Surface Modification of Silicone Elastomer Using Perfluorinated Ether

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The surface properties of a poly(dimethylsiloxane) elastomer have been modified by reacting an allyl amide functional perfluorinated ether (PFE) to the siloxane network by a hydrosilation reaction. Examination of the surface by contact angle and X-ray photoelectron spectroscopy revealed that the perfluorinated ether migrates to the surface of the polymer, thus reducing its surface energy from 22 to about 8 mJ/m^2 without affecting its bulk material properties. The resultant surface however exhibits higher contact angle hysteresis than that seen with the PFE-free elastomer. These results indicate that the higher energy amide functionalities of the perfluorinted ether are available for interfacial interaction, even though they are buried below the PFE layer. This study demonstrates that a high-energy group can be pulled to the free surface of a polymer by the driving forces of the lower energy groups segregating to the surface. The high-energy groups are available for further chemical interactions when the surface reconstructs in contact with a high-energy environment.

Release coatings are generally used at the interface between two materials in order to prevent strong adhesion. Although they are used in the manufacture of a diversity of industrial products, such as mold-release agents, self-adhesive tile-liners, and chewing-gum wrappers,[1−3] the largest market for release coatings, however, is the protection of items coated with pressure-sensitive adhesives (PSAs).[1] Thus, release coatings are important components of products such as self-adhesive label liners and a variety of rolled adhesive tapes (e.g., Scotch tape).

Although a variety of materials, such as polyamines,[4] poly(vinyl alcohol)s,[5] organic sulfides,[6] and perfluorinated polyesters,[7,8] have been used to create release coatings, silicone polymers are most frequently employed for PSA release. This is due to low surface energy (20 mJ/m^2)[9] and high flexibility[9,10] of the silicone network. Patent records contain a wealth of silicone-based release coating recipes. Some are simply polyorganosiloxanes with added resins, made from materials such as polyesters,[11] polyacrylics,[12] neoprene rubber,[13] or styrene−butadiene copolymers.[13] These additives are typically included to improve ease of spreading, optimize curing time, or alter the release properties of the silicone. Others have developed release coatings based on polyorganosiloxanes which have backbones modified with selected functional groups, including ureas,[13] epoxides,[14,15] olefins,[16] amines,[17] and acrylates.[18] In particular, fluoroalkyl-substituted polysiloxanes have been explored,[19−27] frequently as a means to create coatings that exhibit low surface energy. Alternately, fluorine has been introduced into coating formulations by cross-linking a siloxane with a fluoropolymer[28] or by casting a thin fluorocarbon film on top of a silicone-coated substrate.[29] In addition, higher molecular weight perfluoropolyethers have been included in some formulations for easy-release coatings.[28,30−33]

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Clearly, a variety of methods have been used to create release coatings that are effective under specific and limited conditions. There exists, however, a demand for release coatings that can be tailored to various conditions over a wide peel velocity range and whose release properties can be adjusted without adversely affecting the stability, curability, or elastic properties of the material. Examples of such coatings have been disclosed in patent form, consisting of amine-[17] or urea-functionalized[13] siloxanes, fluorine-containing silicones,[12,29] perfluorinated polyesters,[8] and perfluorinated polyethers.[33] These formulations often require large proportions of the modifying agent, leading to significant changes in physical properties of the material. Moreover, many of these modifying functional groups are high-energy moieties and are driven away from the surface of the coating over time; thus, the stability and effectiveness of the release coating are compromised. There are other significant developments[35−43] in the preparation of low surface energy polymeric materials using self-assembly of fluorinated side chains that form uniformly organized array of trifluoromethyl (CF_3) groups. As low as 8 mN/m surface tension can be achieved with these methods.[43]

For the release coating material described here, our approach was to modify poly(dimethylsiloxane) (PDMS) with a perfluoroether additive that contains a large number of low-energy CF_3 groups in its backbone. Because the low-energy CF_3 groups easily migrate to the surface of the silicone film, it is possible to attain significant control on the surface segregation with only a small concentration of the additive. Furthermore, because of high density of CF_3 groups in its backbone, a very low energy surface can be prepared without any structural organization of the molecules on the surface. One added benefit of this is that the surface remains fluidlike, which may be of advantage for certain types of interfacial applications. With this objective in mind, we have modified the surface of a silicone elastomer using allyl amide functional perfluoroether [$F(CFCF_3CF_2O)_7CFCF_3CONHCH_2CH{=}CH_2$, PFE]. The PFE molecules were tied to the network using a platinum-catalyzed hydrosilation reaction. Although a very low surface tension (8 mN/m) was easily achieved, the resultant surfaces exhibited higher contact angle hysteresis and higher adhesion than the unmodified PDMS elastomer perhaps due to the presence of high-energy amide groups near the surface. The control of the adhesive property of the surface using this method is a desirable feature from the point of view of tuning the release property of a silicone elastomer. Subsequently, we realized that we have explored an interesting concept of surface modification—somewhat related to an idea of Koberstein et al.[44]—that is to use the driving force of surface segregation of the lower-energy CF_3 groups to bring a higher energy group, namely amide, close to the air/polymer interface. The resultant surfaces thus exhibit lower surface energy but higher adhesion than the unmodified elastomer. In what follows next, we describe spontaneous surface localization of perfluoroether in PDMS films using X-ray photoelectron spectroscopy and the properties of the resultant surfaces via contact angle and adhesive force measurements.

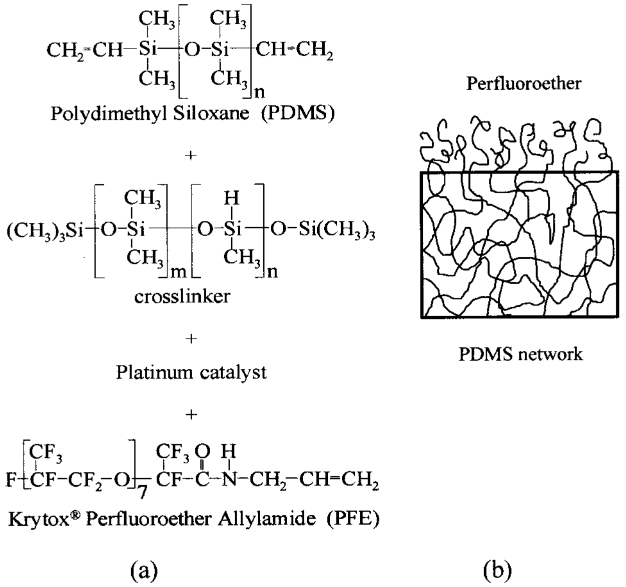

Figure 1. Modification of poly(dimethylsiloxane) by addition of perfluoroether allyl amide. A vinyl-terminated PDMS was reacted with a methyl hydrogen siloxane cross-linker in the presence of a platinum catalyst in order to form the elastomeric network. When a allyl amide functional perflororinated ether is added in the reaction mixture, part of it reacts with the network and segregates to the air/polymer interface (b).

Synthesis of Perfluoroether-Modified Poly(dimethylsiloxane). Poly(dimethylsiloxane) (PDMS) elastomers were synthesized by cross-linking vinyl-terminated PDMS oligomers with methyl hydrogen siloxanes via a platinum-catalyzed hydrosilation reaction as shown in Figure 1. Modification of the PDMS elastomer was achieved by adding small quantities of DuPont Krytox Perfluoroether Allylamide (PFE) to the PDMS mixture prior to curing it. The addition of allyl amide functional PFE was intended to yield the result that the allyl groups would coreact with the SiH groups of the cross-linking agent, while they segregate to the air−polymer interface. The evidence of platinum-catalyzed hydrosilation between allylamide functional PFE and the SiH groups of the methyl hydrogen siloxane was obtained from a separate experiment. In that, the allyl amide functional PFE [$F(CFCF_3CF_2O)_7CFCF_3CONHCH_2CH{=}CH_2$] was reacted with a SiH containing PDMS [$(H_3C)_3Si(OSiHCH_3)_5(OSiCH_3CH_3)_3OSi(CH_3)_3)$] in the presence of a platinum catalyst at 75 °C using toluene as a reaction medium. Reaction was monitored using ^1H NMR. The appearance of peaks due to $-SiC\boldsymbol{H}_2CH_2CH_2NH-C{=}O$ at 0.48 δ and $-SiCH_2C\boldsymbol{H}_2CH_2NH-C{=}O$ at 1.60 δ and disappearance of a peak due to SiH at 4.63 δ indicated addition of SiH to the allyl group of the allyl amide PFE.

During the synthesis of the silicone elastomer, it was noted that the perfluoroether additive exhibits a low solubility in PDMS at room temperature. For lower PFE concentrations (<0.5 wt %), mixtures remained transparent. For higher concentrations (0.5−1.5 wt %), mixtures were cloudy initially but became more transparent upon heating to curing temperature (75 °C). For PFE concen-

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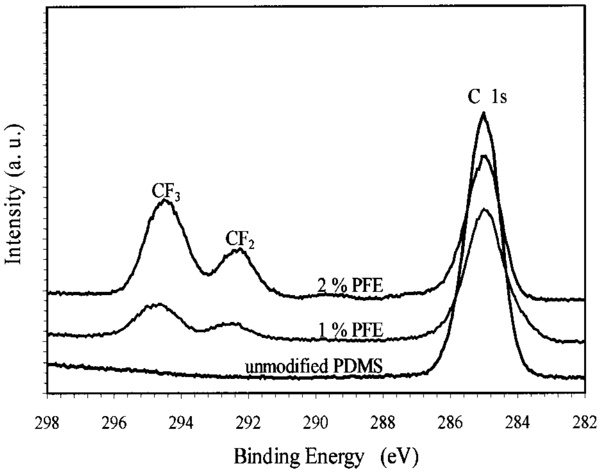

Figure 2. X-ray photoelectron spectra of the C_{1s} region for unmodified and PFE-modified PDMS. The peaks at 292 and 294 eV indicate the presence of PFE groups on the PDMS surface.

trations greater than 1.5 wt %, cured films remained cloudy. This cloudy appearance can be attributed to undissolved PFE remaining in the cured PDMS, which mostly disappeared when the cured elastomers were Soxhlet extracted in chloroform to remove unreacted material. The elastomer was then dried thoroughly before characterizing their chemical, physical, and adhesive release properties.

Evidence of Surface Modification. The surface compositions of modified and unmodified PDMS films were determined using X-ray photoelectron spectroscopy (XPS). All spectra were collected at a low takeoff angle (15°) in order to minimize the penetration depth of the X-ray beam. As a result, the information obtained pertains to regions of the substrate located approximately 30 Å below the surface. Spectra of the carbon (1s) region are shown in Figure 2. The single peak at an electron binding energy of 285 eV verifies that the carbon in unmodified PDMS is predominantly in the form of methyl groups. In the spectra of the PFE-modified PDMS, two additional peaks at 292 and 294 eV appear and are of greater intensity in the 2% PFE case. These peaks correspond to carbon atoms bound to fluorine, specifically, the CF_3 carbon signal appearing at 294 eV and the CF_2 signal at 292 eV. These fluorocarbon groups are attributed to PFE, and their presence provides evidence of significant surface modification. It was not possible to detect any peak due to nitrogen of the amide group due to its very low concentration and the fact that its intensity is attenuated by the PFE layer above it.

Figure 3 shows that the atomic concentration of surface fluorine initially increases with the bulk concentration of perfluoroether (PFE) but reaches a plateau value (30%) when the bulk PFE concentration reaches about 1.5%. The S-shaped curvature of the adsorption isotherm is reminiscent of a type V isotherm indicating cooperative interactions among adsorbed molecules.[34] The picture here is however complicated by other processes. The formation of two phases, one PFE rich and the other PDMS rich, is thermodynamically favorable due to the low solubility of PFE in PDMS. At low bulk PFE concentrations, the PDMS phase can accommodate the PFE molecules, as the system lowers its free energy more effectively by bulk dilution rather than the surface energy minimization. At higher concentrations, the PDMS-rich phase becomes saturated with PFE and the excess PFE phase separates in the forms of emulsions or by migration to the surface.

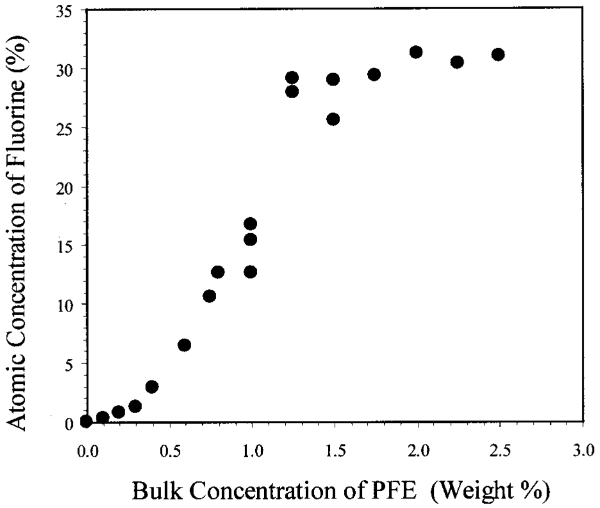

Figure 3. Atomic concentration of fluorine on the surface of the elastomers, which were modified with various amounts of PFE.

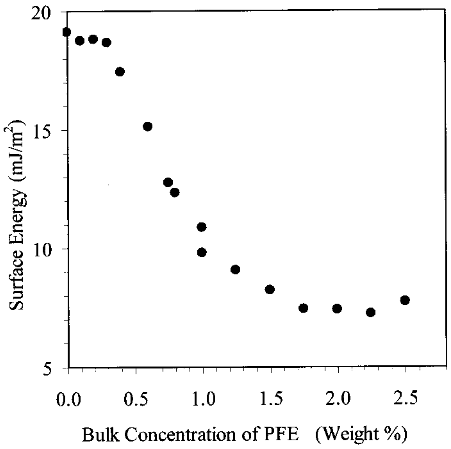

Figure 4. Surface free energies of the PFE-modified PDMS films, determined by static contact angles of hexadecane.

Contact angle and surface free energy measurements supported evidence of increased fluorine concentration at the surface. Contact angles were measured with both water and hexadecane. While both the advancing and receding contact angles could be measured with water as a test liquid, a quasi-static advancing contact angle could only be measured with hexadecane since the polymer swells in oil. A significantly reduced level of swelling was, however, observed in the samples reacted with PFE moieties. To reduce the artifacts due to swelling, the contact angles of hexadecane were measured within 20 s after placing the drops on the polymer samples. The surface energies of the polymers, which were estimated using the contact angles of hexadecane, are summarized in Figure 4. The reduction of the surface free energy from 20 to 8 mJ/m^2 with increased PFE in the bulk of the polymer clearly demonstrates that the surface is highly saturated with CF_3 groups. The lowest surface energy (8 mJ/m^2) obtained from these studies is similar to that of self-assembled monolayers[39,40] of perfluoroalkanes having close-packed CF_3 groups.

Advancing and receding dynamic contact angles of water on these surfaces exhibit very significant hysteresis. The dynamic advancing angle increases from 120° to 140° as the bulk PFE concentration is increased from 0% to 1.25% (Figure 5). Over the same range of PFE concentration, the dynamic receding angle decreases from 90° to 50°.

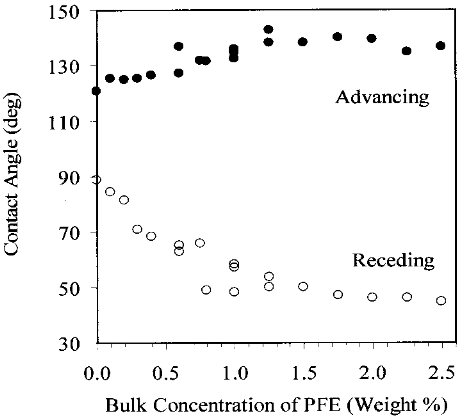

Figure 5. Advancing and receding contact angles of water show that the hysteresis increases with the amount of PFE in the network.

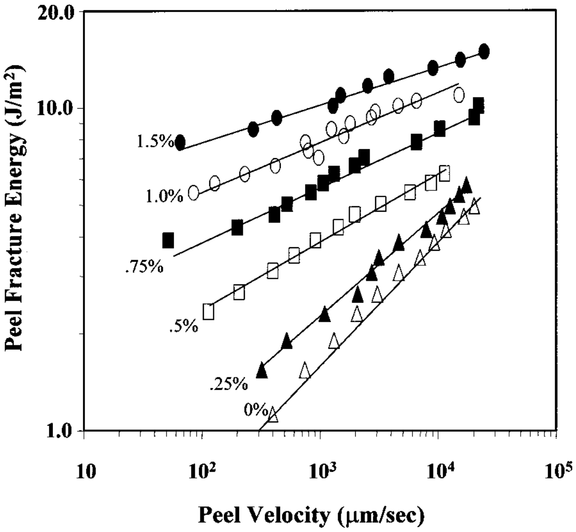

Figure 6. The peel tests of an acrylic PSA on the unmodified and PFE-modified PDMS show that that a small amount of PFE can affect the adhesive fracture energy dramatically. Note that the slopes of the lines are not constant for these samples.

Increased hysteresis from 30° to 90° suggests very significant reorganization occurring on these surfaces, implying the presence of highly polar groups. These are most likely due to the amide groups, which are buried beneath the PFE layer but can be exposed when the surface is in contact with a high-energy medium.

Effect of Surface Modification on Adhesive Release. To elucidate the effect of surface modification of PDMS by PFE, the prepared films were subjected to peel tests using a commercial pressure-sensitive adhesive (PSA). The acrylic PSA tape was applied to each substrate and peeled away at a 90° angle by applying dead loads at the free end of the tape. The peel velocity for each weight was measured, and values of peel fracture energy per unit area were plotted against peel velocity on a log−log scale (Figure 6).

Although the effect of PFE modification was to lower the surface free energy of PDMS, the peel fracture energy increased dramatically with increasing PFE concentration. For a peel velocity of 1000 μm/s, a 5-fold increase in peel fracture energy was observed as the bulk PFE concentration increased from 0% to 1.5%. Further studies (Figure 7) based on dynamic mechanical analysis showed that neither the glass transition temperature nor the dynamic shear modulus of the polymer is significantly altered as a result of the PFE addition to the elastomer. Thus, the surface and the release properties of PDMS can be effectively tuned with very low PFE concentrations without affecting the bulk elastic properties of PDMS.

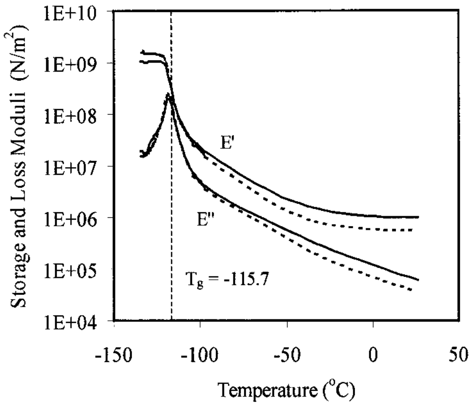

Figure 7. The storage (E') and loss (E'') modulus for the unmodified and PFE-modified PDMS shows that the bulk properties of PDMS are not significantly affected by the presence of PFE in the network. Solid lines correspond to unmodified PDMS and the dashed lines correspond to 1% PFE in PDMS.

Examination of Figure 6 reveals that the peel fracture energy (G) varies with peel velocity (V) following a power law relationship: $G = V^n$. For the unmodified PDMS, n is about 0.38, whereas it approaches 0.13 with increasing concentration of PFE in the bulk of the elastomer. Examination of the failured surfaces by XPS showed that no material was transferred from the PSA to the elastomer or vice versa. Evidently, the failure is interfacial. According to the classical theory of viscoelastic fracture,[45] the fracture energy can be expressed as the product of two terms: one is the interfacial work of adhesion (W) and the other is the bulk dissipation function ($\phi(V,T)$). In our case, the dynamic mechanical analysis revealed that the bulk properties of the elastomer did not change as a result of PFE addition. If the interfacial separation is controlled by equilibrium work of adhesion, the $G-V$ profiles should be parallel to each other. Since the exponent (n) varies, it is possible that the separation of the adhesive occurs via a rate-dependent interfacial process. A nonequilibrium separation of an interface having a dissipative component was envisaged earlier by Kendall,[46] who, following the suggestion of Blake and Haynes,[47] proposed that the interfacial work of adhesion is of the form:

$$W_{\mathrm{I}} = W_0 + A \sinh^{-1}(V\tau/2\delta) \tag{1}$$

where W_0 is the thermodynamic work of adhesion, δ is the characteristic lattice length, and τ is the bond relaxation time, which can be expressed as follows:

$$\tau = \tau_0 \exp(E_{\mathrm{a}}/kT)$$

The activation energy E_{a}, as a first approximation, is proportional to the intermolecular interaction (W_0) between surfaces. Expansion of eq 1 shows that W_{I} varies linearly with W_0 at high velocities but exponentially with W_0 at low velocities. Thus the values of W_{I} for the different surfaces should differ more significantly at low velocities than at high velocities as is the experimental observation.

Summary. Silicone release coatings with tunable release properties were made by reacting allyl amide terminated perfluoroether oligomer with the silicones by

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a platinum-catalyzed hydrosilation reaction. A trace amount of PFE (<1.5%) changes the surface properties of PDMS remarkably without affecting the bulk properties of the PDMS network. The trend of the adhesive release properties of the surfaces is similar to that seen with the contact angle hysteresis of water on these surfaces, the origin of which is thought to be due to the interaction of water and the adhesive with the high-energy amide groups. The ability to pull a high-energy group to the surface by the low-energy PFE groups may be a useful synthetic strategy to consider in the preparation of other types of novel surfaces. These surfaces, having a latent capacity to engage in chemical interaction, are relatively stable on the surface because of the low-energy PFE layer above it, which are therefore suitable for the design of controlled-release coatings.

Experimental Section

General Information. Films of poly(dimethylsiloxanes) were prepared using a commercially available silicone elastomer kit (Dow Corning Sylgard RTV 184). A vinyl-terminated perfluoroether (DuPont Krytox Perfluoroether Allylamide) compound was used to modify the surface of PDMS. XPS spectra were collected using a Scienta ESCA-300 X-ray photoelectron spectrometer. Contact angles were measured using a modified Rame-Hart 100 contact angle goniometer. Water used for the contact angle measurements was distilled and deionized. Dynamic mechanical analysis was carried out using an Acme mechanical property analyzer in torsion mode. A commercially available, acrylic-based, pressure-sensitive adhesive tape (3M Transparent Tape 147) was used for all peel fracture energy tests.

Preparation of Elastomer Films. The Sylgard RTV 184 kit consists of a vinyl-terminated dimethylsiloxane oligomer, a methyl hydrogen siloxane cross-linker, and a platinum catalyst to carry out the hydrosilation reaction. The polymer also contains partially methylated silica resin as a re-enforcement filler. The two parts of the kit are combined in a 10:1 ratio (by weight) and mixed thoroughly in a polystyrene weighing boat. For modified PDMS, PFE was added by weight immediately after mixing the base polymer. The mixtures were poured into 100 mm polystyrene Petri dishes in quantities of 6.0 g (to give resulting films approximately 1 mm thick). The dishes were degassed under vacuum for 45 min and then cured for 3 h in an oven at 75 °C. Cured films were cut into strips (1 in. × 3 in.) and Soxhlet extracted in chloroform for 18 h. The strips were allowed to deswell and then dried under vacuum and stored in a desiccator before use.

XPS Characterization of Surface Composition. The surface composition of the films was determined using X-ray photoelectron spectroscopy (XPS) with a Scienta ESCA-300. X-rays are generated using a water-cooled high-intensity rotating Al Kα anode source, at a power of 4.5 kW. Spectra were collected at a takeoff angle of 15°, to minimize the penetration depth and therefore maximize the signal obtained from surface species. For each sample, high-resolution spectra were taken in four regions: carbon 1s, silicon 2p, oxygen 1s, and fluorine 1s. Compositions were determined by calculating peak areas for each elemental region and then calculating the atomic percentage of each element present.

Surface Energy Measurements. The surface energies of the unmodified and PFE-modified PDMS films were determined by first measuring the static contact angle of hexadecane on each substrate and then calculating the surface energy using Fowkes' equation:[48]

$$\gamma_s = \gamma_l (1 + \cos \theta)^2/4$$

Method Used To Measure Peel Fracture Energy. The substrate was secured to the underside of a flat surface (perpendicular to the normal direction). A commercially available adhesive tape (3M Transparent 147), containing an acrylic pressure-sensitive adhesive, was used for all peel tests. Each test was conducted by placing a fresh piece of tape on the substrate surface, pressing it with a clean PDMS elastomer, allowing a minimum of 30 s to ensure good contact, and then measuring the time required for the tape to peel away over a marked distance under the force of a known weight. From these data, the peel fracture energy and peel velocity were calculated. For each sample, the weights were varied from lowest to highest and then repeated in the same order four times. It was observed that the peel adhesion of the surfaces increase after repeated measurements, suggesting that the surface can reconstruct under stress.

Dynamic Mechanical Properties. Dynamic mechanical analysis (DMA) was performed using a mechanical property analyzer in torsion mode. For these tests, thicker (~3 mm) PDMS substrates were synthesized by following the same procedure described above. Both unmodified and modified substrates were cut and extracted for 48 h and dried thoroughly. Slabs (1 cm × 3 cm) were cut to fit the DMA apparatus. Each sample was first cooled to −140 °C, after which storage and loss moduli were determined at regular temperature intervals from −140 to 25 °C.

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