (Dimension 3100) was used to obtain images of the different surfaces in tapping mode using Si_3N_4 tip under ambient condition. Topography and phase images were collected at the same time. The scan rate is 1–2 Hz. Scan size was ranging from 5 μm to 1 μm.

To characterize wettability, the sessile drop method was used for contact angle measurements at 20 ± 1.5°C using commercial contact angle meter (Solon Tech. Shanghai, China). The diameter of droplet used for the measurement was about 2 mm. Ultra pure water droplets were placed at six different positions for one sample. Then the average value was obtained. The experimental error of the measurements was ± 1°.

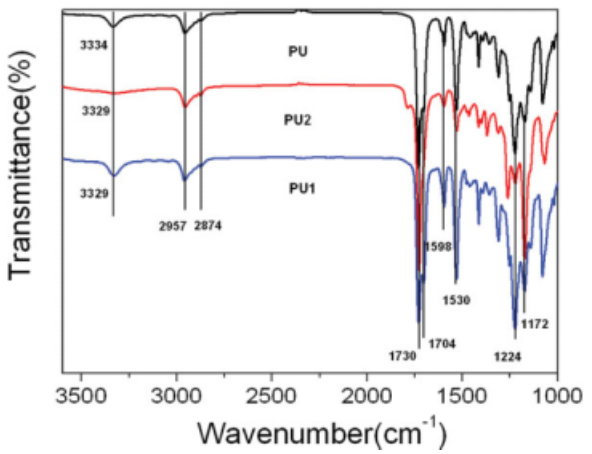

Figure 1 ATR-IR spectra of PU films and PU films after activated treatment by potassium peroxydisulfate or ozone. The PU film after pretreatment of $K_2S_2O_8$ was denoted as PU1; the PU film after pretreatment of O_3 was denoted as PU2. [Color figure can be viewed in the online issue, which is avaialable at www.interscience.wiley.com.]

The lubricity was evaluated by the kinetic friction coefficient of materials which was measured by coefficient of friction tester (DRK127, China) according to a modification of the ASTM D1894-06. In the experiment, the sled is 50 g in weight, and 2 cm × 2 cm in the size of contact section. A smooth support face for the specimen is polished stainless steal. The results were the average value from six examples.

RESULTS AND DISCUSSION

ATR-FTIR spectra

To characterize the surface alteration after grafting, we used ATR-FTIR to measure the chemical structures of PU before and after grafting. Figure 1 shows the ATR-FTIR spectra of PU and PU after activated by O_3 or $K_2S_2O_8$. To the control films, the amide and ester groups in urethane groups shows the absorption at 3335 and 1725 cm^{-1}, respectively; the absorption at 1704 cm^{-1} can be designated to the hydrogen-bond association of ester or amide groups. The absorption bands at 1596 and at 1414 cm^{-1}, from the benzene ring, and at 1530 cm^{-1} from the N—H bending and C—N stretching mode of the urethane group, were strong peak.[15] The multiplet absorption peak at 1255–957 cm^{-1} designated to C—O—C vibration mode. After ozone oxidation, a broad absorption at 3325 cm^{-1} resulted from the superposition of urethane and the peroxides groups. The absorption of the hydrogen-bond association of ester and amide groups decreased. And the absorption of hard segment at 1530 cm^{-1} and 1223 cm^{-1} was also depressed.[16] Moreover, after the PU films were treated by $K_2S_2O_8$, the absorption at 3329 cm^{-1} increased due to the contribution of hydroxyl group, as Figure 1 shown. It indicated that the surface hydrophilicity enhanced after pretreatment.

The spectra of PAA-grafted PU films are demonstrated in Figure 2. The broad and strong peak at 3300 cm^{-1} increased greatly because of abundant carboxyl group on PAA-grafted PU films, and the absorption at 1704 cm^{-1} and 1255–957 cm^{-1} slightly decreased because of the cover of PAA, as can be seen by comparison with Figure 1. Moreover, the intensity of the absorption of carboxyl group on the -PU1 was greater than that on PAA-*g*-PU2, which may be due to the homopolymerization of AA, as can be seen in SEM images. No double bond vibration absorption band of AA was found, which proved that all the monomer was polymerized. Therefore, these results indicated that PAA were grafted onto the PU films successfully.

Surface topography and structure

Surface topography and structure of grafted PU was characterized by SEM (Figs. 3 and 4) and AFM. The low resolution images of PU showed the surface was very smooth and no particular features. But the typical fine structures were found by SEM image with a high resolution in Figure 3(a). This regular structure on a scale is consistent with microphase separation, which was caused by the block copolymers containing hard and soft segments.[14,17] There were no obvious differences in surface nanostructure between PU and hydroxylated PU films as shown in Figure 3(b). When polymer is exposed to ozone gas, peroxides are formed in addition to carbonyl and carboxyl groups. After surface ozone oxidation, the topography of PU films changed, but surface fine structure could still be found, as shown in Figure 3(c). It suggested that both the oxidation capability

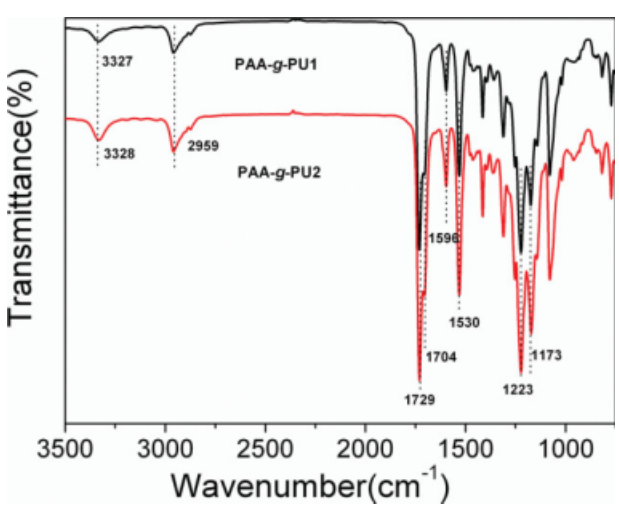

Figure 2 ATR-IR spectra of modified PU by poly(acrylic acid). [Color figure can be viewedin the online issue, which is available at www.interscience.wiley.com.]

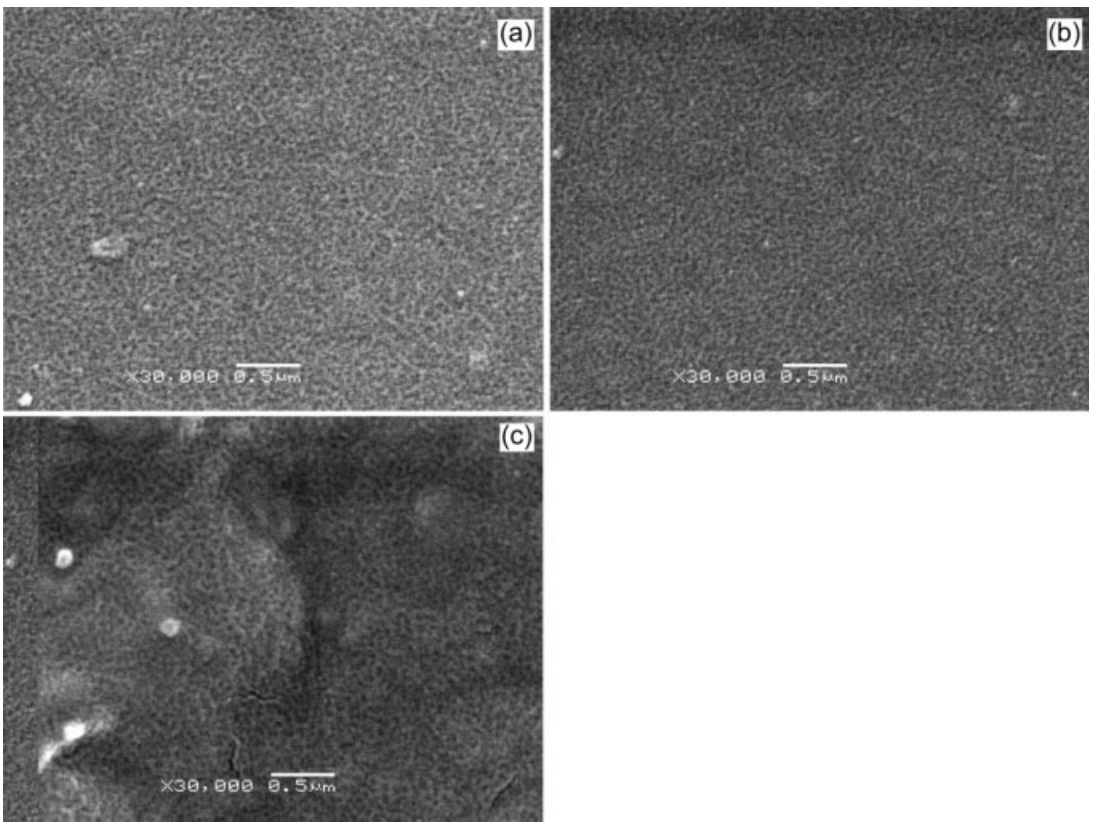

Figure 3 SEM images of PU film before and after pretreatment. (a) PU films, (b) PU1, and (c) PU2.

and the effect on topography of ozone were greater than that caused by potassium peroxydisulfate.

SEM micrographs (Fig. 4) clearly showed that the PAA-grafted PU films were rougher than PU. The PU films were covered with a layer of PAA, and the characterized structure of original PU [in Fig. 3(a)] disappeared. There were some particles on the PAA-*g*-PU1 films, which was caused by polymerization of monomers AA. Compared with PAA-*g*-PU1 films, the surface topography of PAA-*g*-PU2 films were homogeneous, and the PAA-grafted surface by ozone oxidation was smoother than that of PU1.

PU and PAA-grafted PU surface were analyzed using tapping mode AFM in air, as shown in Figure 5. The sample was generally rough at the nanometer scale. AFM images of PU showed that the surface was smoother, and the root mean square (RMS) roughness was 4.2 nm in an area of 2 μm × 2 μm. After the grafting of PAA, the surface roughness was enhanced. The RMS roughness of the PAA-*g*-PU2 films measured on an area of 2 μm × 2 μm averaged out to 12.5 nm, significantly lower than that of PAA-*g*-PU1 films. This is consistent with the results of SEM. The detail data of surface structure

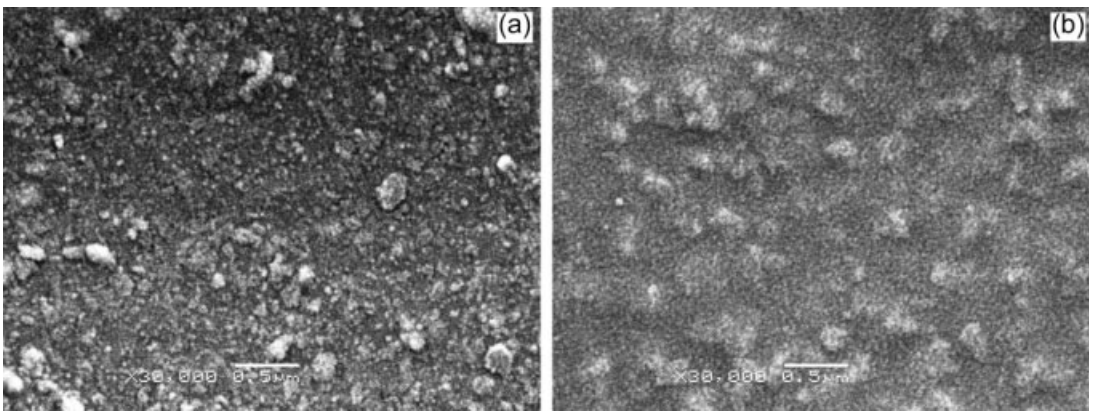

Figure 4 SEM images of PU film modified by poly(acrylic acid) (PAA) after different pretreatment. (a) PAA-*g*-PU1, (b) PAA-*g*-PU2.

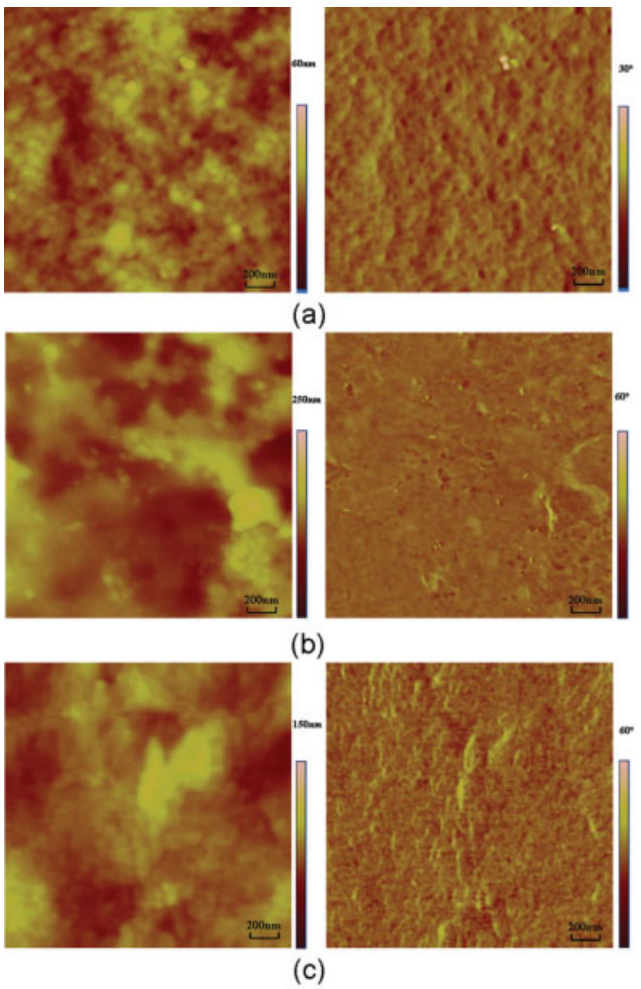

Figure 5 Topographic images (left) and corresponding phase images (right) of (a) PU, (b) PAA-*g*-PU1, and (c) PAA-*g*-PU2 films. The scan area was 2 μm × 2 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was listed in Table I. Phase imaging is a material-sensitive technique in which the distribution of material properties, such as adhesion, friction, and viscoelasticity are mapped.[18] The bright and dark areas correspond to a soft material and a hard material, respectively. The inhomogeneities on the PU surface were visible in the phase image, which was caused by microphase separation. The different structure was at a scale less than 100 nm. It is in good agreement with the SEM image. However, the PAA-grafted PU showed more homogeneous, which proved that the PU surfaces were fully covered by the PAA layer. Based on the analysis of AFM and SEM images, it showed that O_3-treatment can lead to a better grafting results than $K_2S_2O_8$-treatment under the same graft conditions, namely, the PAA-grafted PU2 films were smoother and more homogeneous than PAA-*g*-PU1 films. The GPC data in Table I demonstrated that the molecular weight decreased slightly after surface modification. It implied that surface modification has little effect on the structure of bulk phase.

Surface hydrophilicity

Water plays an important role in determining the blood-compatibility of polymer.[19] In general, the hydrophilic surface could reduce both protein adsorption or cell adhesion on polymeric surface.[20] A lower water contact angle is an indication of a more hydrophilic surface. Figure 6 shows the contact angles data of modified PU films. Bare PU exhibited an average contact angle of 92°, which means it is hydrophobic. After oxidation pretreatment, the contact angle decrease greatly. Moreover, the effect of ozonation was more significant than that of $K_2S_2O_8$. However, contact angle were further decreased due to the grafting of PAA polymer. The PAA-*g*-PU1 and PAA-*g*-PU2 film surface became more hydrophilic with an average contact angle of 32° and 25°, respectively. The variation of water contact angle as a function of time on the PAA-*g*-PU2 films was shown in Figure 6(b). The water contact angle decreased quickly in 1 minute. It demonstrated the films have a good hydrophilicity.

Compared with the UV radiation and gamma-ray radiation, ozonation and $K_2S_2O_8$ are relatively simple and inexpensive methods to uniformly modify polymers by introducing peoroxides and hydroxyl groups, respectively. According to the results of SEM, FTIR and contact angle measurements, the surface roughness, heterogeneity, and hydrophilicty of the PAA-grafted PU film pretreated by ozonation were better than those pretreated by $K_2S_2O_8$. First, the surface of the PAA-grafted polymer pretreated by ozonation was smooth, uniform. It would be benefit for the surface hydrophilicty and lubricity. Second, hydroxyl groups on PU induced by reaction were limited, and it indicated that activated sites are not

TABLE I
Surface Topographical Characteristics and Molecular Weight of the PU and PAA-grafted PU

	AFM data[a]			GPC data	
Samples	RMS roughness (nm)	AVE roughness (nm)	Surface area (μm^2)	M_w	M_w/M_n
PU	4.2	3.2	4.01	8900	0.99
PU1	6.2	4.5	4.04	8500	1.0
PU2	11.3	8.7	4.11	8800	0.99
PAA-*g*-PU1	32.0	26.3	4.29	8900	1.01
PAA-*g*-PU2	12.5	9.8	4.07	8700	1.01

[a] Measured mean values by AFM based on a minimum of three independent measurements. The scan area was 2 μm × 2 μm. RMS roughness: root mean square roughness; AVE roughness: average roughness.

enough to grafting. The limited activated sites could be one of the factors resulting in the homopolymerization and high roughness on PAA-*g*-PU1 films.

Surface lubricity

The lubricity is very important for guidewire, catheter, stent and stent-associated device, endoscopic device, and so on.[21] It was usually evaluated by the kinetic friction coefficient. The lower the friction coefficient is, the more lubricious the material is. This gives lubricious materials a smooth, slippery feel. Figure 7 shows the kinetic friction coefficient of grafted PU by PAA. The PU films show the high friction coefficient. There was oscillation when PU films moved along with hydrophilic surface. The friction coefficients of examples markedly decreased after surface modification. Moreover, the PAA-*g*-PU2 films are the most slippery and smooth, and the friction efficient was closed to 0.1. It would be related with the surface hydrophilicty and roughness.

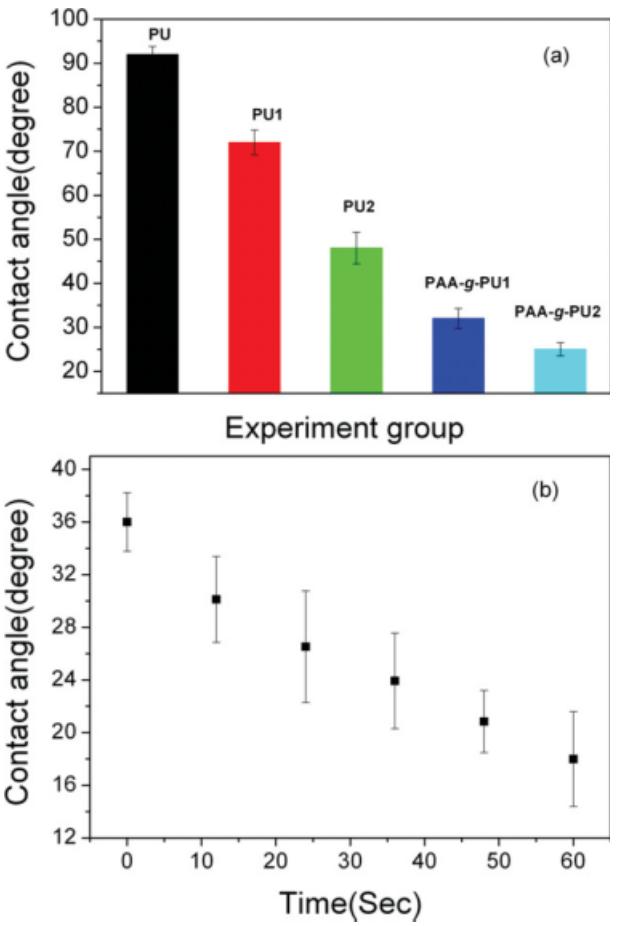

Figure 6 (a) Water contact angle of PU and grafted PU by poly(acrylic acid), (b) The effect of contact time on water contact angle of PAA-*g*-PU2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

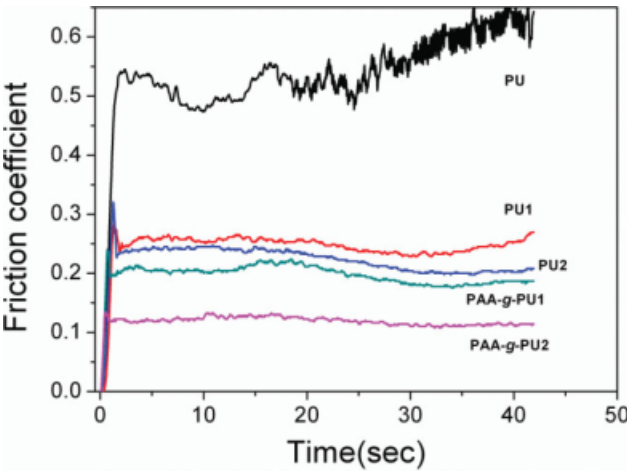

Figure 7 Friction coefficients of PU and grafted PU by poly(acrylic acid). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

PAA was successfully grafted onto medical PU treated by ozonation or potassium peroxydisulfate in advance. The effect of pretreatment on the hydrohpilicity and lubricity had been explored. It was observed that the further grafting of PAA can significantly improve the hydrophilicity of PU after the treatment by ozone.

The surface of PAA-grafted PU films by ozonation demonstrated more smooth and lubricous than those by pretreatment of potassium peroxydisulfate. The friction coefficients greatly decreased after surface modification. Moreover, the hydrophilicity and lubricity of PAA-grafted polymer surfaces depends on both surface functionality and roughness. Compared with the conventional chemical modification, surface ozonation is a better choice for surface treatment of polymer.

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