Synthesis and Surface Energy Measurement of Semi-Fluorinated, Low-Energy Surfaces†

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ABSTRACT: The surface energy and stability of pendent semifluorinated groups (SFG) attached to the surface of PDMS were measured using the JKR technique. SFG, made up of a flexible hydrocarbon segment and a mesogen, i.e., the fluorocarbon segment, combine the low surface energy aspect of a ($-CF_2-$) and ($-CF_3$) surface with a resistance to surface reconstruction. An acid chloride group present on the end of the hydrocarbon segment allowed the SFG to be covalently attached to the surface of hydrolyzed elastomeric PDMS model networks. Whereas the hydrolyzed PDMS surfaces had surface energies of 1−10 J/m^2 and showed large adhesion hysteresis, the SFG-treated surfaces displayed a minimum adhesion hysteresis and had a surface energy of ∼ 14.5 mJ/m^2. This result suggests that in the SFG-modified surfaces both ($-CF_2-$) and ($-CF_3$) groups cover the surface. As the extent of hydrolysis of the PDMS networks increased, the density of attached SFG increased (as shown by XPS results), but the surface energy remained constant. No effect of length of time the networks were kept in contact or the rate of unloading was observed.

1. Introduction

Low-energy polymer surfaces are useful for a number of applications, such as soil-resistant and breathable textiles. While fluorinated surfaces have excellent low energy properties, they must also have a resistance to surface disordering to be useful in such applications. To introduce this necessary quality, we have developed a material with liquid crystalline (LC) characteristics: pendent semifluorinated groups (SFG). Each SFG is of the form: $F(CF_2)_m(CH_2)_nCOCl$ where the lengths of the hydrocarbon and fluorocarbon segments may be varied. It has been shown that if the fluorocarbon segment is long enough, it may act as a mesogen to direct the formation of a LC phase in which the SFGs are closely packed.[1−5] Just as in many LC materials, the flexible spacer allows the mesogen units to align themselves parallel to each other thus facilitating close packing and providing lateral stability in the fluorinated surface. The hydrocarbon units also promote solubility of the SFG.[6] In the best case, the mesogens would be close-packed perpendicular to the substrate. This would result in a surface that would have the greatest stability, and it would be covered by ($-CF_3$) groups, which would provide the lowest surface energy. Thus a well-defined low-surface-energy layer could be created that would cover the entire surface and prevent surface reconstruction.

Wang et al.,[6] have synthesized SFG with various lengths of the flexible spacer group and the fluorinated segment. These SFG were then attached, via the acid chloride group, to anionically polymerized hydroxylated poly(styrene-*b*-1,2,3,4-isoprene). They found that by varying the lengths of the spacer group and the fluorinated segment, the side chains formed different LC phases that in turn changed the surface tension and surface stability. SFGs with 8 and 10 ($-CF_2-$) units were found to form more highly ordered structures than those with fewer ($-CF_2-$) units. Powder X-ray diffraction of the SFG with the longer fluorinated segments revealed a nearly uniform close packed surface. Contact angle measurements of surfaces with these SFG yielded a surface tension of 8 mJ/m^2. These surfaces showed no noticeable surface reconstruction or change in surface tension when exposed to water for 2 weeks. As the length of the hydrocarbon unit increased, the solubility and the thermal stability of the SFG improved. In this paper we will examine the surface energy of the SFG with $m = 8$, and $n = 6$.

To measure the surface energy of this SFG, we utilized the so-called JKR test.[7] This simple technique based on contact mechanics is now well recognized for its ability to quantitatively measure the strain energy release rate, G, required to maintain a radius of contact, a, between two elastomeric hemispheres under a contact force, P. G is described by the following generalized JKR equation which must replace the standard form if G is a function of a[8] or da/dt[9]

$$G(a) = \frac{(P_H - P(a))^2}{6\pi K a^3} \tag{1}$$

where K is a bulk elastic stiffness term ($=2E/(3(1-\nu^2)$, E is Young's modulus, and ν is Poisson's ratio) that is determined from the a vs P data during loading. $P_H = Ka^3/R$ is the Hertz contact pressure (the pressure required to produce the measured radius of contact if there were no adhesive forces, i.e., $G = 0$), and R is evaluated from the combination of the radii of curvature

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of the two hemispheres (R_1 and R_2) as $R^{-1} = R_1^{-1} + R_2^{-1}$. In systems that do not display interface reconstruction under equilibrium loading and unloading of P, G is equal to the work of adhesion, W. The W measured when two identical surfaces are brought together under equilibrium conditions is equal to 2γ where γ is the surface energy.

To use the JKR technique to measure γ of the SFG, they must be attached to the surface of elastomeric hemispheres. Poly(dimethylsiloxane) (PDMS), $T_g \approx -120$ °C, was used to this end. The surface of these model networks was hydrolyzed by immersion in a weak hydrochloric acid aqueous solution. This hydrolysis produces silanol groups that remain just below the methyl-covered surface of PDMS in air. When two such hydrolyzed networks are brought into contact, a surface reconstruction may occur such that the silanol groups from opposite sides of the interface can condense (with water as the leaving group) or form hydrogen bonds. We have seen evidence of these reconstruction reactions in the large adhesion hysteresis displayed by the hydrolyzed PDMS networks.[9] We have also shown that the amount of adhesion hysteresis is directly correlated with the length of exposure time of the networks to the hydrochloric acid solution.

The acid chloride end groups of the SFG can react with the silanol groups, thereby permanently attaching the SFG to the surface. Thus the surface energy of the SFG, and of any chemical moiety, may be measured by the JKR technique by attaching it to a hydrolyzed PDMS surface.

2. Experimental Section

Model PDMS networks were synthesized according to the technique described by Patel et al.[10] The sol-fraction of these networks was less than 1%; nevertheless, all networks were extracted. To hydrolyze the surface of the PDMS, the networks were placed on microscope slides and immersed in a 0.1 M hydrochloric acid aqueous solution for specified lengths of time ranging from 30 min to 12 h. After they were removed, they were allowed to dry in a hood for 12 h, and then they were placed under vacuum for an additional 12 h.

The details of the SFG synthesis may be found elsewhere.[6] Briefly, semifluorinated 1-alcohols are synthesized and then oxidized to create semifluorinated acids. To attach the SFG to a hydrolyzed PDMS surface, these acid end groups were replaced with acid chloride groups by a reaction with thionyl chloride ($SOCl_2$):

$$F(CF_2)_m(CH_2)_nCOOH + SOCl_2 \rightarrow F(CF_2)_m(CH_2)_nCOCl + SO_2\uparrow + HCl\uparrow$$

A 1:3 molar ratio of the semifluorinated acid to $SOCl_2$ was used. This mixture was allowed to stir for 4 h. The excess unreacted thionyl chloride was removed by using low heat while applying vacuum with a base trap and a cold trap. After 10 min, the solution turned from clear to cloudy and its volume was reduced by half. No further solvent removal was noted after 30 min, and the remaining solution was then distilled under vacuum. The end-capping reaction yield was 90%.

To react the acid chloride end group with the hydrolyzed PDMS surface, the SFG was put into solution in dry tetrahydrofuran (THF). These were combined in a ratio of 0.8 g of SFG: 82 mL of THF and stirred for 5 min. Two PDMS surface treatments with this mixture were used. In one, the SFG mixture was quickly pipetted on to the PDMS networks so as to form a "puddle" on top of them. This setup was kept in a desiccator under vacuum for 12 h, at the end of which time the puddle had evaporated, leaving a crust of SFG behind. The second technique was to put the PDMS networks on silicon wafers and immerse them in the SFG−THF solution overnight in an airtight round-bottom flask. After both of these treatments the PDMS networks were rinsed vigorously for 5−10 min with methanol and acetone to remove any residue or unattached groups from the surface. Any residual solvent was removed by placing the networks under vacuum for 12 h. The samples made by the immersion method were found to yield inconsistent results, therefore all data presented here are from networks treated using the "puddle" method.

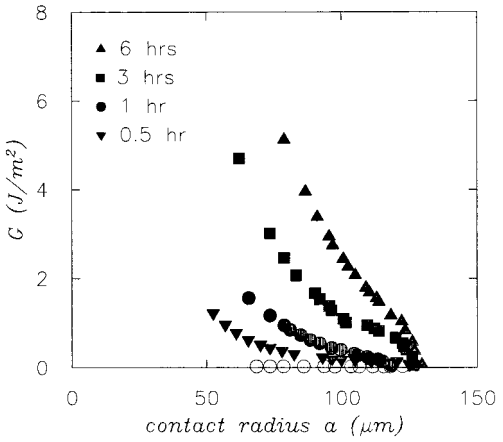

Figure 1. Effect of the exposure time in a 0.1 M HCl solution on the adhesion hysteresis of PDMS networks. The open circles are the unloading and loading data for the model networks before hydrolysis. The filled symbols are the unloading data for networks hydrolyzed for the times shown in the legend.

The JKR technique and apparatus that was used has been described elsewhere.[8,11,12] Briefly, it consists of bringing an elastomeric hemisphere into contact with a similar hemisphere. Both hemispheres have the same treatment history. Unless otherwise noted, a load is applied at a constant rate of ~2.5 μN/s until a maximum load of about 1 mN is reached. The contact is maintained at the maximum load for 6 h and then unloaded at the same rate until the elastomeric hemispheres separate. Throughout the experiment the radius of the area of contact is measured at fixed intervals of applied load. Due to the very low γ of the treated PDMS networks, the hemispheres had to be attached to the testing apparatus via double-sided tape. The samples were in contact with the adhesive tape for the minimum amount of time necessary to perform the experiment; it is unlikely that there was any effect from the adhesive material on the results.

3. Results and Discussion

Figure 1 shows the results of the JKR experiment on the ideal networks before and after hydrolysis. Prior to hydrolysis, G of the PDMS networks was independent of a during both loading and unloading and was equal to ~ 44 mJ/m^2, the value of the work of adhesion for this system. An insignificant amount of hysteresis was observed between the results from the loading and unloading experiments.

After hydrolysis there was a dramatic change in the unloading experimental results. While the loading G vs a curve remained unchanged for all hydrolysis times, the unloading G vs a curves were seen to increase as the length of exposure to the HCl solution increased. Longer treatment times in 0.1 M HCl produced curves that achieved even larger values of G. Subsequent experiments revealed that the adhesion hysteresis is due to the presence of silanol groups in the surface of the network that can form chemical bonds across the interface.[9]

Treatment of the hydrolyzed PDMS surface with the SFG results in almost complete removal of the hyster-

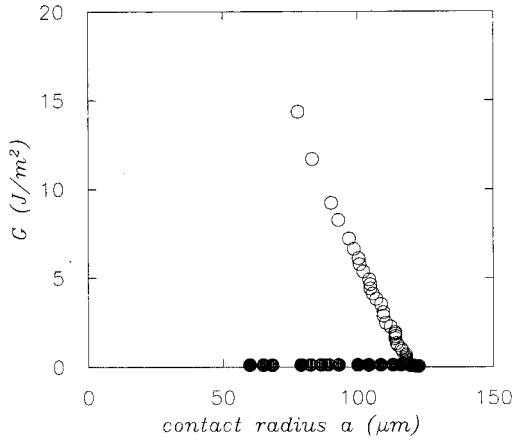

Figure 2. Unloading strain energy release rate vs contact radius curves for PDMS networks hydrolyzed for 12 h in 0.1 M HCl, before (open circles) and after (closed circles) exposure of the hydrolyzed surface to the semifluorinated groups ($m = 8$, $n = 6$).

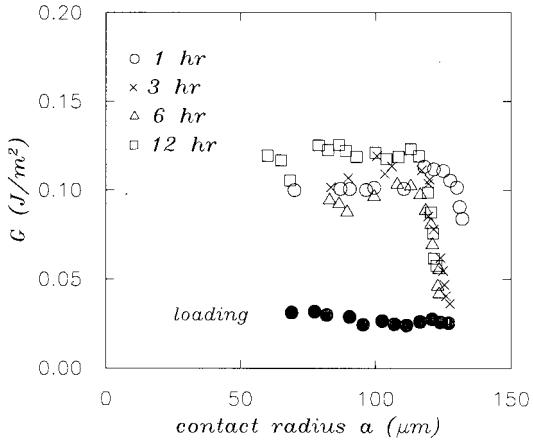

Figure 3. Results from hydrolyzed PDMS networks treated with the SFG, $m = 8$, $n = 6$. The open symbols and crosses represent the unloading data from networks exposed for various lengths of time to the HCl solution. The loading G for all of these samples (closed circles) is constant at ~ 29 mJ/m^2.

esis as shown in Figure 2. More detailed results from these treated networks are shown in Figure 3. The loading curve for the SFG treated networks shows a constant G of ~ 29 mJ/m^2. This corresponds to a surface energy of approximately 14.5 mJ/m^2, which is between the energy of a surface covered with ($-CF_2-$) and ($\gamma = 18$ mJ/m^2) and that covered with ($-CF_3$) ($\gamma = 6$ mJ/m^2) groups.

The unloading G vs a curve for the SFG-treated surface is nearly constant at 100 mJ/m^2, not much larger than the loading G vs a curve. These unloading curves are independent of the length of time the original PDMS surface was hydrolyzed. This indicates that the extent of hydrolysis of the surface after 1 h exposure to HCl produced a sufficient quantity of silanol groups for attachment of the SFG groups to create a low-energy surface.

X-ray photoelectron spectroscopy (XPS) was used to measure the surface composition of PDMS films similarly hydrolyzed and coated with the SFG. A 600 μm^2 area was analyzed with a takeoff angle of 55°, using a SSL-100-3 X-ray photoelectron spectrometer with monochromated Al Kα X-rays (1.4 keV). Typical measurement conditions for analyses included a test chamber (ESCA chamber) pressure of 3×10^{-9} Torr. The X-ray

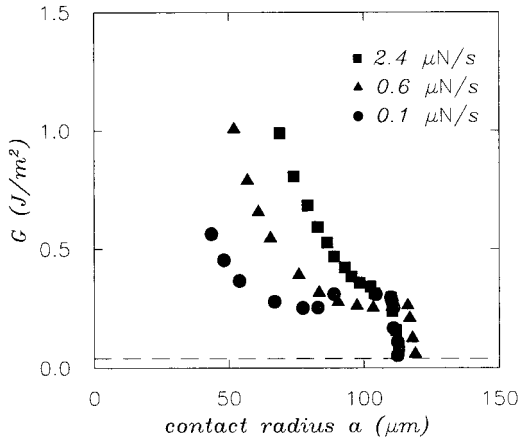

Figure 4. Rate-dependent strain energy release rate vs contact radius curves for PDMS networks hydrolyzed for 1 h in 0.1 M HCl. The dashed line represents the G vs a data during loading, while the symbols show the data for unloading at the rates shown in the legend.

source was operated at 2 kV and 20 mA. XPS results show that the atomic percentage of fluorine atoms within the top 70 Å is 1.8, 2.7, 4.1, and 4.8% for HCl exposure times of 1, 3, 6, and 12 h, respectively.[13] These low compositional percentages imply that the SFG are lying horizontally on the surface of the PDMS, rather than standing in a close-packed arrangement perpendicular to the surface (if the SFG were close packed perpendicular to the surface, the percentage of fluorine would be ~13%). If we consider the top layer containing these SFG to be ~5 Å thick, we can calculate the surface density of the SFG from the measured composition percentages. The amount of fluorine found in the 12 h exposure sample corresponds to a surface that is completely covered by the horizontal SFGs. Therefore we conclude that the surface coverage for this sample is close to 100%. For the exposure times of 6, 3, and 1 h, the surface densities are approximately 85%, 55%, and 37%, respectively. Thus larger amounts of silanol groups allow for greater density of attachment of the SFG; however, the increased number of SFG groups does not seem to affect the energy of the surface (see Figure 3). While one cannot exclude the existence of ordered regions of SFGs, this seems unlikely in view of the rather irregular attachment of these groups on the surface. In our experience, only with dense and uniform substitution do we see such ordered regions.[5]

SFGs are only slightly soluble in both methanol and acetone, so the possibility exists that a tenacious layer of the nonbonded SFG may not have been removed from the PDMS surface by the washing. However, since the XPS results do not show an unreasonable excess of fluorine atoms and the percentage of fluorine increases with hydrolysis time (areal density of silanol groups present), it is reasonable to assume that only the reacted SFG remain on the surface after washing.

In the hydrolyzed PDMS networks a significant effect of the rate of unloading on the G vs a behavior was found.[9] Figure 4 shows the results for networks that have been hydrolyzed for 1 h, loaded to a maximum load required to produce a maximum contact radius of ~120 μm, and then unloaded at rates of 2.4, 0.6, and 0.1 μN/s. In ref 9 we have attributed this rate dependence to the rate of bond dissociation at the interface.

Contrary to the results from the hydrolyzed networks (Figure 4), the SFG treated networks show no depend-

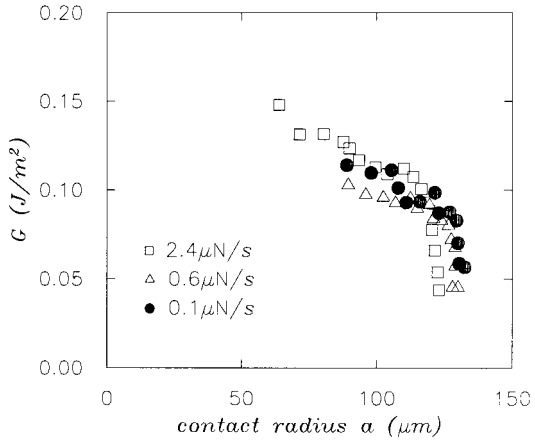

Figure 5. Strain energy release rate vs contact radius for SFG treated PDMS unloaded at different rates. No rate dependence was observable.

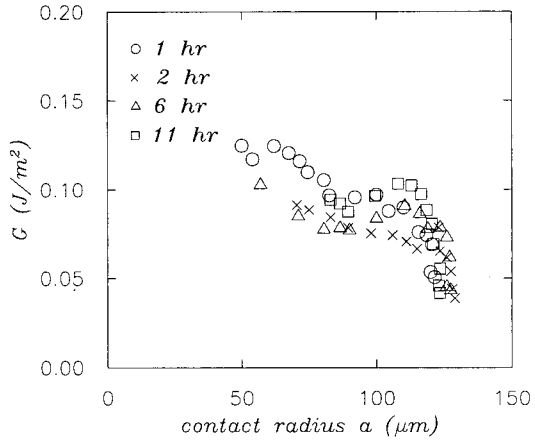

Figure 6. Strain energy release rate vs contact radius for SFG-treated PDMS held at the maximum load for various lengths of time shown in the legend. No dependence on this variable is seen.

ence of *G* on the rate of unloading. This is demonstrated in Figure 5. Moreover, they do not show a dependence on the length of time the networks are held in contact at maximum load before unloading, as shown in Figure 6.

These surfaces do, however, show a small amount of hysteresis between the loading and unloading curves. Not only is this unexpected for fluorinated surfaces, but also the results are consistent over all surface densities of the SFG (as measured by XPS). One possible source of this hysteresis is heterogeneity of the surfaces. As the SFG coverage of the surface decreases, then the contribution of the PDMS substrate to the measured surface energy should increase. Since PDMS has a surface energy of ≈22 mJ/m^2 this would cause the *G* to increase as the percentage of SFG decreased. This behavior was observed by Chaudhury et al.[14] for various concentrations of hexadecylsiloxane self-assembled monolayers on PDMS. However, the loading and unloading *G* data of our samples are independent of the various surface coverages.

A second reason for the observed hysteresis may be an interdigitation of the fluorinated segments. Interdigitation, or slight interdiffusion, between chemical moieties after two surfaces have been brought into contact, may occur when both surfaces have some degree of mobility.[15] The hydrocarbon segments contribute this necessary mobility to the SFG. As the interdigitated

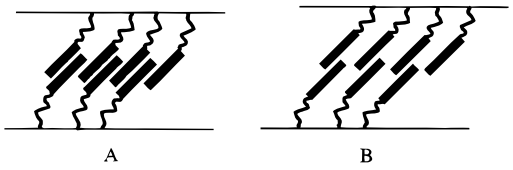

Figure 7. Schematic diagram of how the SFG on the surface can interdigitate on the surface (A). When the surfaces are pulled apart, new surface area is created between each digit, requiring an increase in *G*. Then the SFG interact only at the ($-CF_3$) end-groups (B), and *G* remains constant.

groups move apart, a larger amount of surface is created than that calculated based simply on the contact area. The slight increase in *G* may be due to the added energy needed for the creation of this extra surface (see Figure 7). We believe that this interdigitation of the SFG is the source of the initial hysteresis and the subsequent constant *G* that we observe in our measurements. At higher degrees of coverage, the self-assembly of such SFG might be expected to reduce levels of hysteresis by hindering interdigitation, but that was not observed here.

4. Conclusions

Low-surface-energy SFGs were attached to hydrolyzed model PDMS networks. The JKR technique was utilized to measure their surface energy and stability. It was found that the SFG had a surface energy of ∼14.5 mJ/m^2 during loading. This result suggests that the surface is covered by both ($-CF_3$) and ($-CF_2-$) groups. While increased hydrolysis of the surface led to higher density of the SFG, the surface energy remained the same. The measured surface energy was independent of unloading rate and the length of time the surfaces were kept in contact before unloading. This confirms that these SFG provide a stable surface with a very low surface energy.

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(13) Error for all XPS composition measurements was ±0.1%. The remaining composition of the samples (without H) with 4.8% F was 47.2% C, 23.0% Si, and 25.0% O. No Cl was observable. On the basis of the 4.8% F and the stoichiometry of the attached SFG group and the unmodified PDMS, the theoretical composition should be 4.8% F, 49.5% C, 22.5% Si, and 23.5% O. The increased O and decreased C observed relative to the computed composition probably results from silanol end groups created by the HCl treatment that have not reacted with the SFG groups.
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