Surface Characterization of Plasma-Derivatized Polyurethanes

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SYNOPSIS

The use of plasma deposition to introduce sulfonate groups to the surface of a polyurethane was attempted. In previous work, the bulk incorporation of sulfonate groups was found to improve the blood contacting properties of the base polyurethane but physical properties in the hydrated state were adversely affected. Plasma deposition schemes involving ammonia and sulfur dioxide were utilized in an attempt to incorporate sulfonate groups. Surface characterization by X-ray photoelectron spectroscopy (XPS) and contact angle measurements was used to follow polymer surface rearrangement dynamics and to address the issue of plasma chemistry specificity. Concerns of reaction specificity were alleviated by using the plasma as a pretreatment which is followed by a chemical surface derivatization.

INTRODUCTION

The bulk incorporation of sulfonate groups into a polyether polyurethane via a bimolecular nucleophilic substitution has been shown to improve the blood contacting properties of the underivatized polyurethane biomaterial.[1] Increasing sulfonate content results in better blood contacting behavior but physical properties deteriorate in the hydrated state. At high levels of sulfonate content, the bulk derivatized polyurethanes are water-soluble.

The use of radio frequency plasma treatment to derivatize polymer surfaces appears to be a solution to the difficulties that are incurred with the bulk incorporation of ionic groups into the base polyurethane. Selectively manipulating surface chemistry, so as to enhance blood contacting properties, while simultaneously retaining the good physical properties of the base polyurethane, is an attractive possibility.

Complications that arise from the use of plasma treatments center on issues related to plasma treatment reproducibility, plasma specificity, and polymer surface mobility.

In this investigation, the effects of plasma treatment conditions on surface chemistry were examined by X-ray photoelectron (XPS). Polymer surface dynamics were followed with contact angle and XPS measurements. Finally, a polymer surface derivatization scheme was developed that addresses concerns about plasma chemistry specificity and reproducibility.

EXPERIMENTAL

Polymer Film Preparation

A polyether polyurethane, synthesized in our laboratory, based on a 3/2/1 mole ratio of diphenylmethane diisocyanate/butane diol/poly(tetramethylene oxide) of molecular weight 1000 [MDI-BD-PTMO(1000)] was used in this study.[1,2] The polymer was dissolved in tetrahydrofuran (THF) and was spun-cast into thin films on glass slides or on germanium internal reflection elements. The polymer film thicknesses were measured using ellipsometry and found to be approximately 1000 Å. The polymers cast on glass were used in the XPS characterization whereas the germanium reflection elements were used in contact angle studies and in protein adsorption studies using FTIR spectroscopy.[3]

Plasma Treatment

A plasma reactor has been constructed using a 2-ft long, 1-in. inner diameter quartz tube with externally mounted copper ring electrodes. The vacuum in the system is maintained by a Leybold Model D30AC pump, measured by an MKS Baratron Model 127 pressure gauge, and controlled by an MKS type 252 exhaust valve controller. Gas flow rate is metered by an MKS Model 1160 mass flow rate controller. An EMI Model ACG3 power source is used to produce the plasma at radio frequency (13.5 MHz).

In the plasma treatment, the polymer-coated glass or germanium substrate is centered in the reactor between the two externally mounted copper ring electrodes. The reactor is sealed and evacuated to approximately 2 mtorr. A gas flow rate is chosen on the mass flow controller and then flow is initiated. The pressure established in the reactor at this point results from a balance between the input mass flow rate and the pumping speed. The desired pressure is then set on the pressure controller and the controller is activated. Plasma treatments were performed with pressures in the range of 0.1–0.3 torr whereas gas flow rates were maintained at 10, 20, or 30 standard cubic centimeters per minute (sccm).

After the pressure is stabilized, the power to the electrodes is turned on and set to its chosen value. In this study, power inputs were low and ranged from 10 to 30 W. After a given exposure time, the power is shut off, the pressure controller is deactivated, and, finally, the input gas flow is stopped. The chamber is then evacuated to at least 2 mtorr.

If no further gas treatment is required, the valve between the reactor and the pump is closed. Air is then bled into the chamber and the treated polymer is removed.

If desired, the specimum can remain in the chamber for further treatment. In this study some ammonia plasma-treated polyurethanes were subsequently exposed to flowing sulfur dioxide gas for 5 min, at a flow rate of 20 sccm, and under a controlled pressure of 0.5 torr.

Surface Characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics PHI 5400 spectrometer with a 300 W, 15 kV magnesium anode. The emission angle of the photoelectrons was 45°. The relative atomic percent of each element at the surface was estimated from peak areas using atomic sensitivity factors specified for the PHI 5400.

Contact angle measurements were performed using static bubbles of air and octane introduced from beneath samples submerged in water. The bubbles were photographed and analyzed to determine the contact angles.

Fourier transform infrared spectroscopy with attenuated total reflectance optics was attempted to collect IR spectra of the plasma-treated polymer surfaces. It was not possible to discern spectral differences between treated and untreated polymer samples. The depth of penetration of the IR technique (around 4000 Å) relative to the depth of the plasma treatment (less than 100 Å) suggests that there is not enough surface sensitivity in the IR technique to detect surface chemistry changes due to the plasma treatment methods used in this study.

RESULTS AND DISCUSSION

Use of NH_3 and SO_2 Plasmas

Several approaches were initiated using plasma deposition to introduce sulfonate groups to the surface of the base polyurethane. The first synthesis scheme involved the use of plasma deposition as a precursor to a wet chemistry surface derivatization. An ammonia plasma was used to introduce primary amine groups to the surface of the polymer. These surface amine groups were subsequently reacted with a solution of propane sultone. Despite initial success, the carcinogenic nature of propane sultone was motivation for the pursuit of safer alternatives.

The use of a sulfur dioxide plasma is expected to introduce sulfonic acid groups to the surface of a contacting substrate. Inagaki has performed work in the area of plasma polymerization of monomer/ SO_2 mixtures and reports the presence of sulfonate groups in the deposited films.[4-7]

Initial attempts using sulfur dioxide plasmas failed when the polyurethane films were quickly etched from the supporting germanium reflection elements. The etching of the films can be directly observed since the polymer films are clearly visible when cast on the germanium substrates. The color of the polymer film varies with the film thickness. When the polyurethane is cast on germanium, films that are about 1000 Å thick (as determined by ellipsometry) are gold in color. Blue-colored films are 800–900 Å thick whereas films between 700 and 800 Å are yellow. The decrease in film thickness due to etching can be observed by the changes in color of the polymer film during the plasma treatment.

The etching power of sulfur dioxide is not unexpected since plasmas containing oxygen molecules are often used as etching agents and have been well described in the literature.[8] Plasma deposition is thought to proceed primarily due to the deposition of radicals[9,10] and the presence of oxygen in a plasma can interfere with this.[11] An alternative plan to dilute the etching power of the sulfur dioxide plasma by using a mixture of sulfur dioxide and argon gases was abandoned once reactor operating parameters were found which favored plasma reaction over etching.

The subsequent use of sulfur dioxide plasmas led to some unexpected results. At a given plasma reactor condition (P = 200 mtorr, W = 20 W, F = 20 sccm), it was found that after approximately 3.5 min of sulfur dioxide plasma exposure, the polyurethane films cast on germanium were found to be water-soluble. Exposure of the polymer to the sulfur dioxide plasma for less than 3 min led to the deposition of a significant level of sulfur-based groups, as determined by XPS, but water solubility of the polymer film was not observed. In the work of Lub et al. with ammonia, oxygen, and hydrogen plasma-treated polycarbonate, it was reported that the presence of the aromatic ring in the polymer backbone was a significant factor in chain scission of the plasma treated polymer.[12,13] A combination of the hydrophilicity introduced by the sulfur dioxide plasma treatment and a decrease in the molecular weight of the polymer in the film by plasma etching and chain scission could explain the water solubility of the treated polyurethane.

Specificity and Reproducibility

Two important concerns regarding the use of plasmas for polymer surface derivatizations are reproducibility and chemical specificity. It seems difficult to deposit exclusively one particular functionality, for example, sulfonates from an SO_2 plasma, from all the species generated in the plasma. It is anticipated that the manipulation of plasma processing parameters could influence or control reaction selectivity. An investigation of the effects of various plasma reactor conditions on surface composition was performed. Many previous studies have pursued the quantification of such aspects of plasma processing as deposition rate versus reactor conditions[12] but few have examined the effects of reactor conditions on the surface chemistry obtained. Polyurethane thin films were exposed to sulfur dioxide plas-
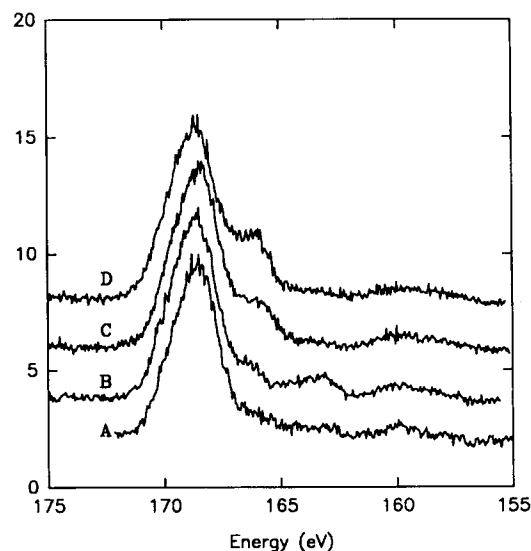

Figure 1 Sulfur region of the XPS spectra of SO_2-plasma-treated polyurethane samples A–D. The ordinate (arbitrary units) of all the XPS spectra shown has been offset to allow easier visualization.

mas under a variety of reactor conditions. The films were characterized using XPS to identify the plasma-deposited species.

The sulfur region of the XPS spectrum of seven sulfur dioxide plasma treated polyurethanes is shown in Figures 1 and 2. The plasma reactor operating parameters used for each treated polymer are shown in Table I. The sulfur region of the spectrum between 155 and 175 eV has two prominent features: peaks near 165 and 168 eV. The lower energy peak near 165 eV has been attributed to sulfur atoms attached to a carbon or one oxygen.[4] The higher energy peak near 168 eV has been assigned to sulfur atoms bonded to two or three oxygen atoms.[4] Figure 1(A) shows only one peak near 168 eV with possibly a shoulder near 165 eV. Under different reactor conditions, different surface chemistries are observed. The spectra in Figures 1(B)–1(D) and 2(E)–2(G) demonstrate the appearance, growth, and dominance of the lower energy sulfur peak near 166 eV. Table II lists the ratio of the XPS peak heights at 165 and 168 eV for the seven treated polyurethane samples of Figures 1 and 2. Figures 1(A)–1(D) and 2(E) all have larger sulfur peaks near 168 eV than at 165 eV, indicating that more SO_2 and SO_3 groups appear on the 1(A)–1(C) polymers. In Figures 2(F) and 2(G), the amount of sulfur attached to carbon or one oxygen atom matches and exceeds, respectively, the amount of sulfur bonded to several oxygens atoms. This can be seen in the
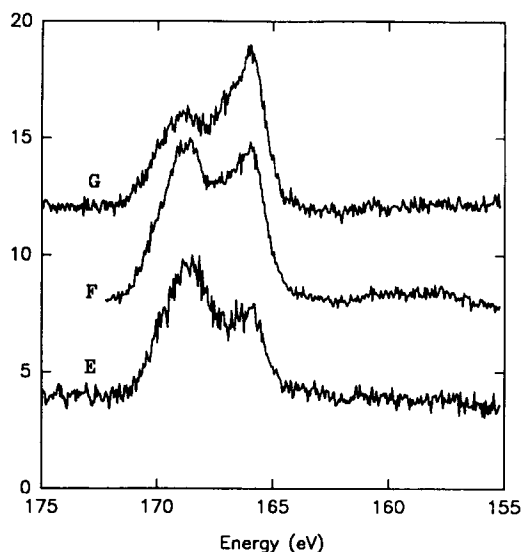
Figure 2 Sulfur region of the XPS spectra of SO_2-plasma-treated polyurethane samples E-G.

increase in 165/168 eV peak height ratio in Table II.

Similar behavior is observed in the oxygen region of the XPS spectra of the same SO_2 plasma-treated polyurethanes. The oxygen spectra also show the presence of at least two peaks. There is a higher energy peak near 534.5 eV and a lower energy peak near 532 eV. The breadth of the higher energy peak relative to the lower energy peak suggests that it may be composed of two overlapping peaks. Oxygen bonded to carbon typically appears near 534 eV whereas oxygen bonded to sulfur can have peaks near 534 and 532 eV.[14] The growth and eventual dominance of the lower energy oxygen peak can be seen in the series of XPS spectra shown in Figures 3(A)-3(D) and 4(E)-4(G) and in the peak height ratio data in Table II. The observations of the peak developments in the oxygen region of the XPS spectra mirror the developments in the sulfur region.

More complex behavior can be observed in the

carbon region of the XPS spectra of the same SO_2 plasma-treated polyurethanes. The carbon region of the spectra contains contributions from at least four peaks. The peak near 285 eV is assigned to aliphatic carbon atoms. The peaks near 289 and 291 eV are assigned to the carbon atoms in ether and carbonyl groups, respectively. Finally, a contribution to the carbon spectrum near 284 eV can be attributed to the presence of carbon attached to sulfur atoms. The growth of this lower energy carbon peak near 284 eV can be followed in the series of XPS spectra shown in Figures 5(A)-5(D) and 6(E)-6(G) and in the 282/285 eV peak height ratio data in Table II. Once again, the observed peak changes mirror those occurring in the sulfur region.

The findings that surface chemistry depends dramatically on plasma processing parameters confirms the expectations that maintaining specificity with plasma treatments is difficult. In response to these complications with the direct use of sulfur dioxide plasmas, an alternative use of plasmas was developed to introduce sulfonate groups to the polymer surface.

This third, less obvious, surface derivatization scheme was developed as the plasma deposition work began. It is based on the fact that a plasma leaves reactive agents, such as free radicals, on a treated polymer surface.[11] The post-plasma treatment reaction of these surface radicals with oxygen in air is often considered to be a troublesome side reaction.[11] Alternatively, these surface radicals can be used to react with some gaseous or liquid derivatization agent in the plasma reactor before exposure to the atmosphere. This technique addresses the problem of chemical specificity in plasma reactions. Instead of using the plasma to attempt to directly introduce a specific functionality to a substrate, the plasma can be used as a pretreatment step with a subsequent derivatization. Since a broad distribution of species is created in the plasma state, a broad distribution of species is created on the polymer surface and concerns of reaction specificity are rea-

Table I The SO_2 Plasma Reactor Conditions Used on the Polyurethane Samples

Sample	Flow Rate (sccm)	Power (W)	Pressure (mtorr)	Exposure Time (min)	Sulfur (%)
A	10	10	100	5	6.09
B	10	10	200	2	7.44
C	30	30	200	5	7.60
D	20	20	200	5	7.38
E	10	20	100	5	4.44
F	10	10	200	5	8.08
G	10	10	300	5	8.65

Table II Peak Height Ratios from the Carbon, Oxygen, and Sulfur Regions of the XPS Spectra of the Polyurethanes Exposed to SO_2 Plasmas at Various Reactor Conditions

Region	XPS Peak Height Ratios		
	Carbon	Oxygen	Sulfur
Sample	282/285	532/534.5	165/168
A	0	0.09	0.12
B	0	0.06	0.08
C	0.36	0.21	0.23
D	0.35	0.36	0.29
E	0.28	0.60	0.54
F	0.94	0.91	0.76
G	0.53	1.38	1.25

sonable. By treating a polymer surface with a plasma to generate surface radicals and then introducing a gaseous or liquid derivatization agent, the generation of a large variety of reactants is avoided and the reaction products are controlled.

To control the reproducibility and chemical specificity in the introduction of sulfur and oxygen based groups to the polyurethane substrates, an ammonia plasma was used to activate the polymer surface and sulfur dioxide gas was then flushed through the plasma reactor system. This introduces a significant amount of sulfur based groups to the surface. The XPS estimated percent surface concentration of sulfur on these ammonia pretreated polymers can be as high as those derivatized by the sulfur dioxide
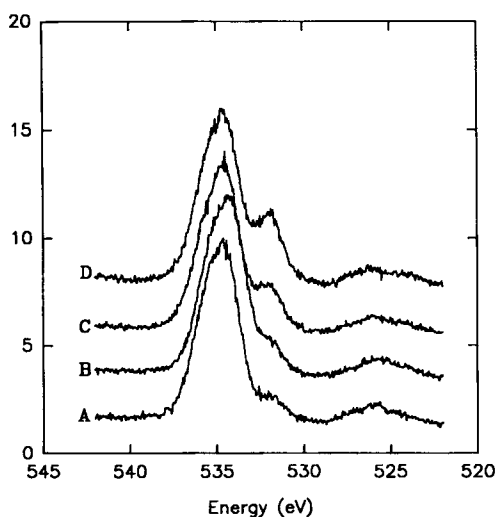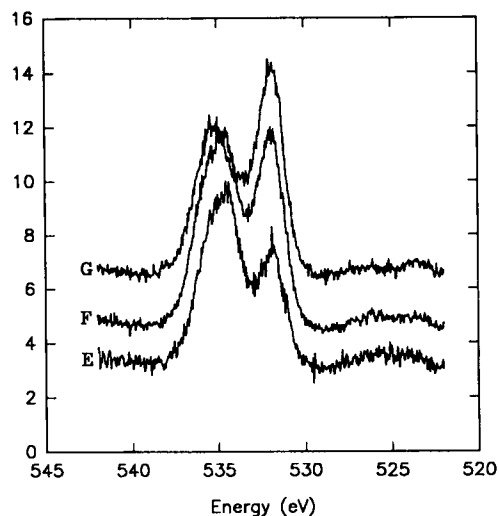

Figure 4 Oxygen region of the XPS spectra of SO_2-plasma-treated polyurethane samples E–G.

plasma. The sulfur, oxygen, and carbon regions of the XPS spectra of ammonia plasma-treated polyurethanes subsequently exposed to sulfur dioxide gas are shown in Figures 7–9. The corresponding plasma treatment and gas flush conditions are shown in Table III. When the spectra are compared to those in Figures 1–6, it can be seen that the variety of species created on the surface was reduced. The sulfur regions of the XPS spectra in Figures 7(A)–7(E) have one peak near 168 eV assigned to the presence of sulfur attached to two or three oxygen atoms. The oxygen regions of the XPS spectra in Figures 8(A)–
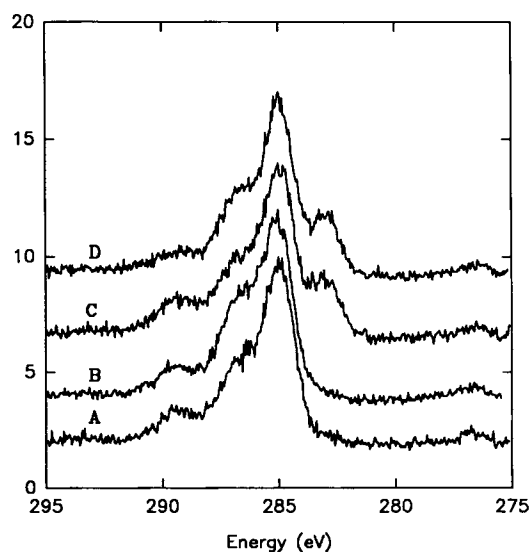

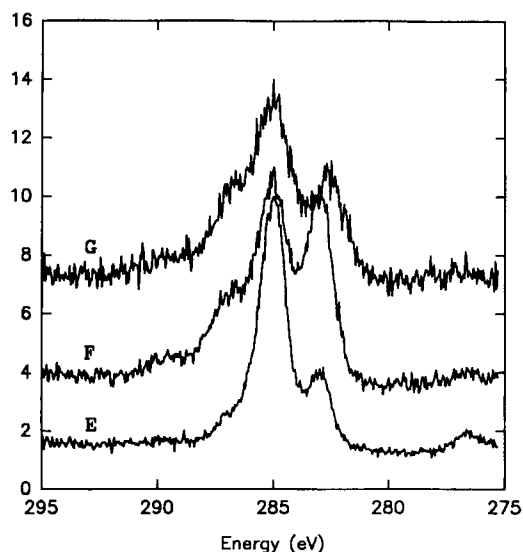**Figure 3** Oxygen region of the XPS spectra of SO_2-plasma-treated polyurethane samples A–D.

Figure 5 Carbon region of the XPS spectra of SO_2-plasma-treated polyurethane samples A–D.

Figure 6 Carbon region of the XPS spectra of SO_2-plasma-treated polyurethane samples E–G.

Figure 8 Oxygen region of the XPS spectra of the ammonia-plasma-treated polyurethanes exposed to SO_2 gas.

8(E) do not show contributions from two different environments and the carbon region of the spectra resembles that of an underivatized polyurethane. These plasma pretreated materials are not water soluble, unlike their SO_2 plasma-treated counterparts.

Effect of Plasma Reactor Operating Parameters

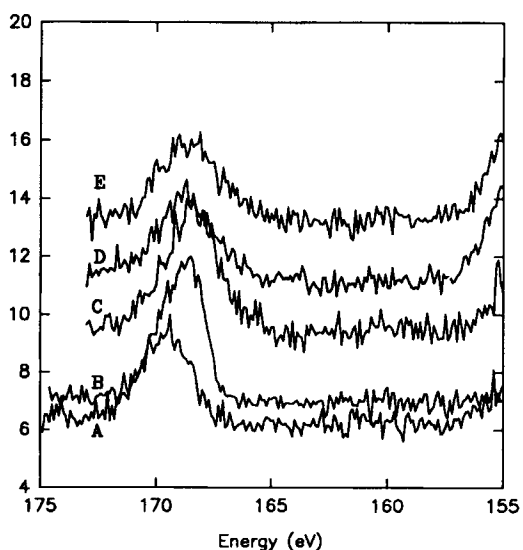The ratio of input power (W) to mass flow rate (FM) is indicative of an energy density and is an important lumped parameter often quoted in the plasma research literature. Many researchers have shown final product properties that have extrema when plotted against W/FM.[11]

The W/FM ratio does not specify a unique plasma reactor condition. The controlled reactor parameters that have an effect on the plasma are power, pressure, flow rate, and the choice of feed gas or monomer. The power input is proportional to the energy of the plasma. The pressure in the reactor is indicative of the amount of gas in the system, i.e., the density or concentration. In many plasma re-

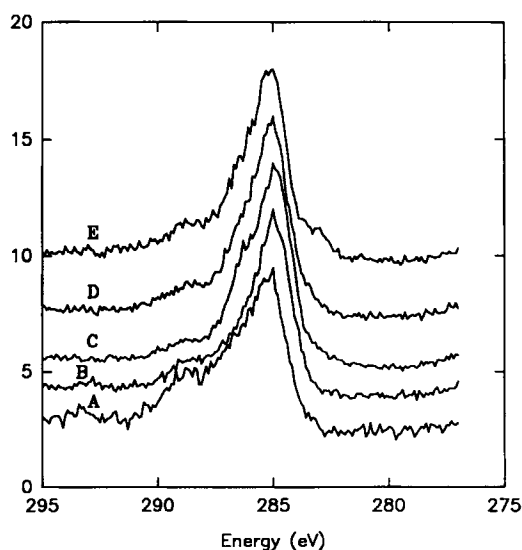**Figure 7** Sulfur region of the XPS spectra of the ammonia-plasma-treated polyurethanes exposed to SO_2 gas.

Figure 9 Carbon region of the XPS spectra of the ammonia-plasma-treated polyurethanes exposed to SO_2 gas.

Table III   The NH₃ Plasma Treatment and SO₂ Flush Conditions Used in the Polyurethane Derivatizations[a]

Sample	Power (W)	Exposure Time (min)	Flush Pressure (mtorr)	Flush Time (min)
A	20	5	500	5
B	30	5	500	5
C	20	2.5	500	5
D	20	5	500	2.5
E	20	5	250	5

[a] Gas flow rate was 20 sccm. Plasma pressure was 200 mtorr.

actors, the pressure is measured but not controlled. A combination of the reactor system pumping speed and the inlet gas flow rate typically determine the pressure in the reactor. The reactor system used in this work independently controls the pressure and flow rate by means of a flow restriction valve. Therefore, our system allows independent manipulation of the density (via pressure) of the plasma and the residence time of molecules in the system (via flow rate). In such a system W/FM is not an appropriate lumped parameter unless the pressure is specified. The same W/FM can be achieved at various pressures yet the pressure can have a large effect on the results of plasma/substrate interactions. W/FM with the pressure stated is sufficient to determine and specify reactor conditions, but, in keeping with the idea of a lumped parameter, W/F_RM is introduced with F_R being an adjusted flow rate which accounts for the pressure in the reactor. Yasuda has shown data that suggest that the plasma polymerization deposition rate is proportional to the pressure during the treatment.[11] Thus W/FM and W/F_RM are related in that F_R is $(P_{atm}/P_0) \times F$, where P_0 is the pressure maintained during the plasma treatment.

To investigate the validity of W/F_RM versus W/FM, polyurethane samples were treated in an SO₂ plasma at various values of W/FM with W/F_RM held constant and at various values of W/F_RM with W/FM held constant. This initial study utilized the XPS-measured surface concentration of sulfur as the independent variable. The results of the study were inconclusive mainly because of the formation of the varied surface chemistry products from the SO₂ plasma reaction with the polyurethane surface. In addition, the surface concentration of a given species may not be the best representation of the transport behavior which W/FM and W/F_RM are intended to describe.

Table I lists the reactor treatment conditions and the resulting level of sulfur incorporation as measured by XPS. Table IV summarizes these data in a comparison of W/FM and W/F_RM versus surface sulfur content. Samples A, F, and G in Tables I and IV represent a series of plasma treatments performed at the same power and flow rate but at different pressures. The level of sulfur incorporation increases with pressure. This result reaffirms the importance of specifying pressure, in addition to flow rate and power, in the description of the plasma treatment. The value of W/FM is constant at 2.09 $\times 10^7$ J/kg for this series of plasma treatments but W/F_RM increases from 2.75 $\times 10^3$ J/kg to 5.50 $\times 10^3$ to 8.25 $\times 10^3$ J/kg for the same series. The magnitude of W/F_RM is obviously much smaller than that of W/FM because of the increased value of F_R relative to F, but it is the trend in the parameter value that is more important that the absolute magnitudes.

Rearrangement

Polymer mobility and surface rearrangements work to hinder surface derivatization efforts. The base polyurethane utilized has both hydrophobic and hydrophilic phases which result in a significant driving force for surface rearrangement depending upon the contacting environment. In a hydrophobic environment such as in air or vacuum, the presence of the nonpolar PTMO soft segment at the air/polymer interface minimizes the solid/vapor interfacial energy. In a hydrophilic environment, the surface enrichment of the polar MDI-BD hard segment is energetically preferred. The kinetics of this rearrangement were probed by contact angle and XPS measurements performed over a period of a week on polyurethane samples which were exposed to various environments. Some samples were left in air or water

Table IV   Comparison of W/FM and W/F_RM versus %S Surface Composition of SO₂-Plasma-Treated Polyurethanes

Sample	W/FM (J/kg) $\times 10^{-7}$	W/F_RM (J/kg) $\times 10^{-3}$	%S
A	2.09	2.75	6.09
B	—	—	—
C	2.09	5.50	7.60
D	2.09	5.50	7.38
E	4.18	5.50	4.44
F	2.09	5.50	8.08
G	2.09	8.25	8.65

for an entire week. Other samples were placed in air for 3 days and subsequently exposed to water for the remainder of the week.

Summaries of the air/water contact angle data are shown in the graphs in Figures 10 and 11. The solid lines represent the results from experiments using the underivatized base polyurethane. The dotted lines represents the data from experiments using a sulfur dioxide (Fig. 10) or ammonia (Fig. 11) plasma-treated polyurethane. The circular data points are used for the experiments using the polymers which were left in air for a week. The square data symbols represent the experiments with polymers which were initially exposed to air but subsequently submerged in water. Finally, the triangular data symbols represent the experiments in which the polymers were submerged in water for an entire week.

The untreated polyurethane is initially hydrophobic, as its high air/water contact angle demonstrates. This is reasonable considering the processing history of the polyurethane film which had only been exposed to air and vacuum environments. After a full week in air, its contact angle does not change much. This suggests that the polymer has obtained some surface composition equilibrium with the hydrophobic air environment. After 3 days in air, if the polymer is then placed in water, it becomes less hydrophobic. The air/water contact angle decreases from 75 to 50°. This increase in hydrophilicity is attributed to the enrichment of the surface with hydrophilic hard segments (MDI-BD). The polyurethane samples which are left in water for 1 week become very hydrophilic.

The continual change of contact angle over the period of 1 week highlights the dynamics of the base polymer. Rapid equilibrium is not achieved upon
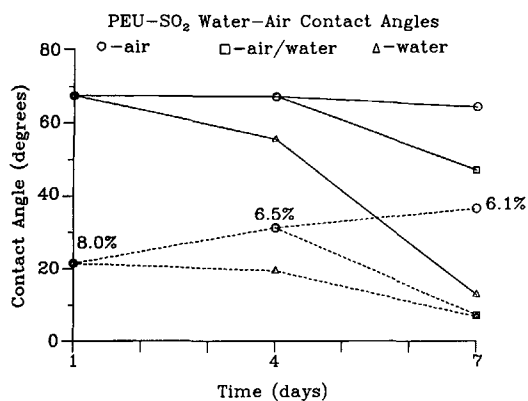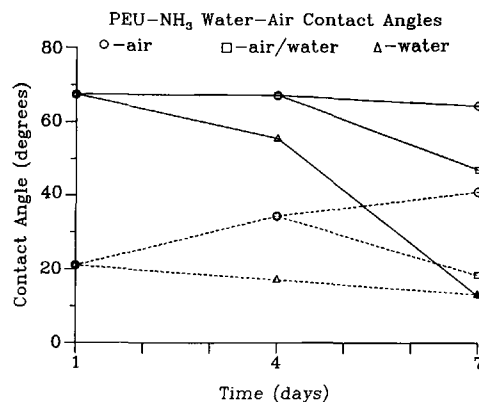

Figure 11   Air/water contact angle of the base polyurethane and the NH_3-plasma-treated polyurethane as a function of time and environment.

exposure to a given environment. Polymer mobility and morphology strongly influence the dynamics. The rate at which hydrophilic hard segments migrate to the surface influences the degree of surface hydrophilicity as determined by contact angle measurements. This diffusion rate is influenced by the polymer morphology, particularly phase separation. There is an expected transport difference between a polyurethane in which the hard segments are aggregated in a multiphase morphology and a polyurethane in which hard segments are dissolved in a soft segment matrix. Evaluation of the bulk morphology of the thin films used in the contact angle experiments was not possible.

Sulfur dioxide and ammonia plasma-treated polyurethane samples were also used in surface rearrangement studies using contact angle and XPS measurements. The contact angles on both surfaces varied similarly over time. The initial air/water contact angles, performed immediately after plasma treatment, were very low. This is indicative of the hydrophilic nature of the plasma-introduced groups. The sulfur dioxide plasma introduces substantial oxygen molecules to the surface whereas the ammonia plasma deposits a significant amount of nitrogen. The plasma-treated polyurethanes that were placed in air for 1 week seemingly lose the effects of the surface treatments and become less hydrophilic over time. This is due to the energetically favorable enrichment of the hydrophobic soft segment at the air/polyurethane interface. A plasma-treated polyurethane sample placed in air for 3 days and subsequently submerged in a water environment regains its hydrophilicity. The hydrophilicity of the plasma-treated materials is maintained by the samples submerged in water for the period of 1 week.

It is not possible to determine by contact angle

Figure 10   Air/water contact angle of the base polyurethane and the SO_2 plasma treated polyurethane as a function of time and environment.

measurements whether the hydrophilic hard segment or the hydrophilic species introduced by the plasma is responsible for the hydrophilic nature of these plasma-treated surfaces. Characterization of the surface chemistry with XPS requires the exposure of the material to a high vacuum environment. The surface rearrangements that occur upon exposure to a hydrophobic environment confound the results of the surface characterization of a material that is initially thought to be in a hydrated state.

XPS was used to measure the sulfur content of the sulfur dioxide plasma-treated polyurethanes that had been placed in air for periods up to 1 week. The XPS estimated sulfur surface percentages are shown on the plasma treated contact angle graph in Figure 10. Immediately after the plasma treatment, the surface is nearly 8.0% sulfur. After 3 days in air, the surface sulfur content is reduced to 6.5% and after 1 week in air, the surface is reduced to 6.1% sulfur. These measurements complement the contact angle data and suggest that the surface loss of hydrophilicity is due to the loss of the sulfur functionality from the surface. This type of XPS analysis could not be performed with the ammonia plasma-treated polyurethane because the signal from the nitrogen content of the base polymer confounded the results.

In addition to a simple measure of the sulfur content on the surface of the plasma treated polyurethanes, the XPS study of these materials revealed complex, time-dependent surface chemistry changes. The sulfur, oxygen, and carbon regions of the XPS spectrum of the freshly treated polyurethane ma-
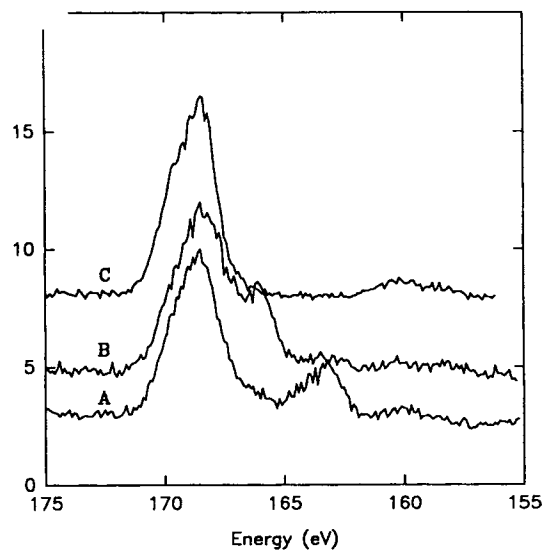
Figure 13 Oxygen region of the XPS spectra of SO_2-plasma-treated polyurethanes immediately after treatment (A), after 4 days in air (B), and after 1 week in air (C).
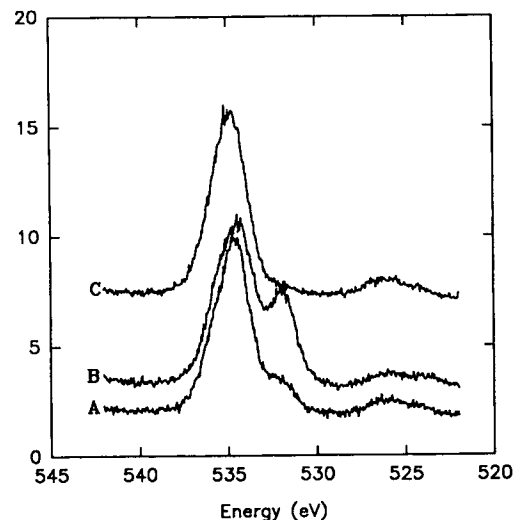
terial are shown in Figures 12(A), 13(A), and 14(A). The two peaks in the sulfur region, resemble previous results shown in Figures 1 and 2. The peaks in Figure 12(A) near 163 and 168 eV are attributed to sulfur atoms attached to carbon or one oxygen and to sulfur atoms bonded to two or three oxygen, respectively. There are also two peaks observed in the oxygen region of the XPS spectra in Figure 12(B) near 532 and 534 eV. The carbon region of the XPS spectrum in Figure 12(C) is complex but includes a peak near 284 eV, assigned to carbon
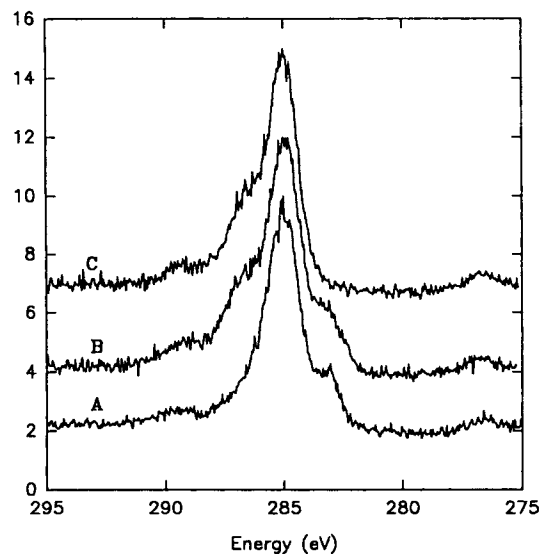
Figure 12 Sulfur region of the XPS spectra of SO_2-plasma-treated polyurethanes immediately after treatment (A), after 4 days in air (B), and after 1 week in air (C).

Figure 14 Carbon region of the XPS spectra of SO_2-plasma-treated polyurethanes immediately after treatment (A), after 4 days in air (B), and after 1 week in air (C).

bonded to sulfur, similar to those in Figures 5 and 6.

After the plasma-treated polyurethane has been in air for 4 days, XPS spectra were again collected. The spectra shown in Figures 12(B), 13(B), and 14(B) suggest that complex changes in surface chemistry are occurring. The lower energy peak in the sulfur region of the XPS spectrum shifts from 163 to 166 eV and increases in magnitude. The lower energy peak in the oxygen region at 532 eV increases. The low energy peak in the carbon spectrum also increases. The increase in the lower energy peaks in the XPS spectra can be seen in the ratios of the XPS peak heights in each of the three spectral regions listed in Table V.

After the material has been in air for 1 week, the XPS spectrum collected demonstrates no evidence of the lower energy peaks in the sulfur, oxygen, or carbon regions. The spectra in Figures 12(C), 13(C), and 14(C) are nearly identical to the spectra shown in Figures 7, 8, and 9, which are of the ammonia plasma-treated polyurethanes exposed to a sulfur dioxide gas flush.

The complex chemistry and morphology of the polyurethane make interpretation of these spectral changes difficult. One possible explanation is the time-dependent oxidation of some of the sulfur- and carbon-based groups. Another, more complex explanation involves the combination of free radical incorporation, surface rearrangement, and radical reaction. Free radicals can be generated in the plasma state but they can also be generated in the polymer substrate. It has been proposed that UV irradiation of a polymer substrate during plasma treatment can generate free radicals in the polymer. Yasuda has shown, using ESR, that such radicals can survive in the polymer substrate without reacting for months.[11] The segment mobility of the polyurethanes could aid the trapped radicals transport to the surface where they may react with oxygen in the air. Further surface rearrangements may drive these hydrophilic groups from the surface.

Interpretation of the XPS data on the polyurethanes in terms of the complicated proposed mechanism of radical incorporation, surface rearrangement, and subsequent reaction is tenuous. But the development of the proposed mechanism is based on a larger series of plasma treatment experiments performed using polyethylene.[15] Those experiments show the same time-dependent XPS peak growth and disappearance. Validation of the proposed mechanism would be difficult on the polyurethane substrates of interest but is being pursued with polyethylene model systems. In the future the mechanism may be put on a more quantitative basis when on-line plasma diagnostics such as optical emission and electron spin resonance spectroscopies become available.

The problem of surface mobility of these polymer systems is difficult to address. The lack of surface characterization techniques designed to function in the aqueous environment compounds the difficulty of investigating the phenomenon. Yet there are methods to circumvent these mobility concerns. Plasma polymerization can be used to deposit a smooth, highly crosslinked polymer film. The large degree of crosslinking insures that polymer surface mobility is decreased significantly. These surfaces can be derivatized via plasma deposition such that surface rearrangement may be minimized.

SUMMARY AND CONCLUSIONS

The use of plasma deposition to introduce sulfonate groups to the surface of a polyurethane has been demonstrated. Concerns of plasma chemical specificity and plasma reproducibility have been addressed with the development of an alternative derivatization scheme. Plasmas have been used as pretreatments to form active free radicals on the polymer film substrates. These films were then exposed to sulfur dioxide gas used as a derivatizing agent. The formation of sulfur-based reaction products on the surface was demonstrated by XPS analysis, which found significant sulfur incorporation on the polyurethane material when this reactive scheme was used.

Table V   Peak Height Ratios from the Carbon, Oxygen, and Sulfur Regions of the XPS Spectra of the SO₂-Plasma-Treated Polyurethanes after 0, 4, and 7 Days in Air

Region	XPS Peak Height Ratios		
	Carbon	Oxygen	Sulfur
Sample	282/285	532/534.5	165/168
A	0.23	0.16	0.29
B	0.23	0.48	0.40
C	0	0	0

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