Water-Induced Surface Rearrangements of Poly(dimethylsiloxane−urea−urethane) Segmented Block Copolymers

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An investigation of the surfaces of linear, segmented block copolymers of poly(dimethyl-siloxane−urea−urethanes) by dynamic contact angle analysis is reported. The polymer films are immersed in water, the time-dependent advancing and receding contact angles are observed, and the contact angle hysteresis is reported. The initially hydrophobic polymer surfaces are observed to become more hydrophilic with long-term exposure to water. The advancing contact angles are relatively constant with immersion time; the receding contact angles decrease to some equilibrium value after a few days' exposure to water. It is proposed that the surfaces reorganize by a mechanism in which the hard block urethane−urea domains migrate through the soft block silicone to the polymer−water interface. The surface reorganization kinetics are discussed in terms of the effects of annealing as well as the average molecular weight of the soft block.

Introduction

The goal of our research is to discern the compositional and morphological features relevant to the formation of minimally adhesive surfaces, which inhibit the settlement of marine organisms. Our work is part of an effort to develop nontoxic, antifouling coatings for use in marine environments.

Historically, successful antifouling marine coatings contain toxicants such as organotin and copper compounds.[1] Such ablative and toxicant-release materials are becoming environmentally unacceptable because of their effects on nontarget marine organisms and the difficulty associated with their disposal. Our research focuses on the need for improved understanding of minimally adhesive materials which would provide nontoxic alternatives to traditional marine coatings.

Prior research has typically revolved around the development of low surface energy materials with the idea of reducing the potential chemical interactions between the fouling organisms and the surface of the coating.[2−6] This is an area pioneered by Griffith et al.[7]

We believe that, in addition to low surface energy, the successful material should satisfy two other criteria. First, it is important that the surface has a low surface glass transition temperature, T_g, to minimize *mechanical* locking of a fouling organism. We suppose mechanical locking arises when a low-viscosity bioadhesive precursor invades surface imperfections, invariably present in real coatings, and cures to a high modulus bioadhesive. The rationale behind requiring a low surface T_g stems from the assumption that it is easier to separate a high-modulus adherend from a low-modulus substrate through the easy deformation of the latter. Second, the surface should remain *temporally stable* in situ with respect to low surface energy and low surface T_g.

To systematically investigate the temporal stability of polymer surfaces in the presence of liquid water, we have begun to characterize a series of linear and network polymers containing poly(dimethylsiloxane) as the surface active component. This paper addresses the in situ behavior of a multiphase linear dimethylsiloxane−urea−urethane that has been synthesized and characterized in our laboratory.[8,9] A number of investigations of surface reorganizations in the presence of water have been reported for polymers.[10−20]

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Segmented block copolymers of dimethylsiloxane−urea−urethanes are known to phase separate in the bulk and at the surface.[9,21,22] Phase separation in the bulk arises from the immiscibility of the urethane segment and the siloxane segment. At the surface, phase separation is enhanced by the cooperative effects of surface free energy minimization and hard and soft segment immiscibility. The result is an increase in the volume fractions of siloxane soft block at the surface and of the urethane hard block at the subsurface.[9] At first approximation then, the polydimethylsiloxane−urea−urethane (PDMS-PUU) segmented block copolymers satisfy the dual criteria of low surface energy and low surface T_g and therefore are potentially good candidates for minimally adhesive surfaces. It is therefore desirable to investigate the time-dependent behavior of the polymer surface in contact with a wetting medium. In the present study, we monitor the in situ temporal stability of the PDMS-PUU polymer surfaces using dynamic contact angle analysis.

Experimental Section

Materials. Poly(dimethylsiloxane-urethane−urea) (PDMS-PUU) segmented block copolymers based on aminopropyl end-capped dimethylsiloxane ($H_2N(CH_2)_3(Si(CH_3)_2O)_nSi(CH_3)_2(CH_2)_3$-$NH_2$), isophorone diisocyanate (5-isocyanato-1-(isocyanato-methyl)-1,3,3-trimethylcyclohexane), and 1,4-benzenedimethanol were synthesized by a two-step polymerization, described previously.[8] Isophorone diisocyanate and benzenedimethanol were purchased from Aldrich Chemical Co. (Milwaukee, WI). Aminopropyl end-capped poly(dimethylsiloxane) oligomers of differing average molecular weights were used. The 2400 ($n = 30$) and 10,000 ($n = 133$) PDMS oligomers were kindly provided by Dr. O. Yilgör of Goldschmidt Chemical Corp. (Hopewell, VA); the 2700 ($n = 363$) oligomer was purchased from United Chemical Technologies (Bristol, PA). Octadecyl-trichlorosilane (OTS, $C_{18}H_{37}SiCl_3$, 95%) and sodium azide (NaN$_3$, 99%) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Reagent-grade tetrahydrofuran and HPLC grade hexane were used as solvents. Glass cover slips (24 × 30 × 0.2 mm^3) were used as substrates and were purchased from Fisher Scientific (Pittsburgh, PA). Water for the dynamic contact angle measurements was purified to type I with a Barnstead Nanopure Bioresearch grade system and had an average resistivity of 18 MΩ cm. The surface tension of the contact angle probe water was checked daily and had a typical value of 72.6 dyn/cm.

Methods. The polymers differed in the molecular weight of the PDMS segments. Molecular weights of 24K, 10K, and 27K PDMS were used in a reaction stoichiometry of 1 poly-(dimethylsiloxane):2 benzenedimethanol:3 isophorone diisocyanate, giving PDMS weight fractions of 0.69, 0.90, and 0.97, respectively.[8]
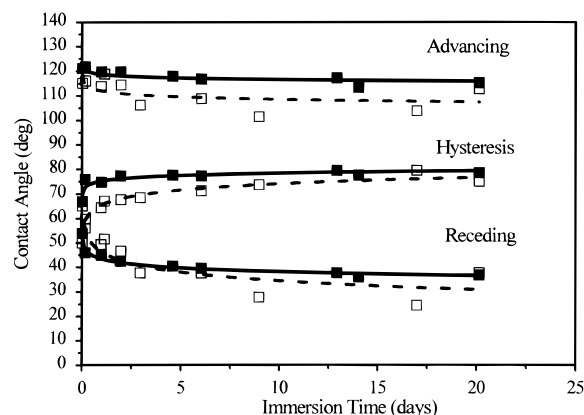
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Figure 1. Contact angle and hysteresis vs immersion time for 2.4K PDMS-PUU: (■) 2.4K nonannealed; (□) 2.4K annealed.

PDMS-PUU films were dip-coated onto glass cover slides from a 2 w/v % tetrahydrofuran solution. To enhance polymer adhesion, the cover slides were made hydrophobic by self-assembly of octadecyltrichlorosilane prior to dip-coating the polymer. The films were air-dried for 24 h and then dried at reduced pressure and room temperature for 72 h. Half of the films were then annealed at 120 °C for 15 min; half of the films were not annealed. The annealing temperature was chosen to be about 25 °C above the highest transition temperature (about 100 °C) detected by dynamic mechanical analysis.[8]

Dynamic contact angle (DCA) measurements were performed on the polymer surfaces using a Cahn DCA Model 312 analyzer (Cerritos, CA). The rates of immersion and withdrawal were 100 μm/s; the top and bottom dwell times were 0 s. Samples were immersed in a 100 ppm NaN$_3$ solution, a known biocide, to prevent the growth of eucaryotic organisms that might affect the contact angle. The samples were removed at regular intervals, rinsed, and advancing and receding water contact angles were recorded. The samples were then placed back in the NaN$_3$ immersion solution. Several duplicate annealed and nonannealed samples were run. Each advancing/receding contact angle data point is the average of the last three out of five immersion/withdrawal cycles. The hysteresis data give the average value, over several samples, of the advancing minus receding contact angles.

Results

Contact Angles. The advancing water contact angle, θ_a, is sensitive to the hydrophobic surface component, and the receding contact angle, θ_r, is sensitive to the hydrophilic surface component.[23,24] The time-dependent contact angle data for the 2.4K, 10K, and 27K PDMS-PUU films are given in Figures 1−3. In the figures, the advancing and receding contact angles were fitted with an equation of the form $y = m \ln(x) + b$, to show trends in the data. Table 1 gives the initial and final values of the advancing and receding contact angles obtained by solving the fitted equation above for $x = 1$ and 20 days. The initial advancing contact angles for all three polymers have similar values, which do not change significantly in the course of the experiment. High-θ_a values show that the polymer surfaces have a hydrophobic component that is temporally stable with respect to water immersion. The high-θ_a value is expected and supports earlier studies that show that

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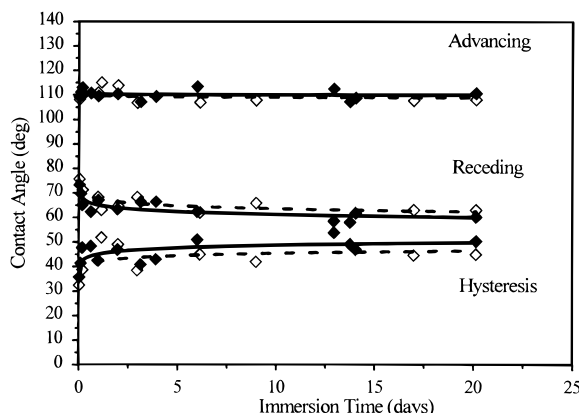
Figure 2. Contact angle and hysteresis vs immersion time for 10K PDMS-PUU: (◆) 10K nonannealed; (◇) 10K annealed.
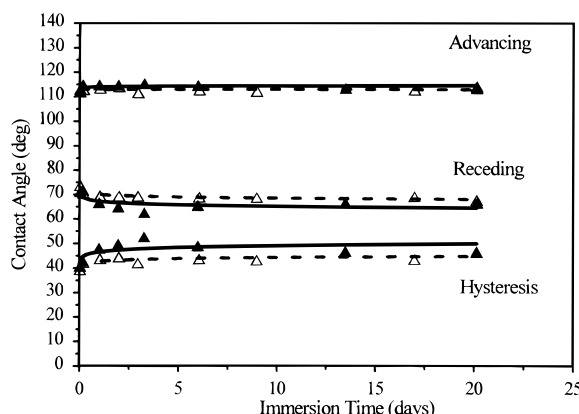

Figure 3. Contact angle and hysteresis vs immersion time for 27K PDMS-PUU: (▲) 27K nonannealed; (△) 27K annealed.

Table 1. Initial and Final Values of Advancing and Receding Contact Angles

	annealed		nonannealed	
	initial	final	initial	final
Advancing Contact Angles				
2.4K	112	108	119	116
10K	110	109	110	110
27K	113	113	114	114
Receding Contact Angles				
2.4K	46	31	44	37
10K	68	62	65	60
27K	70	68	67	65

[a] Contact angles obtained by solving $y = m \ln(x) + b$ for $x = 1$, 20 days. All values in degrees.

many siloxane-containing copolymers phase separate in the bulk and at the surface.[9,25] Surface properties are typically dominated by the surface enrichment of poly-(dimethylsiloxane), and the phase separation may be enhanced by annealing above the T_g or melting point of the hard segment.[9] In the present experiment, significant differences in θ_a due to annealing are observed only in the 2.4K sample.

The receding contact angles, θ_r, for the three films show a greater dependency on time and material. The initial and final θ_r values, given in Table 1, appear to be dependent upon the molecular weight of the soft block. The 2.4K has the lowest receding contact angles; the 10K and 27K values are higher. The similarity of the initial 10K and 27K θ_r values means that these two

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Table 2. Initial and Final Hysteresis Values[a]

	hysteresis values			
	annealed		nonannealed	
	initial	final	initial	final
2.4K	66 (46)	74	75 (64)	78
10K	42 (31)	44	45 (30)	49
27K	43 (39)	44	47 (40)	48

[a] Initial values determined by difference using Table 1. Values in parentheses determined by linear extrapolation of hysteresis vs (time)$^{1/2}$ to time = 0. Final values determined by plotting 1/hysteresis vs 1/time and taking the *y* intercept. Because of differences in fitting methods, the final values above do not exactly coincide with those obtained using Table 1. All values in degrees.

surfaces have similar initial hydrophilic components that somehow differ from that of the 2.4K surface by similar amounts. In each case, θ_r decreases with immersion time. The relative decrease in θ_r is greatest for the 2.4K film, followed by the 10K film. The 27K θ_r is nearly invariant with immersion time. Annealing effects are resolved to the greatest degree in the 2.4K receding contact angle.

Hysteresis. Hysteresis is the difference between the advancing and receding contact angles. Because it includes both θ_a and θ_r, hysteresis is a convenient measure of surface heterogeneity and, when observed over time, a convenient measure of surface change. Taken another way, since θ_a is relatively invariant, any change in hysteresis arises primarily in the θ_r and is linked with an apparent change in the surface high-energy component. The change in θ_r may arise from a change in either the type or the surface area fraction (relative to the hydrophobic component) of the hydrophilic moiety. From Figures 1−3, the hysteresis of each film increases with immersion time. The hysteresis curves show a rapid initial increase, followed by a slow increase toward some equilibrium value. Initial and final hysteresis values are given in Table 2. The hysteresis is dependent upon the material, sample annealing, and time of immersion. The annealed samples show the lowest initial and final hysteresis. In general, the overall hysteresis change is greater for the 2.4K sample than for either of the 10K or 27K samples, and greater for the annealed samples than the nonannealed samples.

Discussion

The value of the DCA measurement is the easy determination of the advancing and receding contact angles. In the DCA method, a relatively large area is interrogated compared with the sessile drop method. Hysteresis is always present in polymer films and is caused by metastable states at the solid-air and solid-water interfaces. Hysteresis has been attributed[26] to surface roughness, chemical heterogeneity, and impurities in the probe liquid. There is a growing body of evidence to suggest that, in the absence of other effects, surface chemical heterogeneity may be the primary cause of hysteresis.[23,27−30] Taken together, θ_a and θ_r (as

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the hysteresis) give a single observable which is both convenient to use and sensitive to small changes in surface hydrophilicity and surface hydrophobicity.

Polymer surfaces generally reorganize in response to a contacting medium.[5,6,10−15] Typically, surface reorganization occurs through hydration and swelling, resulting in the emergence of the swollen part of the polymer at the surface,[16] or by reorientation of the polymer backbone, segments, or pendant groups, resulting in the presentation of different molecular moieties at the surface.[12] Siloxane−urea[25] and polyether−urethane[17] block copolymers have been described as island domains of hard block in a sea of soft block. The matrix mobility of the soft block above its T_g allows for movement of the hard and soft phases relative to one another.[17] In the present paper, we propose that the surface reorganizes through a mechanism in which the hard-block segments of the linear block copolymer migrate to the water surface. Such a mechanism has been described previously by Tezuka[10] and involves the penetration of water through the surface layer of soft-block PDMS, formation of a hard-block PUU−water interface, and the emergence of the PUU domain through the PDMS layer. According to Tezuka, the principal driving force for such a surface rearrangement process is the interfacial free energy gap between the initial and final states of the interfaces.[10] The kinetics of the rearrangement mechanism are not unlike the adsorption of a solute from solution onto an interface.[31] To the extent that the hysteresis is proportional[23] to the amount of hard-block PUU at the surface, one may use the time-dependent value of hysteresis as the observable in a surface-adsorption kinetics treatment.

Heller[32] has examined the time dependence of the adsorption of polymers from solution onto an interface and we have followed his general treatment here. The present hysteresis vs time data may be fit using an equation of the form

$$y = \frac{t}{kt + k'} \tag{1}$$

where y is the hysteresis and t is the time in days. Equation 1 may be rearranged to

$$t/y = k' + kt \tag{2}$$

where k' and k may be obtained from the plot of (time/hysteresis) vs time in Figure 4. The good performance of eq 2 follows from the figure. The values of k and k' obtained are given in Table 3 and are used in eq 1 to fit the raw data in Figure 5. Note the strong dependence of k and k' on the molecular weight of the PDMS and annealing effects. From eq 2, we may determine the rate of hysteresis change using an equation of the form

$$\frac{dy}{dt} = \frac{k'}{(kt + k')^2} \tag{3}$$

The initial rates at time equals zero are given in Table 3. The most rapid change is seen in the nonannealed 2.4K and 27K samples. The annealed 2.4K and 27K samples exhibit the slowest approach to equilibrium; the
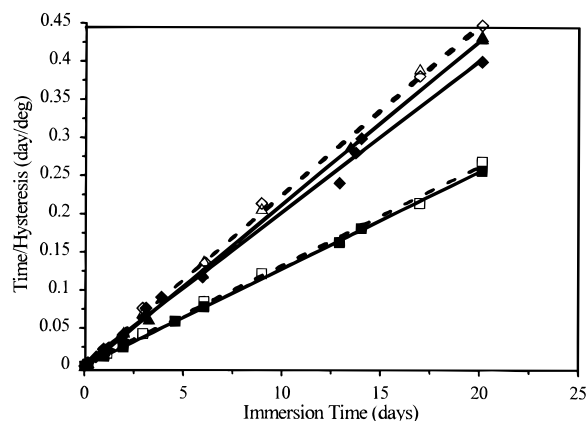
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Figure 4. Test of equation $t/y = kt + k'$: (■) 24K nonannealed; (□) 24K annealed; (◆) 10K nonannealed; (◇) 10K annealed; (▲) 27K nonannealed; (△) 27K annealed; − nonannealed; (− − −) annealed.

Table 3. Values of the Constants k and k'[a]

	$k/10^{-2}$	k' (days)/10^{-3}	rate (day^{-1})/10^2 at $t = 0$
2.4K nonannealed	1.28	0.362	27.6
2.4K annealed	1.34	1.82	5.49
10K nonannealed	2.05	2.39	4.18
10K annealed	2.26	1.03	9.71
27K nonannealed	2.08	0.429	23.3
27K annealed	2.25	1.04	9.61

[a] Values of k and k' are determined from Figure 4, eq 2. Rates of change of hysteresis are derived from eq 3.
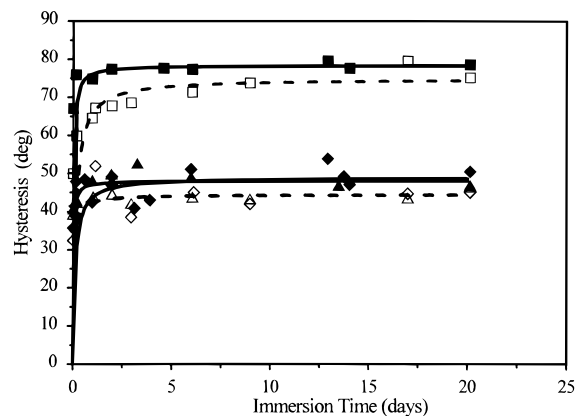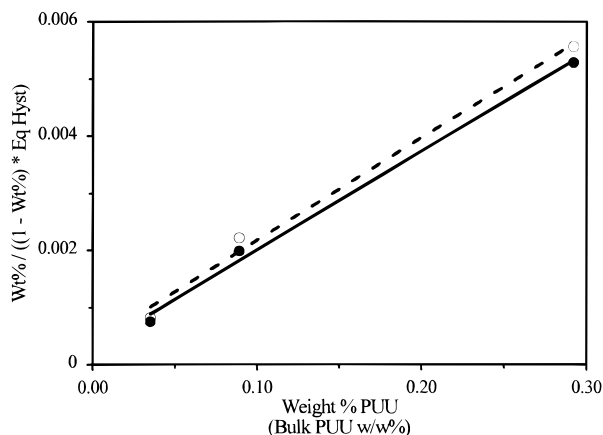

Figure 5. Hysteresis vs immersion time. (■) 24K nonannealed; (□) 24K annealed; (◆) 10K nonannealed; (◇) 10K annealed; (▲) 27K nonannealed; (△) 27K annealed; − nonannealed; (− − −) annealed.

27K being the faster of the two. At present, we are unable to explain the 10K behavior. However, it is interesting to note the similarities between the 10K nonannealed and the 2.4K annealed samples and between the 10K annealed and the 27K annealed samples.

We can determine the equilibrium hysteresis values by taking the y intercept of a plot of (1/hysteresis) vs (1/immersion time) (not shown). The equilibrium hysteresis values are given in Table 2. The equilibrium hysteresis data are consistent with earlier ESCA studies[9] of the present materials. The ESCA data revealed measurable differences between the annealed and nonannealed PDMS-PUU surfaces; the annealed surfaces had a higher percentage of poly(dimethylsiloxane). In addition, the annealed and nonannealed 2.4K samples had a higher surface fraction of hard block than either

Figure 6. Test of BET equation: ($\bullet$) nonannealed; ($-$) nonannealed; $Y = 0.0173X + 0.000285$; ($\bigcirc$) annealed; ($- - -$) annealed; $Y = 0.0179X + 0.000385$.

Figure 7. BET isotherm: ($\bullet$) nonannealed; ($\bigcirc$) annealed; ($-$) nonannealed; ($- - -$) annealed.

of the 10K or 27K samples. In the present study, the difference in hysteresis of the annealed and nonannealed 2.4K samples is greatest in the early period of immersion; a difference that diminishes with increased immersion time. The 10K and 27K samples were nearly indistinguishable from one another in their respective annealed and nonannealed equilibrium states.

At this point, we may begin to develop an adsorption isotherm using the equilibrium hysteresis values. The equilibrium hysteresis values may be fit using a form of the BET equation:[33,34]

$$\frac{x}{n(1-x)} = \frac{1}{cn_m} + \frac{(c-1)x}{cn_m} \qquad (4)$$

where x is the weight percent (w/w%) of the hard block

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in the bulk polymer and n is the equilibrium hysteresis. The BET constant, c, and n_m, which describes the volume of an adsorbed monolayer, though perhaps meaningless in the present discussion, may be evaluated from the slope and the intercept of the linear regression fit of a plot of $(x/n(1-x))$ vs x, shown in Figure 6. The fit is remarkably good, considering the assumptions that have been made during the present treatment. Furthermore, a plot of the (equilibrium hysteresis/n_m) vs weight percent, x, of hard block (Figure 7) has the general shape of a type II or type IV BET isotherm.[33] Such isotherms are common in the case of physical adsorption onto solid surfaces. It is unlikely that a "monolayer" of hard block erupts at the polymer surface. In the present material, perhaps only a small percent of the equilibrated wetted surface is hard block. We attempted to scale the y axis in Figure 7 in order to correlate the observed hysteresis (and contact angle) change to the amount of "adsorbed" hard block at the polymer water interface. Initial ESCA measurements of the water stored polymers were inconclusive, however, which we attributed to the effect of the high vacuum on the samples.

Conclusions

The surface of various segmented block copolymers has been studied using dynamic contact angle analysis. It appears that, from changes observed in the contact angle hysteresis, the polymer surfaces rearrange in response to prolonged contact with water. The time-dependent surface rearrangement is dependent upon the molecular weight of the soft block and sample history. Samples with the highest concentration of hard block showed the highest degree of hysteresis before and after water immersion. Nonannealed samples showed the greatest rate of change in the early stages of immersion and the greatest hysteresis at equilibrium. The equilibrium hysteresis is consistent with previous ESCA data that show a measurable difference between the annealed and nonannealed samples, between the 2.4K samples and the 10K and 27K samples, but not between the 10K and 27K samples. The equilibrium hysteresis may be fit using the BET equation, which suggests that the surface-adsorption kinetic treatment may be valid. To the extent that the contact angle hysteresis is sensitive to the relative amounts of surface hard block and soft block, the change in hysteresis with immersion time may arise from the migration of the hard block to the polymer−water interface in a fashion similar to that of molecules adsorbing onto a surface from solution.