

Surface Modification of a Biomedical Poly(ester)urethane by Several Low-Powered Gas Plasmas

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ABSTRACT: Several low-powered gas plasmas were employed to treat a biomedical poly(ester)urethane using the treatment gases of CO₂, O₂, NH₃, and SO₂ with different treatment time (2, 5, 10, and 15 min). The changes of the physical and chemical characteristics of the biopolymer surface were studied. Surface morphology was evaluated by scanning probe microscopy, which showed increased roughness of the surface after plasma treatment. The wettability of the surface was examined by static water contact angle (SCA) measurements, which presented that there was a decrease of SCA in all plasma treatments compared with the untreated surface and that each gas plasma had an optimum

treatment time accompanied by a minimum contact angle. X-ray photoelectron spectroscopy indicated the changes of the surface functional groups. The data demonstrated that CO₂ and O₂ plasmas resulted in the incorporation of oxygen-containing groups, while NH₃ plasma resulted in the combination of nitrogen-containing groups, and SO₂ plasma resulted in the formation of sulfur-containing groups. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1273–1282, 2006

Key words: poly(ester)urethane; surface modification; gas plasma

INTRODUCTION

Polyurethanes (PUs) are perhaps the most versatile family of biopolymers.¹ In the past few years, they have been widely used in the biomedical areas because of their excellent physical and mechanical properties and relatively good biocompatibility.² However, some of their clinical applications have been limited partly by problems associated with surface-induced thrombosis.^{3,4}

The best protection against thrombus formation, however, is an intact endothelium.^{5,6} Therefore, a surface that can promote the formation of an endothelial layer in shorter time is favorable to decrease the surface thrombogenicity and gain better hemocompatibility.⁷ It is accepted that a biological response of the host to a biomaterial is strongly influenced by the surface properties such as roughness, ionogenicity, hydrophilicity, incorporation of functional groups, and so on.^{8–10} Based on these understandings, an increasing interest for surface modification of biomaterials has been greatly attracted recently.

PUs, with a relatively inert surface, must be carried with a surface modification process to achieve better cell-adhesion. So far, three principal techniques have

been employed for surface modification.¹¹ Firstly, a coating of adhesion-promoting molecules is simply daubed on the biomaterial surface. Examples of these molecules are gelatin, chitosan, fibronectin, or collagen, which contain cell binding domains.¹² Secondly, functional or reactive groups such as hydroxyl, amino, carboxyl, and sulfonic groups can be generated on the biopolymer surface. Thirdly, after surface activation, bioactive molecules like short oligopeptidic sequence (RGD)^{13,14} can be covalently coupled via coupling reagents on the biomaterial surface.

Plasma treatment is one of the most revolutionary techniques allowing such surface functionalization.⁹ This technique exhibits a vast spectrum of physical and chemical surface modification possibilities without altering the bulk properties of materials that affect their functions,^{15–17} since the thickness of the modified layer is typically limited to be several nanometers¹⁸ depending on plasma treatment parameters such as power, flow rate, pressure, treatment time, and gas.¹⁹ Through plasma treatment, oxygen species,^{20–22} nitrogen species,^{23,24} or more complex functional groups²⁵ can be enriched on the surfaces of materials.

In this study, the surface of a biomedical poly(ester)urethane (PEU) was modified by treatment of several low-powered gas plasmas. The surface wettability, morphology, and chemistry of this biomaterial were investigated immediately after treatment. X-ray photoelectron spectroscopy (XPS) has been used to determine changes in surface chemistry, while static water

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contact angle (SCA) measurements and scanning probe microscopy (SPM) have been utilized to investigate changes in wettability and surface roughening, respectively.

EXPERIMENTAL

Materials

The biopolymer studied was a thermoplastic medical grade aromatic poly(ester)urethane (PEU) (Estane 58,277) supplied by Noveon. The PU comprised alternate "hard" and "soft" segments of 4,4-diphenylmethyl diisocyanate (MDI) and polyester adipate (PEA), respectively, with butanediol as the chain extender.

The polymer was dissolved in 1,4-dioxane at 80°C, with a concentration of 10% (w/v) and stirred for complete dissolution and homogenization. Then the mixture was poured into a glass plate ($F = 75$ mm). The glass plate containing the solution was placed with a cover glass in a ventilative box to dry at 50°C, saturated with vapor from the solvent. After the evaporation of the solvent, a transparent film with a thickness of ~ 0.25 mm was obtained. After drying, the film was maintained under a vacuum at 30°C for 72 h to constant weight. Then the membrane was cleaned in alcohol/water (1/1, v/v) solution with a ultrasonic cleaner for 30 min to remove surface contaminants, rinsed with large amount of deionized water, and dried under reduced pressure at 30°C for 24 h to constant weight again.

Four ultrapure grade treatment gases, CO₂: 99.5%, O₂: 99.5%, NH₃: 99.9%, and SO₂: 99.5%, were used in this study.

Plasma treatment

All the plasma treatments were performed in a reaction chamber coupled with a radio-wave generator. The frequency applied was 13.56 MHz with a maximum output of 500 W. The system pressure was monitored by a vacuum gauge connected to the reactor, while the flow rate of treatment gases was measured by mass flow controller. The system pressure before discharge was typically evacuated up to 10⁰ Pa after a PEU film was placed on the holder in the reaction chamber. During treatment, the radio frequency power was fixed at 20 W, while the pressure in the plasma tube and the flow rate of treatment gases were kept constant at 50 Pa and 30 sccm, respectively. The treatment time (2, 5, 10, and 15 min) and the gas species admitted to the reactor (CO₂, O₂, NH₃, and SO₂) were the variable parameters in this research. After treatment, the sample film was left in the reactor for at least 10 min to terminate as many of residual

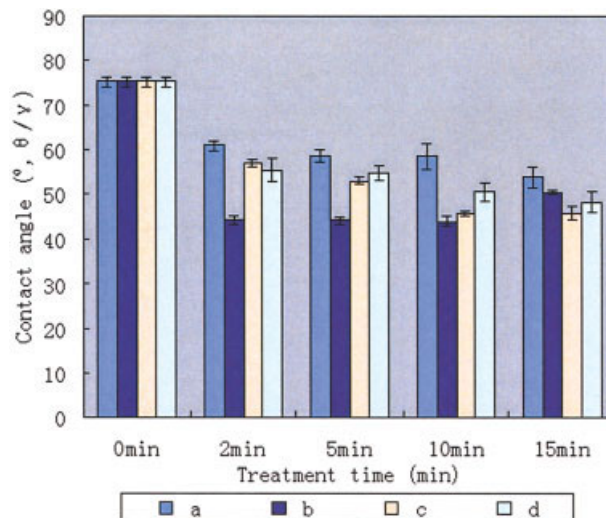


Figure 1 SCA at different treatment time for (a) CO₂ plasma treated, (b) O₂ plasma treated, (c) NH₃ plasma treated, and (d) SO₂ plasma treated PEU surfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reactions as possible prior to exposure to the atmosphere.

Scanning probe microscopy

The surface morphology of the PEU was examined on a submicro scale by scanning probe microscopy (SPM)^{26,27} to evaluate the effect of the surface modification. A HL-II Scanning Probe Microscope from Chinese Scientific Electromechanical Instruments was employed to obtain the images of the surface morphology in contact mode in air with a triangular cantilever supporting an integrated pyramidal tip of Si₃N₄. The scanning range was $16 \times 16 \mu\text{m}^2$ and all the tests were repeated over approximately three sample areas to improve the reproducibility of the results. All the data, like roughness, were evaluated by the 8 bit SPM software.

Static water contact angle

Static water contact angles (SCAs) were used to determine the hydrophilicity of the PU surface and the effect of plasma treatment on surface wettability. The contact angles were measured by depositing a drop of 0.6 μL of deionized water on the treated and untreated surfaces, using a Dataphysics OCA-15 Contact Angle System with a CCD Camera. To verify the contact angle value reproducibility, the measurement was done on five samples of each PEU film surface.

X-ray photoelectron spectroscopy

Detailed characterization of the untreated and modified surfaces was carried out using X-ray photoelec-

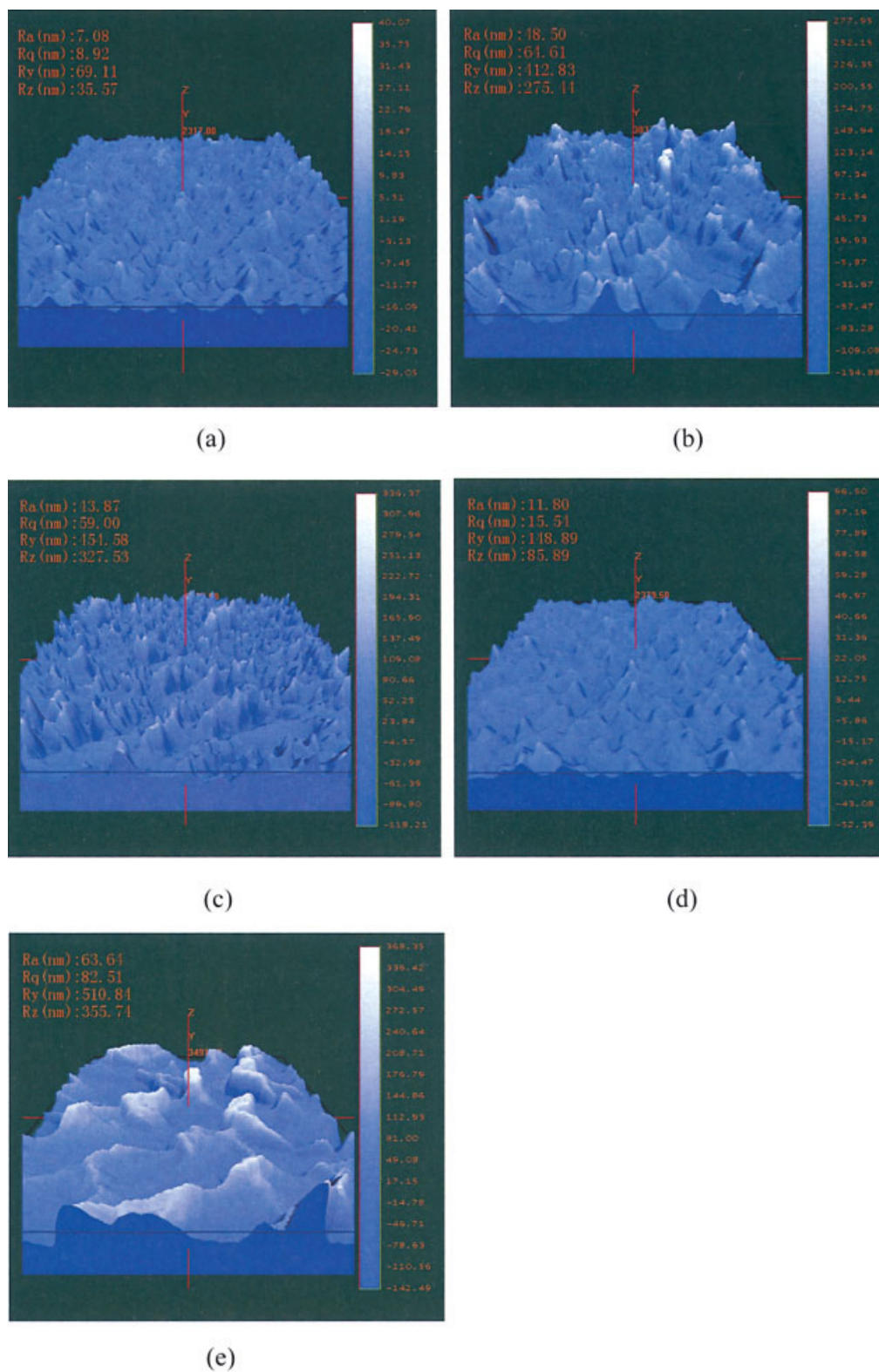


Figure 2 SPM three-dimensional micrographs of the surface morphology of (a) untreated, (b) CO_2 treated for 15 min, (c) O_2 treated for 10 min, (d) NH_3 treated for 10 min, and (e) SO_2 treated for 15 min PEU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Effect of Plasma Modification on the Surface Elemental Ratios of PEU Films

Treatment	Elemental ratios			
	O/C	N/C	S/C	O/N
Untreated	0.322	0.048	N/A	6.723
CO ₂ treated for 15 min	0.411	0.016	N/A	25.017
O ₂ treated for 10 min	0.463	0.060	N/A	7.691
NH ₃ treated for 10 min	0.307	0.156	N/A	1.971
SO ₂ treated for 15 min	0.445	0.069	0.041	6.485

tron spectroscopy (XPS) to evaluate the elemental and chemical groups present in the surface.¹⁰ A PHI 5300 spectrometer (Ö Physical Electronic) with a 250 W Al K α radiation source was used to obtain spectra. The operating pressure was maintained under 10⁻⁸ torr enabling the field emission gun to deliver a primary beam current of 25 nA onto the sample as a 40 nm spot size. A pass energy of 89.45 eV was used to record the widescan spectra (0–1000 eV) and 35.75 eV for high-energy resolutions scan. All measurements were obtained at a take-off angle of 45°, corresponding to an approximate depth profile of 10 nm. Binding energies were calibrated using the C_{1s} binding energy peak for CH₂ in polymers at 285.0 eV as a reference,²⁸ with FWHM of 0.8 eV, so that surface elemental compositions could be calculated from the relative peak areas. The C_{1s}, N_{1s}, O_{1s}, and S_{2p} spectral envelopes were analyzed and peak-fitted using Gaussian–Lorentzian function obtained from the ORIGINLAB software.

Infrared attenuated total reflectance spectroscopy

A ZnSe (45°) parallelepiped internal reflection element (IRE) was used in infrared attenuated total reflectance (ATR) analysis. The native and plasma-treated PEU membranes were pressed against the IRE under a constant torque using a torque wrench and placed in an ATR accessory made by Bio-Rad. Infrared spectra were obtained at a resolution of 2 cm⁻¹ on a Digilab FTS 3100 fourier transform infrared spectrometer (Bio-Rad). The intensities of the peaks in the ATR spectra were used to identify the concentrations of chemical groups.

RESULTS AND DISCUSSION

Static water contact angle

Water contact angle analysis provides information about the surface hydrophobicity/hydrophilicity and molecular mobility at the air–solid–water interface.²⁹ It is sensitive to both chemical and physical changes in the first few monolayers of the surface. For biomaterials, water contact angle is an important parameter corresponding to their biocompatibility. In general, the water contact angle is lower, the biocompatibility is better.

Figure 1 shows the effect of different treatment gases and treatment time on the SCAs of the PEU surfaces. It is noticed that the virgin PU exhibited a relatively hydrophobic surface. However, as we expected, the water contact angles of all the plasma-

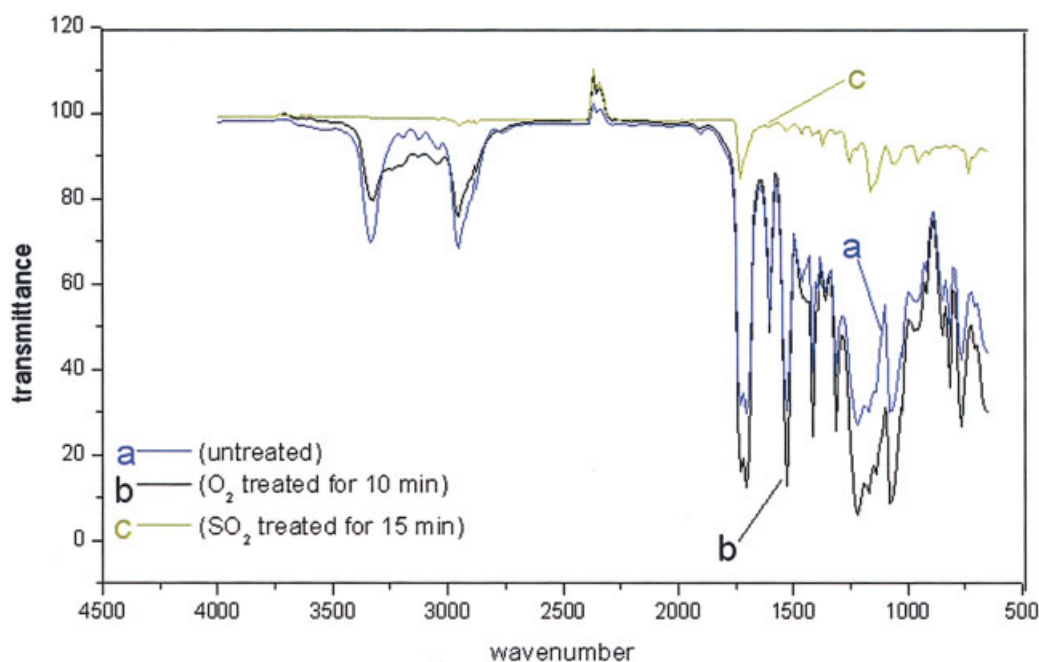


Figure 3 ATR spectra for (a) untreated, (b) O₂ treated for 10 min, and (c) SO₂ treated for 15 min PEU films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

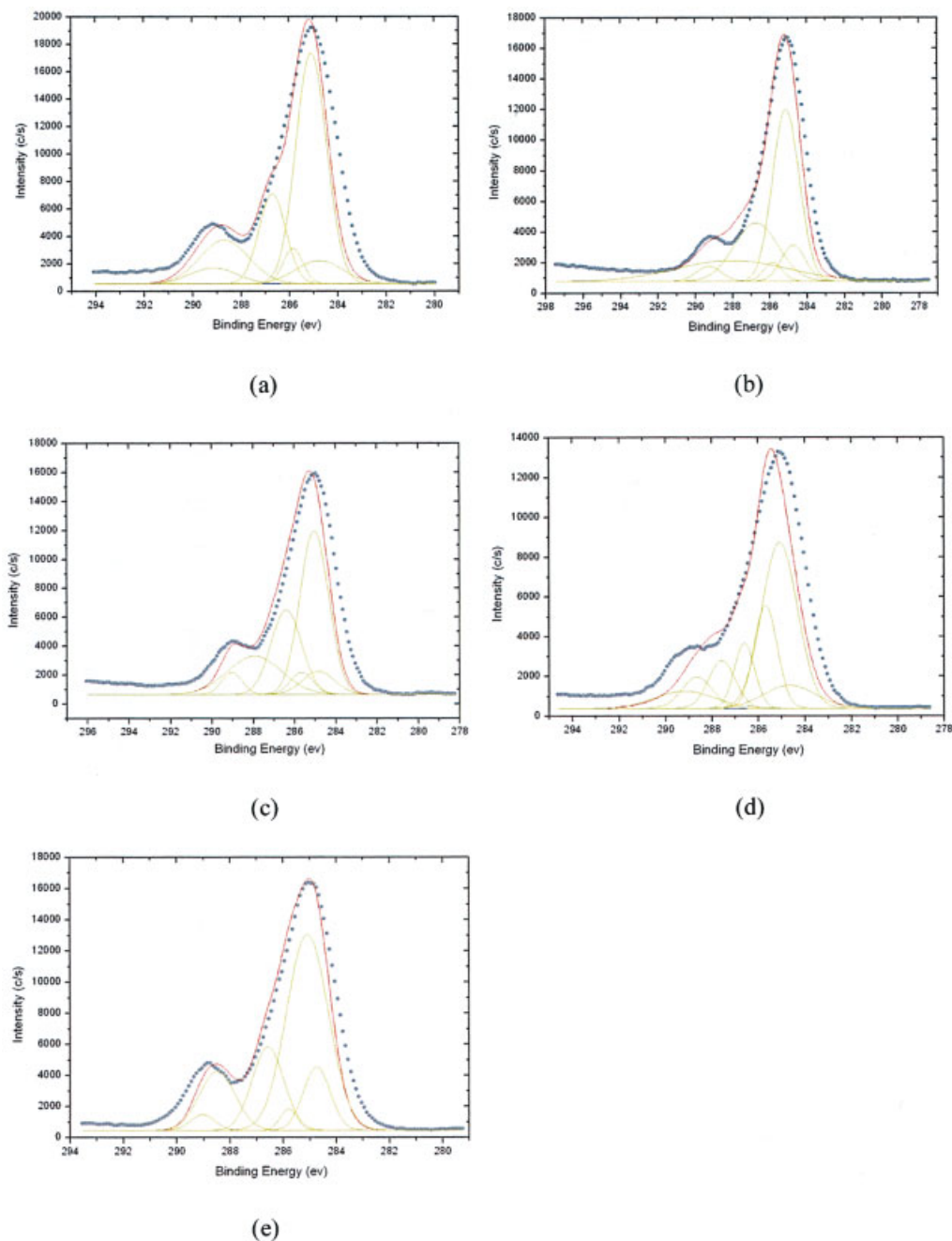


Figure 4 High-resolution XPS spectra of C_{1s} peak for (a) untreated, (b) CO_2 treated for 15 min, (c) O_2 treated for 10 min, (d) NH_3 treated for 10 min, and (e) SO_2 treated for 15 min PEU films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

treated PEU surfaces considerably decreased due to the changes of the surface functional groups and roughness that are helpful to improve the wettability of the PU.¹⁰ Furthermore, we can also conclude that a minimum value of the water contact angle is presented in each plasma treatment. For CO_2 and SO_2 plasma treatments, the minimum contact angles of 53.82° and 48.40° appeared when the treatment time was 15 min, while in O_2 and NH_3 treatments, the contact angles first decreased respectively, to a mini-

imum of 44.02° and 45.66° as the treatment time reached 10 min, and then began to increase. The results may indicate that etching and ablation occurred more and more on the PEU surfaces with the increasing treatment time. After the etching and ablation reached some extent, the PEU surfaces were overlaid with the deposit caused by etching and ablation. Therefore, the wettability decreased since the overlayer prevented the contact between the hydrophilic functional groups and the water droplet.

TABLE II
Representative XPS High-Resolution Peak Fitted Components of C_{1s} Spectra for Untreated and Plasma-Treated PEU Surfaces

Treatment	C=C or C=S	C—C or C—S	C—N	C—O	C=N	C=O	$\begin{array}{c} \text{O} \\ \\ \text{—HN—C—O—} \\ \\ \text{C} \end{array}$
Untreated (binding energy (ev), area %)	284.78, 7.60	285.09, 50.02	285.76, 5.19	286.72, 17.32	N/A	288.70, 14.68	289.15, 5.18
CO ₂ treated for 15 min (binding energy (ev), area %)	284.78, 8.03	285.13, 41.98	285.84, 3.30	286.74, 22.83	N/A	288.05, 20.40	289.28, 3.46
O ₂ treated for 10 min (binding energy (ev), area %)	284.86, 6.50	285.05, 43.34	285.67, 4.35	286.48, 23.36	N/A	288.00, 18.15	289.05, 4.30
NH ₃ treated for 10 min (binding energy (ev), area %)	284.74, 5.38	285.09, 43.28	285.69, 17.66	286.71, 10.02	287.59, 10.23	288.56, 8.81	289.03, 4.62
SO ₂ treated for 15 min (binding energy (ev), area %)	284.75, 11.43	285.15, 52.37	285.79, 2.57	286.59, 17.35	N/A	288.39, 13.70	289.03, 2.58

Scanning probe microscopy

Figure 2 shows the domain morphology of the PEU surfaces before and after plasma treatments. The three-dimensional image of native PEU [Fig. 2(a)] clearly demonstrates numerous stone-like protrusions on the polymer surface. The particular topographical structure is mainly attributed to the microphase segregation between the hard and soft segments of the PEU due to the difference in the interfacial energy of the two components.^{30,31} At the polymer surface, the soft segments are flexible enough to allow the protrusions formation such that the hard segments corresponding to the concave zones are only visualized between the protrusions.

All the plasma treatments modified the surface morphology of the PEU. Figure 2(d) illustrates the surface topography following NH₃ plasma treatment and indicated the mildest modification within the surface region compared with other three plasma treatments. The resulting surface shows a fine stone-like texture with little change from the original morphology, which suggested that a little etching occurred during the treatment process throughout the hard and soft segments. The bombardment of the plasma species mainly caused the increased surface roughness. However, the rather pitted patterns resulted by CO₂ [Fig. 2(b)] and SO₂ [Fig. 2(e)] plasma treatments show a marked variety of surface roughness and indicated a great etching to the polymer segments. The most interesting phenomenon is the effect of O₂ plasma treatment. After modified by O₂ plasma, a pinnacled structure with a regular arrangement [Fig. 2(c)] substituted the primary structure of the native PEU. According to Coen et al.,³² such topographical change was attributed as a result of polymer surface crosslinking. All these observations from SPM demonstrate that

through plasma treatment, the surface roughness of the PEU membrane was favorably increased.

X-ray photoelectron spectroscopy

Widescan and high-resolution XPS spectra of the PEU material were investigated to determine the functionality present in the surface region and illuminate the changes of the species introduced by each plasma treatment. Peak fittings of the C_{1s} , O_{1s} , N_{1s} , and S_{2p} spectral envelopes were employed in XPS to evaluate the proportions of different carbon, oxygen, nitrogen, and sulfur bonds at the surface of the PEU films.

Table I shows the surface atomic ratios determined from the relative areas of C_{1s} , O_{1s} , N_{1s} , and S_{2p} peaks for the native and modified PEU. The data exhibits that after plasma treatments, the proportion of each element was redistributed at the surface. Following O₂ and SO₂ plasma treatments, the values of N/C increased in some extent. According to the results of ATR (Fig. 3), after O₂ plasma treatment, the absorption strength for the deformation vibration of N—H (1520 cm⁻¹) existing in hard segments increased, which indicated an increase of the detected nitrogen in the PEU surface. Therefore, it can be inferred that a relatively more etching and ablation of the soft segments occurred during the treatment of O₂ plasma. However, after the treatment of SO₂ plasma, the absorption strengths for the deformation vibration of N—H (1520 cm⁻¹) and stretching vibration of C=O (1720 cm⁻¹) both sharply decreased, this result suggested that the increased value of N/C might be mainly caused by the coating and reaction of sulfur-containing species. In the case of CO₂ plasma treatment, the value of N/C decreased as expected. This result indicated a more supplement of carbon element through CO₂ plasma

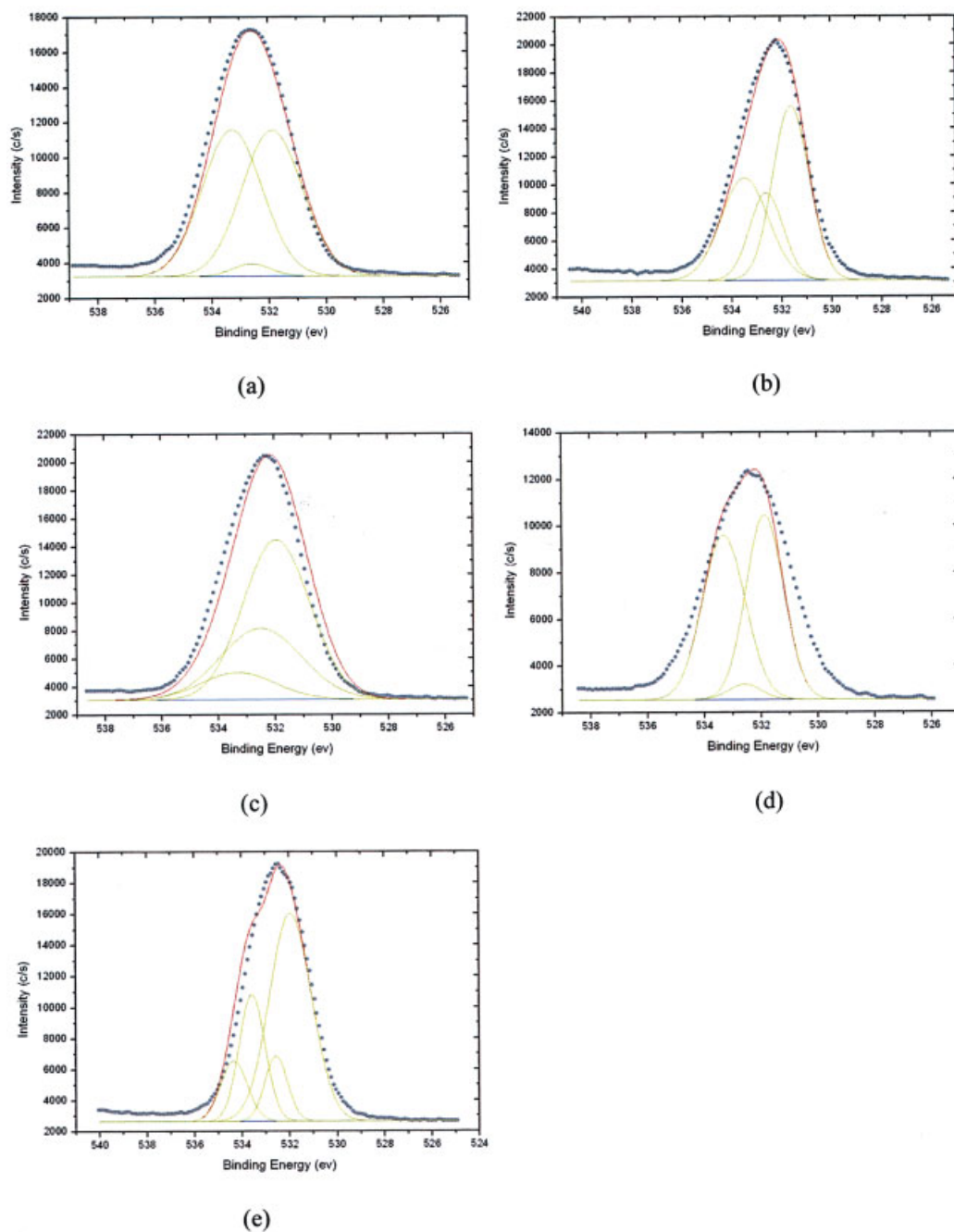


Figure 5 High-resolution XPS spectra of O_{1s} peak for (a) untreated, (b) CO_2 treated for 15 min, (c) O_2 treated for 10 min, (d) NH_3 treated for 10 min, and (e) SO_2 treated for 15 min PEU films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

treating than its loss caused by etching. In addition, we can also see that NH_3 plasma obviously caused the increase of nitrogen content and SO_2 plasma successfully introduced sulfur element to the PEU surface.

High resolution of C_{1s} spectra for the native and plasma-treated PEU films are shown in Figure 4. The relative percentages of each component analyzed by Gaussian and Lorentzian peak fitting algorithms are summarized in Table II. The C_{1s} peak for the unmodified PEU surface can be resolved into six component

peaks [Fig. 4(a)] at 284.78, 285.09, 285.76, 286.72, 288.70, and 289.15 eV. These peaks correspond to the aromatic $C=C$, aliphatic $C-C$, $C-N$, $C-O$, and unsaturated $C=O$ in adipate and carbamate separately.^{28,33,34} The latter two functionalities are an integral part of the repeat unit for the soft and hard segments. Plasma modification induced significant changes in the relative intensities of all peaks. Following treatment by CO_2 and O_2 plasmas, there was a decrease in relative intensity of $C-C$ bond accompa-

TABLE III
Representative XPS High-Resolution Peak Fitted Components of O_{1s} Spectra for
Untreated and Plasma-Treated PEU Surfaces

Treatment	$\text{O}=\text{C}$ or $\text{O}=\text{S}$	$\text{HO}-\text{C}$	$\text{O}-\text{C}=\text{O}$	$\text{HO}-\text{S}(\text{O})_2-\text{C}$
Untreated (binding energy (ev), area %)	531.88, 48.87	532.62, 2.63	533.28, 48.50	N/A
CO ₂ treated for 15 min (binding energy (ev), area %)	531.62, 45.12	532.61, 21.10	533.48, 33.78	N/A
O ₂ treated for 10 min (binding energy (ev), area %)	531.95, 57.92	532.51, 31.18	533.32, 10.90	N/A
NH ₃ treated for 10 min (binding energy (ev), area %)	531.87, 48.32	532.59, 3.51	533.31, 48.17	N/A
SO ₂ treated for 15 min (binding energy (ev), area %)	531.96, 56.62	532.58, 10.21	533.59, 22.23	534.35, 10.95

nied by an obvious increase in C—O and C=O. This was due to oxidative reactions of the oxygen-containing plasma species with the PEU surface. Furthermore, the relative intensity of carbon in C=C after CO₂ plasma treatment had a small increase. According to a previous report on plasma treatment of PU,⁸ the increase in C=C could be attributed to double bond formation at the surface due to radical reaction induced by the carbon-containing radicals. The susceptibility of this PEU to NH₃ plasma can be interpreted by the significant incorporation of nitrogen-containing groups. The C_{1s} peak can be deconvolved into seven peaks as illustrated in Figure 4(d). A new peak that was consistent with the formation of imine groups (C=N) appeared at 287.59 eV as well as a notable increased intensity of 17.66% in C—N was observed. In addition, the reduced intensities of the groups containing oxygen such as C—O and C=O indicated a partial substitution of oxygen moieties by nitrogen moieties. In the case of SO₂ plasma treatment, the relative intensities in 284.75 and 285.15 eV increased markedly. Since the binding energies of C—C and C=C are very similar to C—S and C=S, it is considered that the increased intensities in 284.75 and 285.15 eV were mainly resulted by the formation of C—S and C=S. Consequently, we can confirm that some sulfur-containing groups were indeed introduced to the PEU surface.

Figure 5 and Table III respectively, show the high resolution of O_{1s} spectra and relative percentages of each component for the untreated and plasma-treated PEU membranes. The O_{1s} spectrum of the virgin PEU can be deconvolved into three peaks [Fig. 5(a)] corresponding to O=C (531.88 eV), HO—C (532.62 eV), and O—C=O (533.28 eV). After treating by CO₂ and O₂ plasmas, there are no new peaks present in the high-resolution of O_{1s} spectra [Fig. 5(b,c)]. As we expected, rather quantities of hydroxyl groups were introduced to the PEU surface. It is noticeable that al-

though the relative percentage of oxygen in O—C=O reduced after both treatments, this reduction was much less in the treatment of CO₂ plasma compared with that in O₂ plasma treatment. Furthermore, the relative intensity in O=C increased after O₂ plasma treatment followed by a decrease after CO₂ plasma treatment. It could be inferred that during the treatment of CO₂ plasma, some carboxyl groups were formed to complement the lost ester groups in the etching of soft segments, which resulted a relative less reduction of the intensity for O—C=O oxygen. However, following O₂ plasma treatment, carbonyl groups were produced due to the oxidative reactions which directly led to the increased intensity of O=C peak. In the case of NH₃ plasma treatment, the high resolution of O_{1s} spectrum and relative percentages of each component are nearly consistent with that of native PEU ([Fig. 5(d)] and Table III). Through the treatment of SO₂ plasma, the O_{1s} spectrum had wider binding energy range than that of the original PEU. A new peak at 534.35 eV [Fig. 5(e)] corresponding to the oxygen of HO—SO₂ appeared and an increased intensity by ~8% at 531.96 eV was observed as well. Both the results indicated an incorporation of sulfonic groups on the PEU surface.

The N_{1s} spectra of all the PEU films except those treated by NH₃ plasma only consist of one peak for the urethane nitrogen at about 400.50 eV. After modified by NH₃ plasma, the binding energy range of the N_{1s} spectrum was broadened and it could be deconvolved into three peaks [Fig. 6(a)], 399.45 eV (45.53%) for the nitrogen of HN=C, 399.95 eV (30.88%) for the nitrogen of H₂N—C, and 400.51 eV (23.59%) for the HN—COO nitrogen. The S_{2p} high-resolution spectrum following the treatment of SO₂ plasma can be resolved into four peaks [Fig. 6(b)] corresponding to simple sulfur at 164.51 eV (5.71%), S=C at 166.54 eV (6.21%), HS—C at 168.21 eV (29.67%), and HO₃S—C at 169.40 eV (58.43%). These results agree with the conclusion of

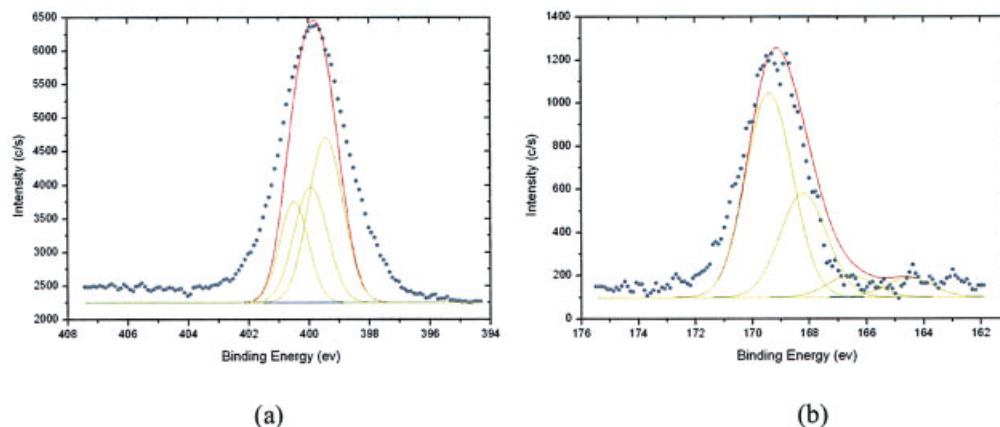


Figure 6 High-resolution XPS spectra for (a) N_{1s} peak of NH_3 treated for 10 min and (b) S_{2p} peak of SO_2 treated for 15 min PEU films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Cao et al. for the modification of PU by SO_2 plasma.³⁵ The appearance of simple sulfur peak indicated a complete decomposition of SO_2 partially occurring during the discharge, and as a result, it is essential to clean the treated PEU surface prior to processing it with cell culture.

Through the characterization of XPS, we can conclude that for all the plasma treatments, there was a decrease in the relative percentage of C—C bond at the PEU surface. However, some polar groups such as hydroxyl, amino, carboxyl, and sulfonic groups were introduced to the PEU membranes, which could be beneficial for cell-adhesion to this material. Besides, the successful incorporation of sulfonic groups with PEU surface can greatly enhance the resistance against thrombus formation of this material.³⁶

CONCLUSIONS

The results obtained in this study demonstrate that the PEU films were significantly modified by plasma treatment via inducing some complex chemical and physical changes at the surface. The different morphologies exhibited in SPM indicate that the surface became rougher due to the reactions and etching at the surface caused by the energy imparted to the polymer during plasma treatments. For all the treated surfaces there is an increase in the polar character as displayed by an increase in wettability. Moreover, during each plasma treatment, a minimum water contact angle appeared indicating a competition between incorporation of polar functional groups and etching to the surface. XPS spectra showed that the technique of plasma treatment has been successful in the formation of functional species that are not seen in the unmodified PEU surface. For instance, following CO_2 and O_2 plasma treatments, —COOH and —OH functionalities ap-

peared, while — NH_2 as well as — SO_3H came into being respectively, after NH_3 and SO_2 plasma treatments.

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