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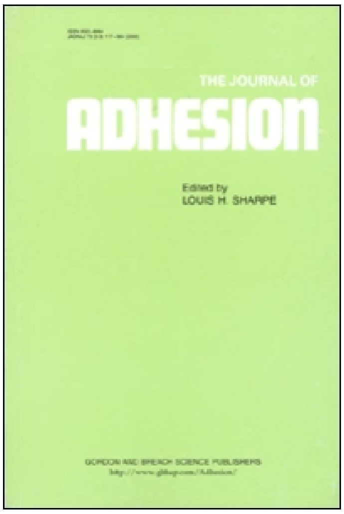

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Surface Restructuring of Polyurethanes and its Control by Plasma Treatment

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It was shown that when polyurethanes designed for use in biopolymer applications were immersed in orienting fluids, significant increases in their non-dispersive surface energies took place. The kinetics of the surface energy response were found to be a function of the immersion medium's acid-base interaction potential. Restructuring from the as-cast state, similar to that reported for two-component polyurethane adhesives, occurs in response to thermodynamic demands and is attributable to a preferential concentration of low energy segments in the surface region. Since shifting surface energies in polyurethanes may pose problems in biological applications, an attempt was made to crosslink the surface of the polymers by the use of cold, microwave plasma discharges with Argon as the treatment gas. Plasma treatments proved to be successful, in that polyurethane surfaces so modified responded much more weakly to changes in the polarity of contact media.

KEY WORDS: Polyurethanes; biopolymer applications; orienting fluids; surface free energies; acid-base interaction potential; microwave (cold) plasma; surface restructuring; surface crosslinking; surface modification; characterization by IGC.

INTRODUCTION

Polyurethanes (PUr) are among the synthetic polymers most frequently used in biological and biomedical applications. In this context it has long been recognized[1–3] that polymer surfaces should remain uncontaminated by the adsorption and adhesion of certain proteins. However, one of the characteristic features of two-component PUr esters and PUr ethers is that they tend to be phase separated into micro-regions where hard and soft segments predominate.[3–5] The separation confers considerable mobility to the polymer at temperatures above the glass transition. Accordingly, appreciable differences exist between bulk and surface compositions; for example, as was shown previously,[6,7] when PUr films are formed in air, in order to minimize the surface free energy, the lower energy soft segment tends to occupy

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the surface layer preferentially. The preferential surface localization of a hydrophobic component appears to be a significant factor in the preferential adsorption of certain plasma proteins and the resulting blocking of other protein molecules and platelets, notably serum albumin.[8] The mobility of PUr, akin to that of other polar group-containing polymers, also makes them subject to surface restructuring. That is, when PUr surfaces are exposed to liquid or solid "orienting" media, then significant compositional changes take place, driven by the new thermodynamic command to minimize the pertinent interfacial tension. The restructuring phenomenon, of obvious importance to all surface-sensitive properties of a polymer, has been the subject of considerable recent attention.[6,9–11] A change in surface composition toward an increase in hydrophilic constituents may be undesirable from the viewpoint of biomedical applications but, in the case of PUr adhesives, such a shift can benefit the application range of the polymer.[7] Time-dependent changes in surface composition, driven by the orienting nature of the substrate in contact with PUr, or other orientable polymers, imply, *inter alia*, accompanying changes in such properties of assemblies as adhesive bond strength, barrier and mechanical properties.

The objectives of the present research are based on the preceding considerations. They are to establish the restructuring capability of PUr specimens intended for biomedical use, and to explore surface modification strategies capable of stabilizing preferred surface compositions by the elimination or reduction of restructuring events.

EXPERIMENTAL SECTION

Materials

Two polyether urethanes samples were used throughout this work. Coded PUr-U1 and PUr-U2, they were supplied as aqueous dispersions by Becton Dickinson Inc. Analyses of the polymers resulted in characterization, reported in Table I. The nominal hard segment content in each is 37%, but with different soft segment molecular weights, as shown. DSC analysis defined T_g values for the soft segment. Surface

TABLE I
Structural Characteristics of Polyurethanes

sample	PUr-U1	PUr-U2
Nominal % hard segment	37	37
MW soft segment	1000	2000
Soft Segment T_g	−60°C	−70°C
Calculated ave. size of hard block	42 A°	63 A°
Hard/Soft segment ratios:*		
Surface region	0.10	0.055
Wt% hard segment, surface	35	19
Wt% hard segment, bulk	42–55	37–49

*From elemental analysis.

composition in samples prepared for XPS analysis was calculated from N/C—O ratios. PUr-U2 responded strongly to the non-polar air and vacuum environments involved in preparing for and undergoing the analysis, with a reduction in the hard segment content of the surface region. In the case of PUr-U1, the preparation of this sample produced only slight differences between bulk and surface compositions within the roughly 50–70 A° depth sensed by present XPS measurements.

Procedures

Surface restructuring in these polymers was studied by the immersion of dried PUr specimens in orienting and non-orienting media. Films of the PUr were prepared by placing the liquids onto degreased (acetone), washed (distilled water) and dried (120°C/20 min) microscope glass slides. They were then dried at 50°C/48 h and 0% relative humidity (R.H.) in a desiccator, followed by an additional 50°C, 48h. exposure in air at 50% R.H. Film thicknesses throughout were 0.15 ± 0.02 mm, as observed on fracture surfaces by microscopic (Dectac) analysis.

Surface energies of the starting materials were obtained from static contact angle measurements, using the Rame-Hart goniometer. Wetting fluids were *n*-decane, glycerol, formamide, α-bromonaphthalene, ethylene glycol and water. Following recently described procedures,[12] contact angles were measured as a function of contact time, and the value extrapolated to zero time was used as the characterizing parameter. Determination of dispersive and non-dispersive surface energies, (γ^d) and (γ^{nd}), followed from application of the harmonic mean approximations.[13] Reported surface energy data bear an uncertainty of ±8%. Contact angle data were the source of identification of restructuring capability for the PUr surfaces. These data were redetermined on specimens which had been exposed for specified periods to the following orienting fluids: water, benzene, formamide, and tetrahydrofuran (THF). The fluids were chosen because they have been designated as Lewis acids and bases by Gutmann's theory,[14] and assigned quantitative electron acceptor and donor numbers, AN and DN, respectively. Exposure was at controlled temperatures and contact with the orienting medium extended to 18 days. After removal from the immersion liquid, specimens were wiped with lint-free paper to remove excess liquid, then dried in a vacuum oven at 60°C for 48 h.

Dispersive surface energies $(\gamma)^d$ for the polymers were evaluated also by the method of inverse gas chromatography (IGC). IGC also generated values of the polymers' acid and base interaction constants, Ka and Kd respectively. The experimental protocols for these determinations have been fully discussed in the recent literature.[15–17] Briefly, the PUr were dried and conditioned by the same temperature/time/R.H. regime as described earlier. The dried films were comminuted manually to powders passing 80 mesh screens and packed in previously degreased, washed and dried stainless steel columns, 0.4 cm in diameter and 35 cm in length. The mass of polymer was 1.206 g for PUr-U1 and 1.177 g for PUr-U2. A Perkin–Elmer Sigma 2 gas chromatograph, equipped with hydrogen flame and hot wire detectors, was used in IGC determinations of retention volumes for the following vapor probes: the *n*-alkanes from C_5 to C_8, representing vapors interacting through dispersion forces only, acetone, diethyl ether, ethyl acetate, chloroform and

THF representing vapors again designated as acid, base or amphoteric.[14] Retention volumes, *Vn*, were obtained in triplicate over the temperature range 60–110 °C. Throughout, quoted values of *Vn* were reproducible within less than 4%. The link between *Vn* and the polymer γ^d was the previously justified[16,17] expression:

$$RT \ln Vn = 2N\,a(\gamma_1^d)^{1/2} \cdot (\gamma^d)^{1/2} + C \qquad (1)$$

where N is the Avogadro number, a is the area of cross section of the vapor molecule, γ_1^d is the dispersion surface energy of the vapor in the liquid state, C is an integration constant and RT have their usual meaning. The polymer γ^d was obtained from slopes of linear plots of $RT \ln Vn$ *vs* $a(\gamma_1^d)^{1/2}$ for the alkane vapors. The position relative to the alkane lines of *Vn* for the polar probes defined their non-dispersive contribution to the free energy of adsorption, and that value was then used according to the literature[15–17] to evaluate the polymer Ka and Kd. These interaction parameters are valid for the investigated range of T.

Attempts to control the restructuring of PUr surfaces made use of cold, microwave plasma (MWP) discharges. The principle of such discharges is now well-known;[18] in the present case, the aim was to promote surface crosslinking without the introduction of significant chemical changes to the PUr surfaces. In this regard we followed the concepts of CASING treatments, described some time ago by Schonhorn and coworkers,[19] and used Ar as the discharge gas. The apparatus used was modelled after that described in Ref. 18. It housed PUr films deposited on glass slides (as in the procedure for contact angle work). At the time of MWP treatment the polymer surfaces were either in their equilibrium states with respect to the non-polar air environment, or in the corresponding equilibrium state with respect to orienting media, as attained by previous immersion in water. MWP treatment was at 2.45 GHz, with the Ar gas pressure at 0.75 Torr. The applied power was 250 W. Plasma treatments were of 30–120 sec. duration, but the present account is restricted to samples that had received 60 sec. exposures. Following plasma treatment, the reactor vessel was brought to atmospheric pressure by a flow of Ar, and the treated specimens were transferred rapidly to desiccators under an Ar atmosphere where they remained for 24 h., in order to minimize oxidative reactions upon their re-entry to ambient conditions. The effectiveness of surface modifications was assessed by calculations of γ^{nd}, using contact angle determinations, as already described.

Diagnoses of surface composition, based on ratios of N/C—O, were from XPS spectra, obtained with an VG-ESCALAB 3 MK II instrument, and spectral deconvolution procedures which have been described elsewhere in detail.[20]

RESULTS AND DISCUSSION

IGC Characterization

The surface energetics and interaction capabilities of the polyurethanes were characterized by IGC, with results illustrated in Figure 1 for PUr-U2 at 60°C. Typical is

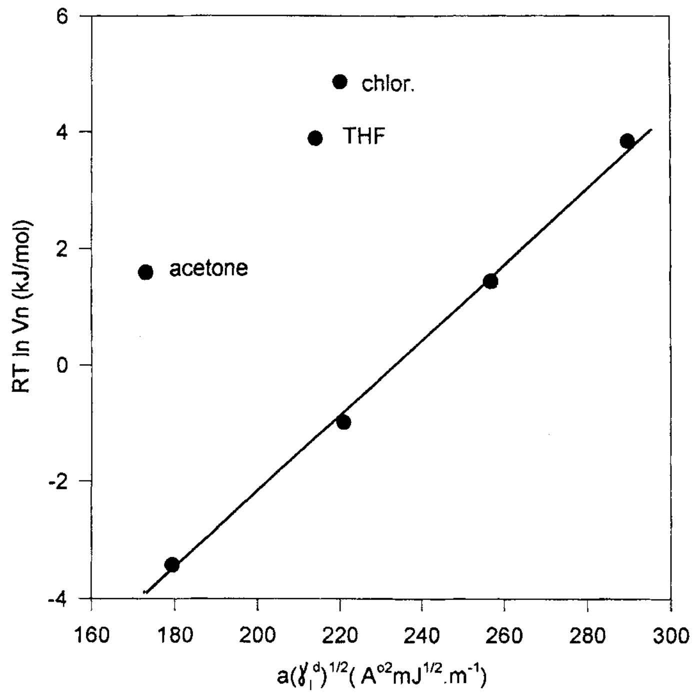

FIGURE 1 Retention volume *vs.* probe molecule area and surface tension for polymer PUr-U2 at 60°C; unlabelled circles are for *n*-alkane probes.

the excellent linearity generated by the alkane data, as well as the distinct deviation from the reference line of data produced by the polar probes. Evidently, this polyurethane behaves as an amphoteric product, the surface being able to interact strongly with both acid and base vapors.

A detailed view of surface properties is to be found in Table II. This presents, in the upper section, Gutmann's designation of AN and DN values for the vapor probes, enthalpies of adsorption and the Ka, Kd indexes for the polymers. These express, respectively, the solid's electron acceptor and donor potentials. In the lower section of the table are given the polymer γ^d values over the investigated temperature range. There are some differences between PUr-U1 and PUr-U2. The latter is the more balanced material, with significant values of both Ka and Kd, albeit with the balance of interaction forces shifted towards basicity. PUr-U1 registers as a base, without significant electron acceptor potential. As shown by the sum of interaction constants, the overall interaction potential of the two polymers is equal. The dispersion surface energy values are roughly similar to those reported for 2-component PUr adhesives.[7] That of PUr-2 is somewhat higher, perhaps due to the preferential accumulation of hydrophobic soft-segment component in its surface, as indicated by the diagnostic data in Table I. As expected, the γ^d values decrease monotonically with rising temperature in the 60–105 °C range.

TABLE II
Surface Characteristics of Polyurethanes and Vapor Probes

			ΔH**		Ka		Kd	
Polymer:	AN*	DN*	U1	U2	U1	U2	U1	U2
A: Acid-Base Parameters:								
Probe:								
Acetone	12.5	17	7.7	16.2	0.0	0.25	0.96	0.67
THF	8.0	20	15.2	9.2				
Chloroform	23.1	0	17.9	12.5				
Ether	3.9	19.2	3.0	7.7				
Ethyl ac.	9.3	17.1	10.0	13.8				

*Gutmann designation **Units are Kcal/mole

B: Dispersion Surface Energies:[+]

Temp. °C:	U1	U2
60	31	36
70	29	35
80	28	33
90	25	31
105	22	27

[+]Units are mJ/m^2

Contact Angle Results and Restructuring Events

Surface restructuring was followed, as noted earlier, by the sequential evaluation of surface energy data for samples that had been immersed in orienting fluids. Both PUr-U1 and -U2 were found to restructure under these conditions. The data in Figure 2 illustrate the point for PUr-U2, on immersion in water at 38.5, 60 and 83°C. The data follow patterns similar to those previously published for PUr adhesives.[6,7] A brief induction period is followed by a substantial increase in surface polarity, as indicated by the γ^{nd} datum. A steady state γ^{nd} was attained in about 100 h at the highest *T*, and near 180–200 h at 60°C. The rate of increase in γ^{nd} near room temperature is slow, and the experiment was discontinued prior to attaining the characteristic plateau. In earlier work,[6] the changes in γ^{nd} were attributed to the time-dependent diffusion of hard segments into the surface region of the PUr, driven by the demand to minimize the system's free energy, that is to say, essentially the interfacial tension with the polar medium. There it was observed also that the total surface energy remained roughly constant, in spite of the redistribution of hard and soft segments in the surface region. The close similarity between the present and earlier data suggests that, in the polymers synthesized for potential use as implant materials, a similar restructuring mechanism is in existence. The similarity alluded to is further demonstrated by the data in Table III. The constancy of the total surface energy is noted; the diminution in γ^d with increasing exposure time in the water medium is reasonable, in light of the proposed migration to the surface of the polar hard segment. The near constancy in γ^d and γ^{nd} in the first 2 days of immersion, also observed earlier,[6] may be attributed to a gradual plasticization of the polymer by

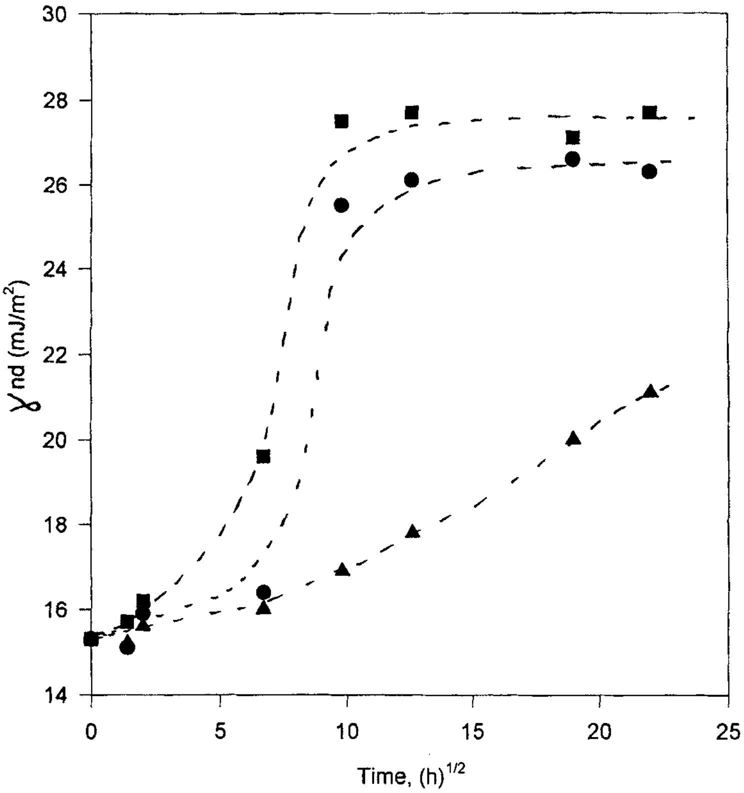

FIGURE 2 Showing time-dependent change in non-dispersive surface tension of PUr-U2 as a result of immersion in water. ■ 83°C; ● 60°C; ▲ 38.5°C.

water. Only after a sufficient increment in free volume has occurred, as a result, can the hard segment migration process come into effective operation.

An additional point is noteworthy: It concerns a comparison of γ^d values obtained from IGC (Table II) and from the contact angle measurements. An extrapolation of IGC data to 30°C places γ^d of PUr-U1 at 36 mJ/m^2, about 11 mJ/m^2 higher than the relevant contact angle datum in Table III, the difference being well above experimental uncertainties. Differences of this kind are to be expected from measurements on surfaces with significant variations in surface site energies.[21] The IGC measurement, utilizing a small quantity of molecular probes, is able to characterize selectively the presence of high energy surface sites. The contact angle datum, based on the use of a bulk droplet, reports an average value. On that basis, PUr-U1 displays a significant degree of surface heterogenenity. This is not unreasonable, given a surface composition combining the soft and hard segments of the polymer.

Alternative origins could be postulated for changes in the surface composition of urethane polymers. One of these is the possible chemical reaction between the polymer and the immersion medium; for example, an enolisation of the hard segment. Such origins would, of course, render the restructuring irreversible. Experimental

TABLE III
Surface Restructuring in Water (Immersion $T = 60°C$) Polymer PUr-U1

Imm.Time (h)	γ^d(mJ/m^2)	γ^{nd}(mJ/m^2)	γ_t(mJ/m^2)
0	24.9	18.1	43.0
2	25.1	18.2	43.3
4	24.1	18.6	42.7
44	20.6	18.9	39.5
96	18.2	24.4	42.6
160	17.6	24.9	42.5
360	17.7	26.3	44.0
432	17.2	26.3	43.5

evidence is to the contrary, however, as shown in Figure 3. Here, PUr-U2 has again been brought to its "restructured" equilibrium γ^{nd} by immersing the polymer in water at 60°C. Following that exposure, the polymer was placed immediately in contact with *n*-octane at 60°C, and the course of γ^{nd} values was followed for 30 days. The restructuring effect is reversible, at least partially. The surface energy parameter, at 19 mJ/m^2, was some 2.5 mJ/m^2 higher than the original value before contact with water; however, as shown in the figure, the experiment was discontinued before a

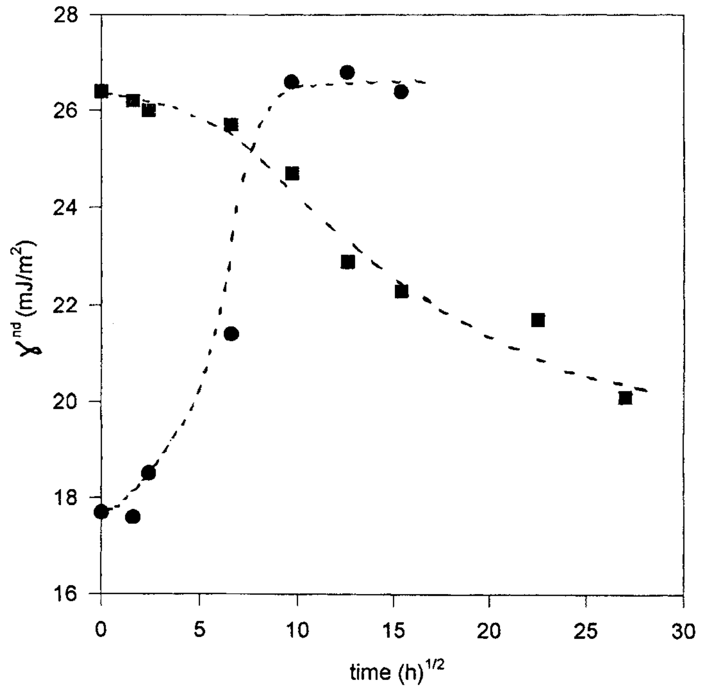

FIGURE 3 Showing the apparent reversibility of surface restructuring. ● PUr-U2 in water @ 60°C; ■ in *n*-octane @ 60°C.

steady state had been attained. The restructuring phenomenon, therefore, may be judged as substantially reversible.

Additional evidence may be offered to support the physical origins of surface restructuring. Logically, the strength of a thermodynamic drive for minimizing the interfacial tension between PUr and the immersion medium should vary with the orienting strength of the medium. The supposition may be tested by measuring the times needed to attain steady state values of γ^{nd} when the polymer is immersed in liquids with polarities ranging from the non-polar alkanes to the highly polar water. Samples of PUr-U2 were, therefore, immersed in THF, formamide and benzene, in addition to water and octane. These fluids may be characterized by Gutmann's AN, DN numbers. The sum of these numbers ranks water highest at 59, THF at 28 (see Table II), formamide at 11, benzene at 6 and, of course octane at 0. A reasonable expression of orienting strength then may be the sum of their Gutmann indexes. The times required to bring γ^{nd} to an equilibrium state in each of these fluids (at 60°C) was evaluated experimentally and the resullts expressed as a function of AN + DN in Figure 4. In the figure the restructuring time datum for octane (approx. 1050 h) has been extrapolated from a regression curve fitted to data of the polar media. The well-defined relationship shows that (isothermal) restructuring kinetics of these polymers are predictable, once the acid/base orienting potential of the contacting medium has been determined. That potential also affects the overall shift in γ^{nd}. For

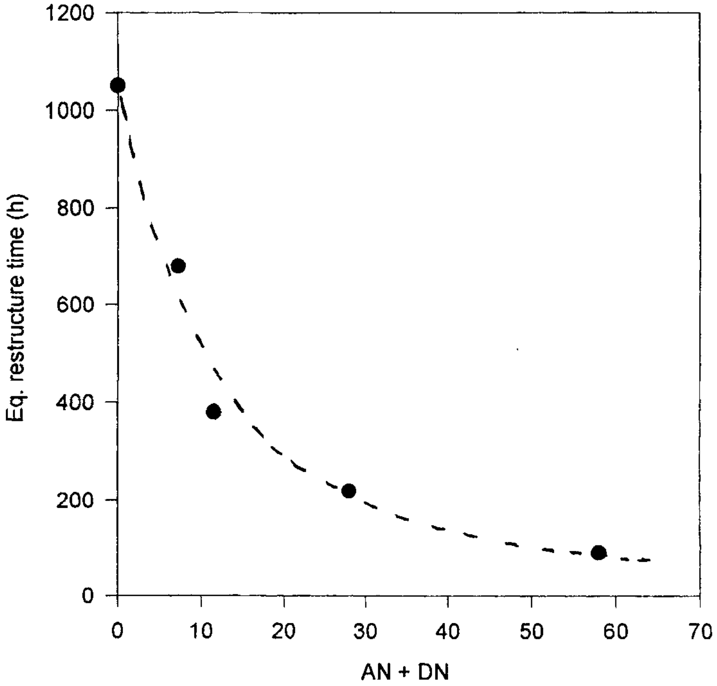

FIGURE 4 Restructuring time as a function of the medium's acid/base interaction potential. Polymer is PUr-U2 @ 60°C.

example, in the case of PUr-U1, water shifts the value to 26.3 mJ/m^2 (see Table III), THF to 21.7 mJ/m^2, while formamide and benzene lead to values of 20.5 mJ/m^2.

Effects of Plasma Treatment

An objective of our study, as stated earlier, was to explore the possibility of controlling surface restructuring by immobilizing the polymer surface in preferred states of surface composition and/or configuration. Surface crosslinking through the use of MWP treatments was the route selected to the goal. Polymer PUr-U1 was used in this portion of the work. The selection of Ar as the plasma gas was made in order to minimize any chemical changes in the surface composition. XPS analyses, reported in Table IV, substantiate the notion. The effect of plasma treatment on the N:C—O ratio is very slight, and the small decrease in the ratio is probably caused by some oxidation of the plasma-treated sample following its exposure to air. Immersion in water does lead to a minor increment in the ratio, and this may be interpreted as a rise in the surface concentration of the hard segment of some 7%. The increase seems too small to account for the massive changes in γ^{nd} observed when untreated PUr-U1 is immersed in water. Plasma treatment of the sample following extended exposure to water does not produce further changes in the apparent composition of the PUr surface. The XPS results then suggest that an appreciable degree of surface stability was conferred on the polymer by the MWP exposure, without completely eliminating its sensitivity to the contact medium. Further refining of plasma treatment variables is expected to produce superior results.

The effectiveness of plasma treatment is more obvious from an inspection of data in Figure 5. Here are plotted the paths of γ^{nd} for specimens which had been plasma treated in the extremes of PUr-U1 surface compositions and configurations. The air-dried sample (solid circles) shows a rise in γ^{nd} of less than 2 mJ/m^2 upon immersion in water, a much smaller increment than the 8 mJ/m^2 reported in Table III for the same polymer in the unmodified state. The plasma-treated sample that had first been brought to $\gamma^{nd} = 27.5$ mJ/m^2 by water immersion (solid squares, Fig. 5), again

TABLE IV
Effect of Immersion and of Plasma Treatment on Surface Composition of PUr-U1

Sample history	Surface N: C—O	Surface wt% hard segment
Original sample (*I*)	0.11	36
Bulk of original sample		39
I + plasma treat*	0.10_6	36
I + W Immersion 60°C		
2 h.	0.11	36
44 h.	0.12	38
360h. (*II*)	0.14_4	43
II + plasma treat*	0.14_0	43

*Refers to Argon plasma @ 150 W, 60 sec., 0.7 Torr

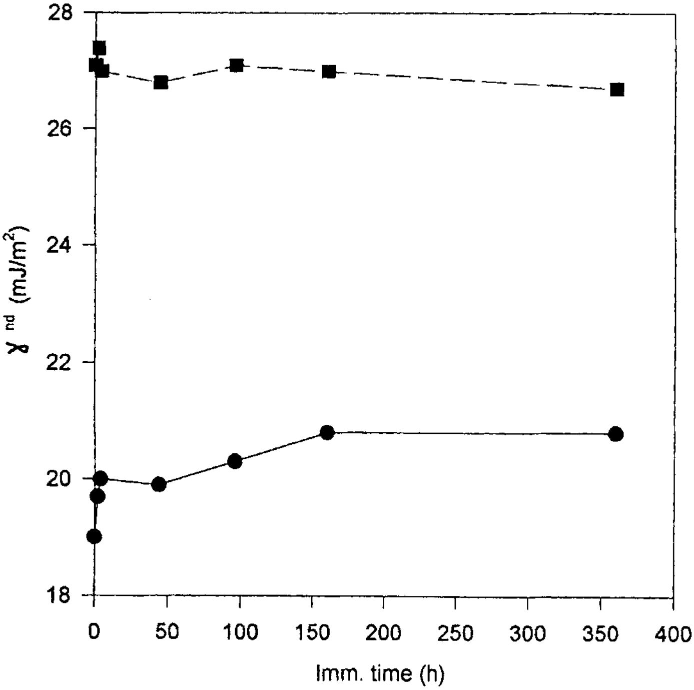

FIGURE 5 Apparent immobilization of surfaces by plasma treatment; response of PUr-U1 to immersion in orienting media: ● air dried sample, MWP-treated, immersed water, 60°C ■ sample equilibrated in water, MWP-treated, then immersed in octane, 60°C.

shows considerable stability when immersed in *n*-octane, the surface energy parameter decreasing by less than 1 mJ/m^2, as compared with >5 mJ/m^2 for an untreated specimen (see Fig. 3). Clearly, plasma treatment has led to a considerable stabilization of the PUr surface structure in both the more and less polar states. Again, additional refining of plasma treatment variables should lead to protocols which fully immobilize the polymer surface. It would seem possible, therefore, to use plasma treatments similar to those explored here to tailor the surface composition and configuration of PUr for superior performance in applications calling for the prevalence of either the soft or hard segment. Moreover, polymers so modified should be generally insensitive to changes in the polarity of environments with which they are in contact. In turn, this should reduce or eliminate property changes normally associated with surface restructuring phenomena.

CONCLUSION

* Polyurethanes evaluated for potential use in biomedical applications have been shown to undergo surface restructuring when placed in contact with media of known polarity, as characterized by their acid/base interaction potential.

- * The presence of the soft segment of PUr is favored in the surface region by contact with non-polar media; when in contact with polar fluids, the hard segment is preferentially oriented in the surface region.
- * The kinetics of the surface restructuring in polyurethanes have been shown to vary with the acid/base interaction potential of the contact medium.
- * Microwave plasma treatments, using Ar as the discharge gas, have been applied to polyurethane surfaces in both the soft segment-rich and the hard segment-rich states of composition. Following plasma treatment, polymer surfaces were partially immobilized, greatly reducing their restructuring tendencies.
- * Surface immobilization seems to offer an attractive route to tailoring PUr surfaces for the requirements of defined applications.

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