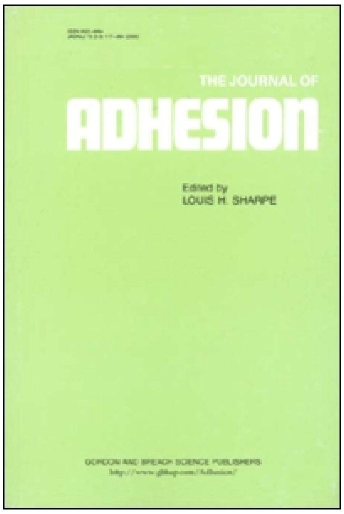

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Modulation of Adhesion at Acrylic Adhesive-Silicone Elastomer Interfaces

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Modulation of Adhesion at Acrylic Adhesive-Silicone Elastomer Interfaces

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We have recently reported a systematic investigation of the role of MQ resins (small silica-like nanoparticles) in the modulation of adhesion at silicone elastomer lens—nanometric thin acrylic surface anchored layer deposited on a silicon wafer through loading and unloading JKR experiments. This particular system was chosen as it allowed one to vary the MQ resin content in the elastomer, and to test its resulting effect on both the thermodynamic work of adhesion and the adhesive strength at elastomer—acrylic layer interfaces, avoiding any complication due to bulk mechanical properties of a relatively thick (in the micron range) acrylic layer. We present here a complementary investigation, aimed at understanding the role of the resins in the development of specific interactions at the interface. To do so the adhesive energy between silicone elastomers containing various amounts of MQ resins and model substrates made of self-assemble monolayers of thiol molecules with various amounts of carboxylic terminations have been measured through JKR tests. We show that the level adhesion at these interfaces results from a competition between increased interactions and decreased mobility associated with the incorporation of the resins inside the elastomer.

Keywords: Acrylic adhesives; Adhesion mechanisms; Dissipation; Interfacial interactions; JKR test; Silicone elastomers

INTRODUCTION

In a number of weakly-adhering adhesive systems it is desirable to adjust precisely the level of adhesion as, for example, in repositionable

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devices, for which one may wish to easily peel apart the two partners, while avoiding spontaneous delamination. This can be achieved by using silicone elastomer coatings in contact with acrylic adhesives. The level of adhesion is usually too low if pure silicone elastomer is used. Thus, in a number of practical systems, the silicone elastomer is chemically modified by incorporation of silicone MQ resins (small silica like nanoparticles) to adjust the level of adhesion. It is commonly assumed that the role of the MQ resins is to enhance interfacial interactions due to their slightly higher polarity compared with pure silicone elastomer. It is now known, however, that the incorporation of the MQ resin significantly affects the mechanical properties of the elastomer, increasing the storage modulus and, still more significantly, modifying the loss modulus and the frequency response [1]. These modifications of the elastic properties of the elastomer should affect the whole mechanical response in any adhesive test. It is, thus, not obvious that the observed adhesion modulation associated with the incorporation of the MQ resin in the silicone elastomer results from enhanced interactions at the interface. In order to try to better identify and understand the molecular mechanisms involved in such modulation of adhesion we have undertaken a systematic investigation of the respective roles of interfacial interactions and bulk dissipations in fixing the level of adhesion at silicone elastomer—acrylic adhesive interfaces. In a previous article we have reported a systematic investigation of both G_0, the adhesive strength at zero fracture velocity, and G(V), the velocity dependent fracture toughness through JKR analysis of the contact between small elastomer lenses put into contact with a molecularly thin acrylic layer, deposited on a silicon wafer. We chose in a first approach to thin down the thickness of the acrylic adhesive layer in order to minimize dissipation in the adhesive acrylic layer and focus on the silicone elastomer side. Both G_0 and G(V) were observed to depend strongly on the MQ resin content and on the contact time, suggesting the progressive building of strong interactions between acrylic and elastomer chains. Due to the rather complicated chemistry of the system, we were, however, unable to clearly identify which interactions were predominant and how they could be controlled [1]. We present here the second part of this work in which model substrates have been tested against the same silicone elastomers containing various amounts of MQ resins, again through JKR tests, in order to shed light on the role of the resins in providing enhanced adhesive strength in the presence of known interactions at the interface. To do so self-assembled thiol monolayers with various amounts of carboxylic acid terminations have been formed on a gold evaporated layer at the surface of silicon wafers. We shall present the results of the JKR experiments performed on these assemblies without entering into a detailed description of the elastomer properties and of the JKR procedures used as they have already been described [1], but rather to show how the kinetic information easily obtained through the JKR test can allow one to elucidate the two competing roles played by the MQ resin regarding adhesion modulation, that is to say favoring interactions with polar groups and reducing mobility inside the elastomer, thus, preventing interactions with polar groups to develop.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Silicone Elastomers and MQ Resins

The characteristics of the MQ resins and of the silicon elastomers used in the present study have already been described in detail [2,3]. We just briefly recall here what is necessary for an easy understanding of the presented results.

Silicone Substrates

Silicone elastomers were prepared using polydimethylsiloxane (PDMS) and MQ silicone resins in various proportions. The divinyl terminated PDMS ($M_n = 17000\,\mathrm{g/mol}$ by titration, $I = M_w/M_n = 1.3$ by GPC) was obtained after several precipitations in acetone of a commercial grade silicone oil (Rhodia 621V200, Rhodia Silicone, Saint Fons, France). The silicone $MD^{Vi}Q$ resin (Rhodia Silicone, Saint Fons, France) was used as received. Its chemical composition was estimated using ^{29}Si NMR ($M = \mathrm{Me_3SiO_{1/2}}$: 47.3 wt%, $D^{Vi} = \mathrm{ViMeSiO_{2/2}}$: 9.1 wt%, $Q = \mathrm{SiO_{4/2}}$: 43.6 wt%). The ratio O/Me is close to unity and, thus, the resin is expected to be less apolar than PDMS which has two methyl groups for one oxygen. From Small Angle X-Ray Scattering experiments we know that the resin particles have compact structures with radii of gyration $R_g = 1\text{–}2\,\mathrm{nm}$. The corresponding average molecular mass is in the range 3000–5000 g/mol. Blends of PDMS and resin (0 wt% up to 40 wt% in resin) were prepared and the concentration of vinyl groups was titrated. The catalyst (Karstedt's Pt), Sigma-Aldrich, st. Quentin de Fallovier, France, is added using 20 ppm of Pt for 10^{-4} mol of vinyl groups. After addition of 1,3,5,7 tetramethyltetracyclosiloxane ($D'4$) which acts as a tetra functional crosslinker, the mixture is stirred for 15 min, degassed, and deposited on fluorinated glass slides to form small spherical caps, following the technique first introduced by Chaudhury and coworkers [4]. In the case of the mixture without

$MD^{Vi}Q$ the potlife at ambient temperature is short; therefore, the stirring after addition of $D'4$ is performed at $-15°C$ under dry nitrogen atmosphere. The samples are cured overnight at 100°C. The relative quantity of D′4 is adjusted to minimize the sol fraction ($r = [SiH]/[C = C] = 1.2$ for pure PDMS and $r = 1.7$, 1.8, 1.95, 2.2 for 10, 20, 30, and 40 wt% resin, respectively). Thick ribbons of the same elastomers are also formed simultaneously and used either to test the mechanical properties of the elastomers or to avoid finite size effects in the JKR test [5]. Dynamic mechanical properties, probed with a Rheometrics RSAII solid analyzer (TA Instruments-Rheometrics, Guyancourt, France) at 25°C using thick ribbons (1 mm) have been reported in detail in [3]. The storage moduli, E', increase from 8×10^5 Pa for pure PDMS elastomers up to 6×10^6 Pa for an elastomer filled with 40% (by weight) in MQ resin. The loss moduli, E'', increase much more, gaining three decades between small resin content ($\sim 10^3$ Pa) and 40 wt% resin content ($\sim 10^6$ Pa). All elastomers remain, however, essentially elastic since $tg\delta = E''/E'$ remains smaller than 0.1. Surface energies were characterized by dynamic tensiometry using H_2O and tricresylphosphate. In contrast to bulk mechanical properties the surface energies appear rather independent of the resin content. The dispersive component of surface energy is equal to $\gamma^D = 21 \pm 1$ mN/m for all samples, while the non-dispersive component slightly increases from $\gamma^{ND} \sim 0$ to 2 ± 1 mN/m between 0% and 40% resin content. This is certainly indicative of the fact that, when in contact with air, the MQ resins tend to escape from the surface and remain inside the more polar PDMS elastomer, thus, they only weakly contribute to surface energy. For an optimized crosslinking reaction as used here, however, they cannot go very far below the surface, as they are attached to the crosslinks. They are, thus, ready to move toward a more polar surface when a contact with an acrylic adhesive layer is formed, the kinetics of which is affected by the MQ resin content in the elastomer as we have shown measuring the zero velocity adhesion energy, G_0, as a function of contact time and resin content [1].

Self-Assembled Thiol Layers

Two thiol terminated molecules have been used: 1 1-mercaptoundecanoic acid and 1-dodecane thiol. Their formulas are presented in Figure 1a and 1b, respectively. They were used as received (Sigma-Aldrich). A self-assembled monolayer was formed by incubating (immediately after a UV-ozone cleaning treatment) silicon wafers covered with a thin evaporated gold film (sputtering, nanometric roughness as seen through AFM) in ethanol solutions of mixtures of these two molecules

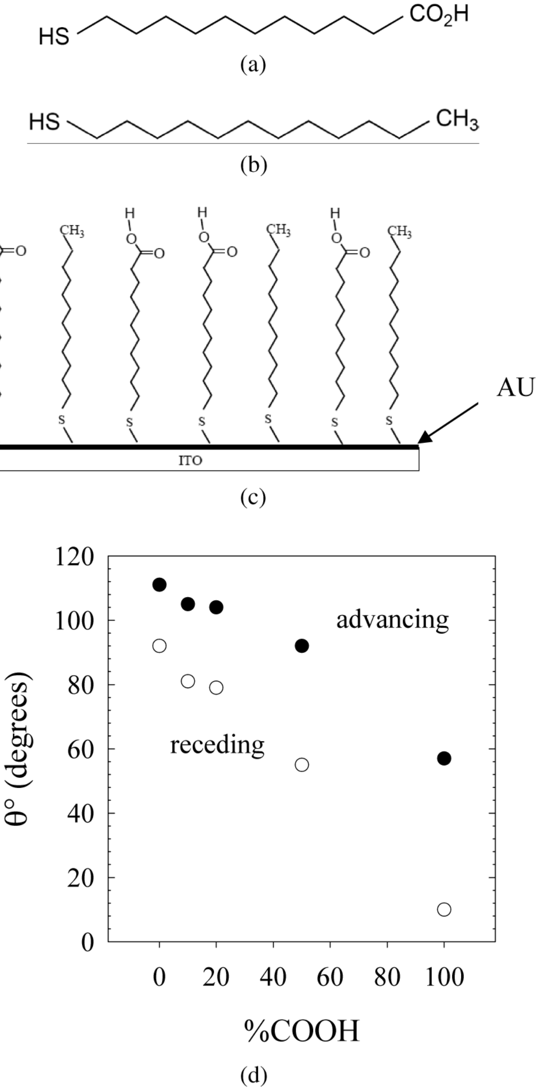

FIGURE 1 Characteristics of the self-assembled monolayers. 1a and 1b: Schematic formulae of, respectively, mercaptoundecanethiol and undecanethiol. 1c: Schematic representation of the mixed self-assembled monolayer, forming a carpet of CH_3 and COOH extremities, in a proportion fixed by the ratio of mercapto/undecanethiol in the incubation bath used to form the monolayer. 1d: Advancing and receding contact angles of water as a function of the ratio of COOH and CH_3 terminated chains in the incubation solution used to form the thiol self-assembled monolayer.

at various relative concentrations, to form a mixed layer, as schematically shown in Figure 1c. The self-assembled layers were then characterized, first by measuring their thickness, through ellipsometry, which was close to the extended length of the molecules, and then by measuring advancing and receding contact angles of water, which both monotonically decrease when increasing the COOH content and the polarity of the surface, as shown by the typical results reported in Figure 1d.

JKR Test

The detailed description of the JKR apparatus we have developed has been given in [1]. We just recall here what is necessary to understand how the results presented below were obtained. Our apparatus allows one to monitor continuously the radius of the contact area, a, the load, P, and the deformation of the elastomer lens at the centre of the contact, δ, while a small spherical lens of elastomer (typical radius in the millimetre range) is pushed onto the substrate under investigation (loading step) or pulled apart from the substrate (unloading step). We first proceed to the loading, imposing successive inward displacements to the plate holding the lens, then waiting for a given contact time under the maximum load, and then proceeding to the unloading step, imposing successive outward displacements to the lens holder, and waiting for the immobilization of the contact line before proceeding to the next step. After one unloading displacement step, the contact area evolves and the velocity of the contact line progressively decreases to zero. Monitoring this evolution with time of the radius of the contact area, a, along with the corresponding evolution of the load, P, allows one to extract the adhesive energy as a function of time, through the JKR relation [6] applied at each time,

$$G(t) = \frac{\left(P(t) - Ka(t)^3/R\right)^2}{6\pi K a(t)^3} \tag{1}$$

and, thus, also the evolution of the adhesive energy with the velocity of the contact line obtained by a numerical derivative of the curve $a(t)$ [1]. In Equation (1), K is the elastic rigidity of the elastomer lens, obtained by adjustment of the loading curve to the JKR equation with $G = W$ the thermodynamic work of adhesion (in fact both K and W are obtained by adjustment to the JKR law), and R the radius of the lens, measured independently. The most direct data obtained from the test are thus G(V) curves. Results presented below will be first displayed in terms of G(V) curves and then analyzed in terms of cuts at fixed velocities as a function of either composition of the underlying thiol monolayer or composition of the elastomer in MQ resins.

RESULTS

In Figure 2, data for the evolution of the adhesive energy, G, with the velocity of the fracture have been reported for pure PDMS elastomer lenses put into contact with a series of grafted surfaces for which the relative composition of CH_3 and COOH extremities in the thiol layer was varied between 0 and 1. All experiments were performed after a contact time at the maximum applied load of 2 hours. The striking

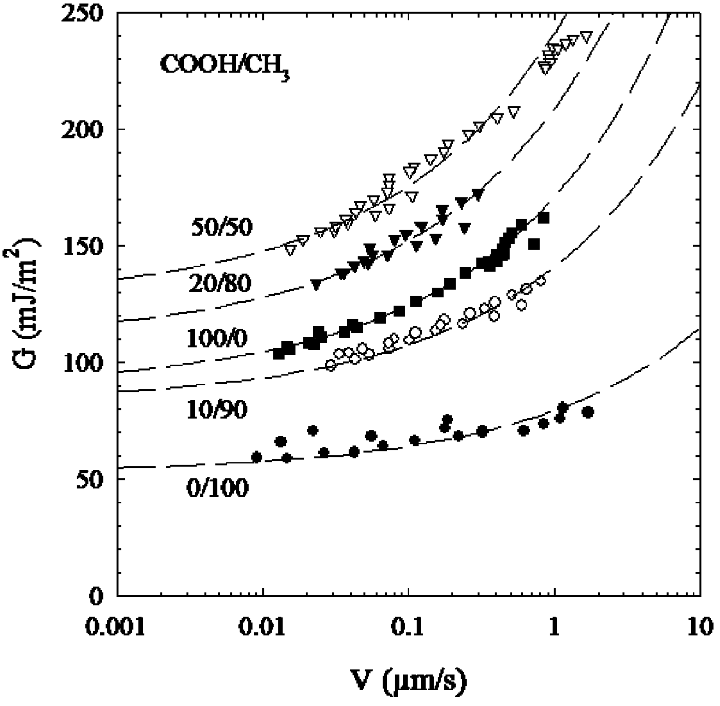

FIGURE 2 G(V) curves for an elastomer of pure PDMS (no resin) in contact with various substrates made of a thin film of gold deposited on a silicon wafer, on which thiol self-assembled monolayers have been formed, with various compositions in, respectively, mercaptoundecanoic acid and 1-dodecane thiol. The composition of each layer is characterized through the ratio of the concentrations of COOH and CH_3 terminated chains. All data were taken after a contact between the elastomer and the layer of two hours.

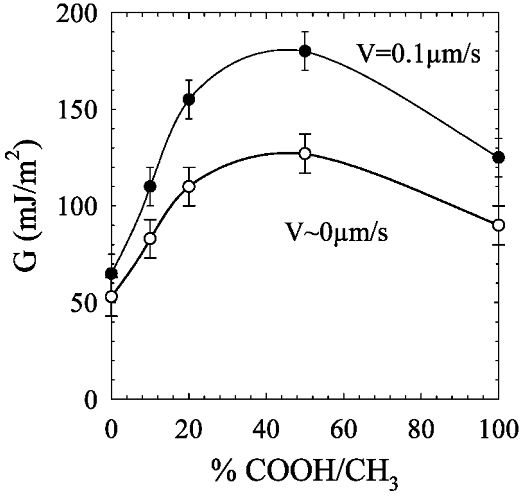

FIGURE 3 Selected data from Figure 2, now reported in terms of adhesive energy, G, as a function of the composition of the layer characterized through the ratio of the concentrations of COOH and CH_3 extremities for two velocities of the advancing fracture.

result is the clear non-monotonic evolution of the adhesive energy with the proportion of polar groups in the layer, for all investigated velocities, as illustrated in Figure 3, where the same data for two velocities are now represented in terms of the ratio [COOH]/[CH_3]. We have also investigated the effect of the contact time. The strength of the contact increases with contact time, as illustrated for layers with a ratio [COOH]/[CH_3] = 20/80, in contact again with a pure PDMS elastomer, in Figure 4.

In order to understand the mechanisms by which MQ resins incorporated into the PDMS elastomer could produce enhanced adhesive strength, the model substrates formed by the silicon wafers covered with thiol layers of various compositions were put into contact with elastomers lenses containing various amounts of MQ resins (the compositions are indicated in weight% of resin in the elastomer). We concentrate here on results obtained at a fixed [COOH]/[CH_3] ratio of 20% in the thiol layer. Again, we were surprised to observe a non-monotonic variation of the adhesive strength with the amount of MQ resin in the elastomer, as reported in Figure 5, even after a rather long contact time (more than 15 hours), while a naïve interpretation in terms of increased polarity in the elastomer due to the incorporation of the MQ resin would have led one to expect a progressive increase of

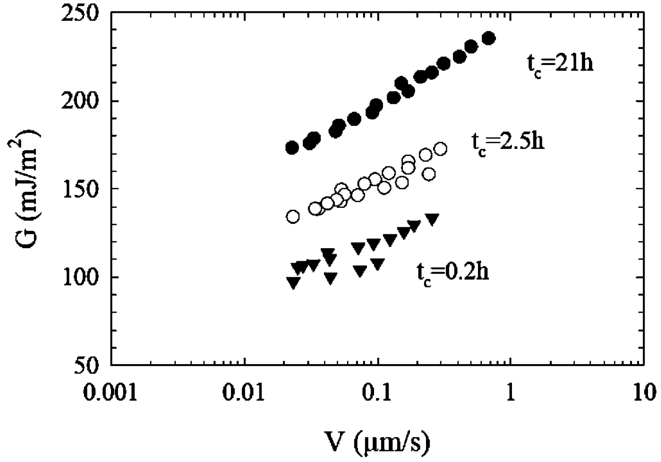

FIGURE 4 G(V) curves for an elastomer without resin and a layer with a ratio $[COOH]/[CH_3] = 20/80$ for different contact times between 0.2 hour and 21 hours.

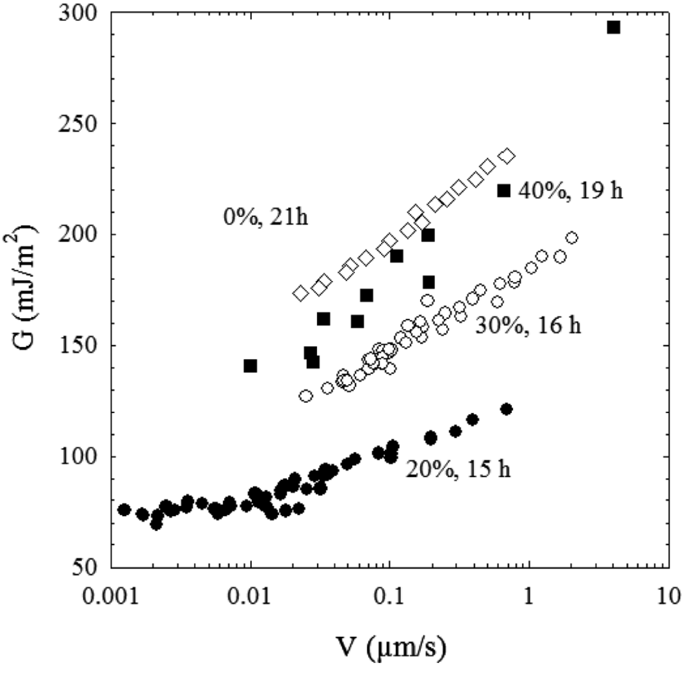

FIGURE 5 G(V) curves showing the influence of the resin content in the elastomer on the adhesive energy for layers with a ratio $[COOH]/[CH_3] = 20/80$ and a time under contact of overnight (15–19 hrs).

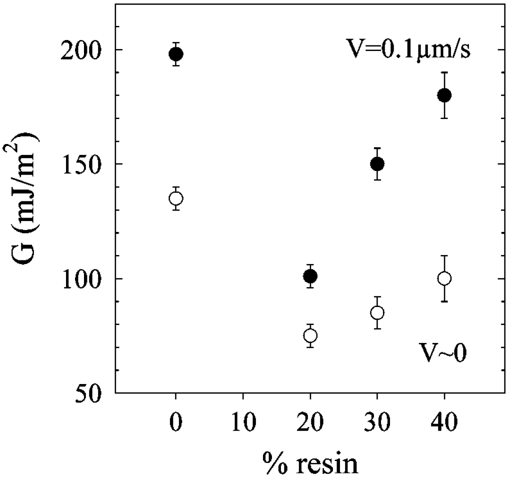

FIGURE 6 Selected data from Figure 5 demonstrating the nonmonotonic evolution of the adhesive energy on layers with a ratio [COOH]/[CH_3] = 20/80 with the resin content in the elastomer.

the adhesive energy when going from 0% to 40% resin content. This surprising result is clearly illustrated in Figure 6, where the data of Figure 5 are reported for two velocities of the fracture in terms of adhesive energy as a function of the resin content in the elastomer.

In order to check how the above results depended on the contact time we investigated in a systematic way the evolution of the adhesive energy for elastomers with 40% resin content on layers with a ratio [COOH]/[CH_3] = 20/80. The results are reported in Figure 7 in terms of G(V) curves and, again, quite surprisingly, the adhesive energy appears slightly larger at short contact times than at longer ones. In Figure 8 we have gathered data showing the sensitivity of the adhesive energy for a 40% resin content elastomer *versus* the composition in polar groups in the surface layer by comparing G(V) curves obtained on layers with the ratio of [COOH]/[CH_3] equal to, respectively, 0/100 and 20/80. Not only the adhesive energy, but also its velocity dependence, appear strongly affected by the composition of the layer in polar groups.

DISCUSSION

All above reported data demonstrate that the adhesive energy on the same series of substrates is highly affected by the incorporation of MQ resins into the elastomer.

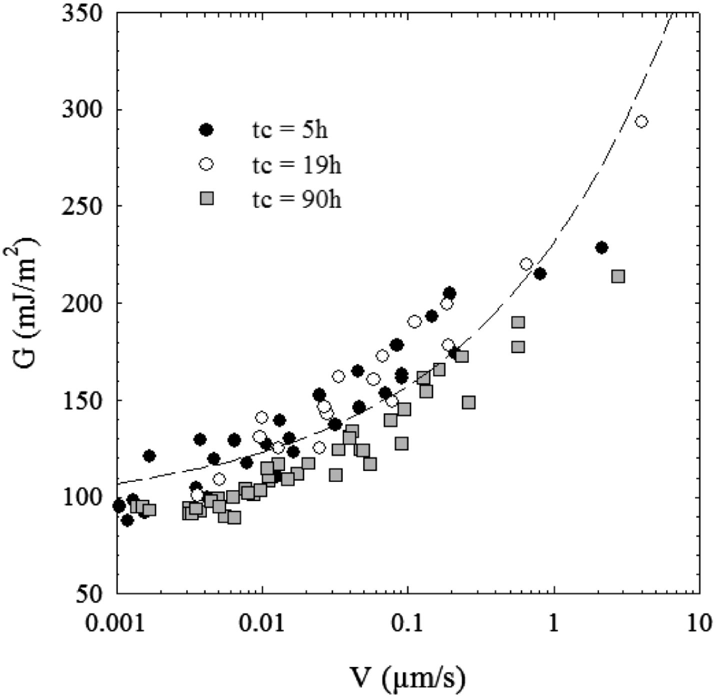

FIGURE 7 Influence of the contact time on the velocity dependence of the adhesive energy between an elastomer with 40% resin content and a layer with a ratio [COOH]/[CH_3] = 20/80.

For a pure PDMS elastomer we have seen that the adhesive energy depends on the proportion of polar groups in the layer. Following Ulman [7], the nature of the interaction between both surfaces is the formation of hydrogen bonds between a carboxylic acid group and oxygen of the backbone of the PDMS chains. One may also think that interactions between the dipole of the C = O and that of one Si-O-Si group could play a role. Experiments have shown that the adhesive strength was not increasing linearly with the concentration in acid groups. Such an effect could be due to the relative flexibility of the C_{11} chains in the thiol layer, which could allow double hydrogen bonds to form inside the thiol layer when the concentration in CH_3 becomes insufficient to separate chain extremities. The corresponding COOH groups are then not able to interact with the oxygen of the backbone of the PDMS chains, which behaves as a weak base, and the high [COOH]/[CH_3] ratio layers lose their efficiency to produce adhesion, as schematically illustrated in Figure 9. On layers of more rigid

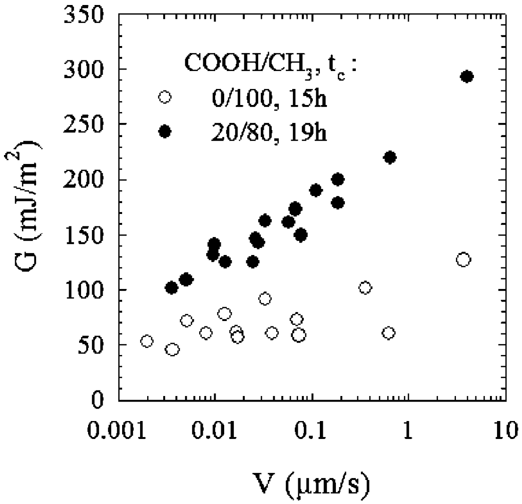

FIGURE 8 G(V) curves for an elastomer with 40% resin content demonstrating the sensitivity of the adhesive energy to the composition of acid groups of the layer.

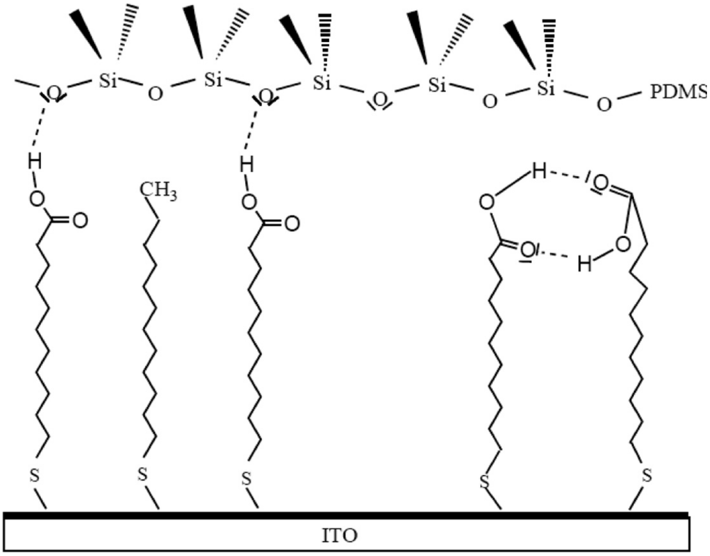

FIGURE 9 Schematic representation of the possible interactions between a mixed thiol monolayer and a PDMS chain along with an illustration of the possible interactions between COOH groups inside the monolayer for large enough concentrations in COOH groups.

biphenyl thiols Ulman has observed a linear variation of the adhesive strength [7] and we do observe a linear variation at low COOH concentration in the layer. Similar non-monotonic variations have indeed been reported by Wool *et al.* [8,9] for elastomers in contact with substrates having variable amounts of acid-base receptors.

The second striking experimental fact is the apparently weaker interaction for elastomers containing resins compared with the case of elastomers without resins, when in contact with surfaces at fixed composition in the thiol layer. Again, a naïve expectation would have been that, due to the increased oxygen concentration inside the elastomer associated with the presence of the resin, the elastomers with the larger resin content give the larger adhesive energy. This is clearly not the case. A possible explanation is a reduced mobility of the polymer chains when resin is incorporated into the elastomer, which could limit the possibilities of local reorganization at the surface, preventing the PDMS chains connected to the resin particles and to the network to find the correct orientation to form the hydrogen bond. One can then think that the adhesive strength between an elastomer containing resin and a surface results from a compromise between oxygen content and mobility of the chain segments inside the elastomer. Data in Figure 6 suggest that the composition in oxygen wins, finally, as the adhesive strength starts increasing again above 20% in resin. One can then think that adding more mobility in the surface layer by increasing, for example, the length of the chains grafted to the solid surface and bearing the COOH groups could lead to a better efficiency *versus* adhesion modulation, as long as the concentration of polar groups at the surface is small enough so that they do not bind together inside the layer (as suggested in Figure 9).

CONCLUSION

We have shown that increasing in a controlled manner the polarity of the substrate could allow one to identify that the enhancement in adhesive energy produced by incorporating MQ resins into PDMS elastomers was the result of a compromise between two effects: increased oxygen content, due to the presence of the resins which tends to favor hydrogen bond formation and dipolar interactions at the interface, and reduced mobility of the PDMS chains in the elastomer, due to the replacement of flexible segments between crosslinks by the rigid nanoparticles of the resin. Such a rigidification can inhibit chain reorganizations under contact and bond formation.

In practical situations where silicon MQ resins are used to adjust adhesive strength *versus* acrylic adhesives, it is certainly quite important to introduce mobility of interacting groups at the surface, with polar groups fixed on flexible long chains inside the acrylic adhesive layer, and, thus, compensate for the rigidification of the PDMS chains associated with the MQ resins.

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