

## Rate-Dependent Fracture at Adhesive Interface

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Schallamach's theory of rate-dependent bond dissociation is used to understand the fracture of a polymer–glass interface. The model system consists of an elastomeric film (20  $\mu\text{m}$  thick) of poly(dimethylsiloxane), chemically bonded to a silanized glass substrate. The fracture energy of the interface varies logarithmically with velocity, which is consistent with Schallamach's theory of forced bond scission. The activation energy (151 kJ/mol) of siloxane bond scission, as inferred from this study, is similar to that (147–180 kJ/mol) obtained from thermal de-polymerization and stress relaxation kinetics of the siloxane polymers. It is shown that the equilibrium threshold toughness of an interface is simply the product of the areal density of the polymer chains and the energy to dissociate a single bond. The well-known Lake–Thomas amplification of fracture energy by the number of bonds per chain can be understood only on the basis of the nonequilibrium aspects of the bond dissociation phenomena.

### Introduction

Two questions that are frequently asked in the context of the adhesion and fracture of polymeric materials are: why does the adhesion energy depend on the molecular weight of the polymer and why does it depend on the rate of separation. Based on the typical number of chains ( $10^{18}/\text{m}^2$ ) that cross a fracture plane and the energy needed (400 kJ/mol) to break a single chemical bond, the total energy of fracture should be only about 1 J/m<sup>2</sup>, which is significantly smaller than the experimentally observed values of 10–1000 J/m<sup>2</sup>. An answer to this discrepancy was provided by Lake and Thomas,<sup>1</sup> who recognized that the fracture energy in a polymeric system is amplified, because all the bonds of the polymer have to be activated even though only one bond ultimately breaks. The Lake–Thomas theory, however, does not explain why the fracture energy is rate dependent. The dependency of the fracture energy on the rate of separation is usually ascribed to bulk viscoelastic processes<sup>2–5</sup> or mechanical entanglement<sup>6–10</sup> near the interface. There are however several examples in the literature where it is clear that the rate dependent fracture is related to the chemical kinetic processes<sup>11–18,30</sup> at the interface. Recently, several other studies have pointed out that the de-bonding<sup>19–22</sup> forces in biomolecules can be successfully modeled using a kinetic theory of fracture. The starting point of all of these methods is the absolute reaction rate theory of Eyring,<sup>23</sup> according to which a bond breaks by a thermally activated tunneling mechanism. The rate dependent detachment of polymer chains using the reaction rate theory of Eyring was elegantly formulated by Schallamach<sup>24</sup> in developing an adhesion-based theory of rubber friction and, by Evans et al.<sup>21,22</sup> in dealing with the detachment forces in a single polymer chain.

The application of chemical kinetics to the studies of interfacial problems has a rather long history.<sup>13–15</sup> It has, in fact, been the basis with which to view the dynamic behavior of wetting,<sup>15</sup> and adhesion<sup>13,14</sup> as well as friction<sup>11</sup> in an unified manner. When the interaction at the interface is weak, the adsorption–desorption processes occur at segmental levels. In that case, the movement of a segment under an external force

( $F$ ) is viewed as a biased random walk, where  $F$  can be expressed as follows:<sup>13,15</sup>

$$F = (2kT/\delta) \sinh^{-1}(V\tau/2\delta) \quad (1)$$

$\delta$  is a characteristic lattice length,  $V$  is the net velocity, and  $\tau$  is the relaxation time of bond dissociation. Based on this concept, the interfacial viscous force for a moving contact line,<sup>15</sup> adhesive fracture energy<sup>13</sup> at rubber–glass interface as well as the dynamic frictional stress<sup>16</sup> at weak polymeric junctions are found to be proportional to  $\sinh^{-1}(V\tau/2\delta)$ . Expansion of  $\sinh^{-1}(V\tau/2\delta)$  shows that the dynamic components of adhesion, friction, and the resistive force at a moving contact line vary linearly with velocity when  $V \ll 2\delta/\tau$ , but vary logarithmically with velocity when  $V \gg 2\delta/\tau$ , which is a common observation.

In contrast to the cases cited above, Schallamach studied the problem of strong adhesion, in which the polymer chains stretch significantly.<sup>24</sup> In what follows next, we first present a simplified version of the theory of Schallamach with some modifications and then use it to elucidate some experimental results of rate dependent fracture involving a polymer-oxide interface.

**Thermally Activated Bond Dissociation and Fracture.** According to Eyring, a force ( $F$ ) applied to a chemical bond modifies the activation energy of the bond dissociation by  $-F\lambda$ .  $\lambda$  is the activation length of the bond,<sup>19,24</sup> the value of which was found by Evans et al.<sup>21,22</sup> to be in the range of 0.1 to 3 nm for some biopolymers. When a force ( $F$ ) is applied to an interface, the number of chains bridging the two surfaces decreases according to the following equation:

$$-\frac{d\Sigma_b}{dt} = \tau_-^{-1} n \Sigma_b \exp\left(\frac{F\lambda}{kT}\right) - K_+ \Sigma_u \quad (2)$$

$\Sigma_b$  and  $\Sigma_u$  are the number of polymer bridges in the bonded and nonbonded states respectively,  $k$  is the Boltzman constant,  $T$  is the absolute temperature,  $K_+$  is the rate constant of bond association.  $\tau_-$  is the characteristic time of bond dissociation,

which can be expressed as

$$\tau_- = \left(\frac{h}{kT}\right) \exp\left(\frac{E_a}{kT}\right) \quad (3)$$

$E_a$  is the activation energy of bond dissociation and  $h$  is Plank's constant. The factor  $n$  in eq 2 is due to the fact that any of the bonds in the polymer chain can dissociate. Thus the overall dissociation rate is amplified by the number of bonds ( $n$ ) per polymer chain. Let us consider a polymer chain of force constant  $M$  is stretched with a velocity  $V$  in the bridging zone. Since the force ( $F = MVt$ ) on the bond increases with time  $t$ , the rate of bond cleavage is described by the following nonlinear equation:

$$-\frac{d\Sigma_b}{dt} = \tau_-^{-1} \Sigma_b n \exp\left(\frac{MVt\lambda}{kT}\right) - K_+(\Sigma_o - \Sigma_b) \quad (4)$$

$\Sigma_o$  is the total numbers of chains at  $t = 0$ . The rate constant of bond association ( $K_+$ ) can be expressed as follows:

$$K_+ = \tau_+^{-1} \exp\left(-\frac{M_1 X_1^2}{2}\right) \exp\left(-\frac{M_2 X_2^2}{2}\right) \quad (5)$$

$\tau_+$  is the characteristic time of bond association,  $M_1$  and  $M_2$  are the spring constants of two reassociating polymer chain fragments,  $X_1$  and  $X_2$  are the lengths by which the polymer chain fragments have to extend from their relaxed positions in order to reassociate. It is straightforward to show that  $M_1 X_1^2 + M_2 X_2^2 = MV^2 t^2$ ; hence, eq 4 becomes

$$-\frac{d\Sigma_b}{dt} = n\tau_-^{-1} \Sigma_b \exp\left(\frac{MVt\lambda}{kT}\right) - \tau_+^{-1} (\Sigma_o - \Sigma_b) \exp\left(-\frac{MV^2 t^2}{2kT}\right) \quad (6)$$

The average time of bond survival can be expressed as follows:

$$\bar{t} = \int_0^\infty \left(\frac{\Sigma_b}{\Sigma_o}\right) dt \quad (7)$$

Once the average time of bond survival is estimated from equations 6 and 7 the average force on a chain before it breaks into two parts can be expressed as  $F = MV\bar{t}$ .

Numerical simulation showed that the chain association rate in eq 6 is considerably smaller than the chain dissociation rate and can be neglected. The solutions of equations 6 and 7 thus can be expressed as the following exponential integral function.<sup>24</sup>

$$\bar{t} = \left(\frac{kT}{MV\lambda}\right) \exp\left(\frac{nkT}{MV\lambda\tau_-}\right) \int_{\frac{nkT}{MV\lambda\tau_-}}^\infty q^{-1} \exp(-q) dq \quad (8)$$

Another level of simplification of eq 8 is possible when  $nkT \ll MV\lambda\tau_-$ . In that case, the exponential-integral function becomes

$$\bar{t} = \left(\frac{kT}{MV\lambda}\right) \left[ \ln\left(\frac{MV\lambda\tau_-}{nkT}\right) - \gamma \right] \quad (9)$$

where  $\gamma$  is Euler's constant (0.55), the value of which is negligible compared to the leading logarithmic term. According to eq 9, the average force ( $MV\bar{t}$ ) on a chain varies logarithmically with the stretching velocity. Recently, Evans et al.<sup>21,22</sup> reached a similar result by maximizing the time-dependent bond dissociation rate,  $\Sigma_b'$  (eq 6). Indeed, eq 9 (without the Euler's

constant) can be easily recovered from eq 6 by setting  $\Sigma_b''(t)$  equal to zero.

Once the average force ( $F = MV\bar{t}$ ) to dissociate a bond is known, the elastic energy stored in the polymer chain up to its breaking point is  $\epsilon = F^2/2M$ . This much energy will be converted to irrecoverable work when the bond breaks and the chain relaxes under zero load. Total energy dissipation can be obtained from the product of  $\epsilon$  and the number ( $\Sigma_o$ ) of chains crossing the fracture plane per unit area.

$$G_{el} = \left(\frac{\Sigma_o}{2M}\right) \left[\frac{kT}{\lambda}\right] \ln\left(\frac{MV\lambda\tau_-}{nkT}\right)^2 \quad (10)$$

The spring constant of a polymer is inversely proportional to the number of monomers ( $n$ ) in the chain, whereas  $\Sigma_o \sim n^{-1/2}$ . We thus have from eq 10  $G_{el} \sim n^{1/2}$ —the classical Lake–Thomas<sup>1</sup> result ( $G \sim n^{1/2}U$ ). However, the bond dissociation energy  $U$  of the Lake–Thomas theory is now replaced with a function that contains kinetic parameters.

**Lake–Thomas Theory Is Incompatible with the Notion of Equilibrium Fracture.** The Lake–Thomas theory of polymer chain dissociation is often used to describe the equilibrium threshold toughness of an interface. It can, however, be shown that if the kinetic effects are ignored, there is no molecular weight dependent amplification of fracture energy. This can be shown by rewriting eq 6 as follows:<sup>20</sup>

$$-\frac{d\Sigma_b}{dt} = \frac{n\Sigma_b}{\tau_-} \exp\left(\frac{MX\lambda}{kT}\right) - \frac{(\Sigma_o - \Sigma_b)}{\tau_+} \exp\left(-\frac{MX^2}{2kT}\right) \quad (11)$$

where  $X$  is the extension of the polymer chain in the crack tip region. Since  $\exp(-MX\lambda/kT) \ll \exp(-MX^2/2kT)$ , the equilibrium value of  $\Sigma_b$  is

$$\Sigma_b = \frac{\Sigma_o}{1 + n \exp\left(\frac{MX^2}{2kT} - \frac{U}{kT}\right)} \quad (12)$$

where  $U$  is the bond dissociation energy. When a crack propagates at vanishing speed ( $V \rightarrow 0$ ), the bonded and unbonded chains are in chemical equilibrium; thus the fracture energy becomes

$$G = M\Sigma_o \int_0^{X_m} \frac{X dX}{1 + n \exp\left(\frac{MX^2}{2kT} - \frac{U}{kT}\right)} \quad (13)$$

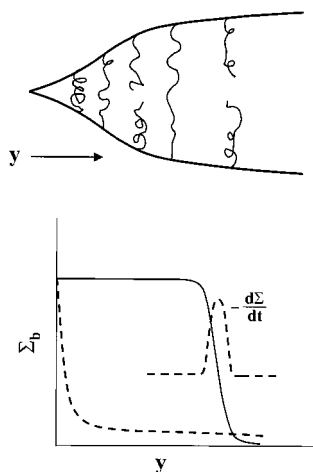
where,  $X_m$  is the maximum extension of the polymer chain before fracture, which may be obtained from the relationship:  $nU = MX_m^2/2$ . Equation 13 can now be integrated to obtain eq 14

$$G = \Sigma_o nU - kT\Sigma_o \ln\left[\frac{1 + n \exp\{(n-1)U/kT\}}{1 + n \exp(-U/kT)}\right] \quad (14)$$

Usually,  $U/kT \gg 1$ . Hence, eq 14 yields

$$G = \Sigma_o U - \Sigma_o kT \ln(n) \quad (15)$$

The second term, which arises because of the fact that a polymer chain can break at any of the bonds in its backbone, is usually negligible in comparison to the first term. We thus find that the equilibrium (threshold) fracture energy is a simple product of the areal chain density and the energy needed to dissociate a single bond. The classical Lake–Thomas amplifica-



**Figure 1.** Schematic of the crack tip region showing how the density of the bonded chains varies as a function of distance from the crack tip region. The dashed line indicates equilibrium distribution and the solid line indicates nonequilibrium distribution.

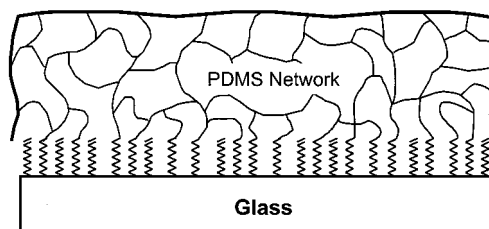
tion factor ( $n$ ) has disappeared from the final equation. Clearly the notion of equilibrium threshold toughness is incompatible with the Lake–Thomas effect, according to which the fracture energy is amplified by the number of bonds in a chain. The Lake–Thomas amplification however arises because equilibrium is not achieved in most realistic fracture experiments. The distribution of chains in the crack tip region for both the equilibrium and nonequilibrium situations are shown schematically in Figure 1. At equilibrium, the density of chain falls off rapidly with the distance  $y$  from the crack tip. Under a kinetic crack growth situation, the chain density remains almost constant over a certain distance ( $y$ ) along the crack tip and then decreases at a catastrophic rate only after a critical length  $y_m$  is reached. Consequently, the crack tip stores and subsequently dissipates more elastic energy (eq 10) under the kinetic crack growth condition than under equilibrium condition.

The molecular weight dependence of the fracture energy has been examined in detail by several authors.<sup>25–28,31</sup> Here we examine the velocity dependence of the fracture energy with a simple experiment, in which a crack grows at extremely slow velocities ( $1 \text{ \AA} < V < 1000 \text{ \AA}$ ).<sup>29</sup>

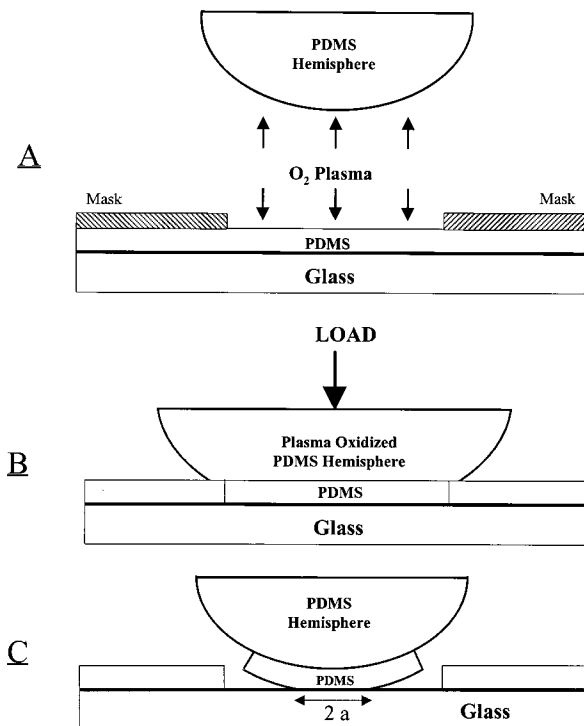
## Method

**Rate Dependent Fracture at the Interface of Glass and Poly(dimethylsiloxane).** The test case involves a thin film of silicone elastomer (Dow Corning Sylgard-184) chemically bonded to a glass slide, which was primed by reacting it with the vapor of undecenyltrichlorosilane. The silane chemisorbs<sup>30</sup> onto glass to form a thin film whose olefin functionalities are available for further reaction.<sup>31</sup> A thin film ( $20 \mu\text{m}$ ) of the liquid polymer was cross-linked onto this primed glass slide at  $75 \text{ }^\circ\text{C}$  for about 1 h and then it was stored in the laboratory atmosphere for 3 days before fracture experiments. Sylgard-184 contains vinyl-terminated silicone oligomer, a methyl hydrogensiloxane cross-linker and a platinum catalyst to carry out the hydrosilation reaction. It also contains silica resin for re-enforcement. The resultant polymer is an elastomer with a glass transition temperature of  $-116 \text{ }^\circ\text{C}$ . The elastic modulus of the polymer is 1 MPa. During cross-linking, some of the SiH groups of the polymer react with the olefin groups on the primed glass slide, thus establishing chemical adhesion of the two materials (Figure 2).

The interfacial fracture energy in the above system was estimated using a modified JKR method (Figure 3). In that, the

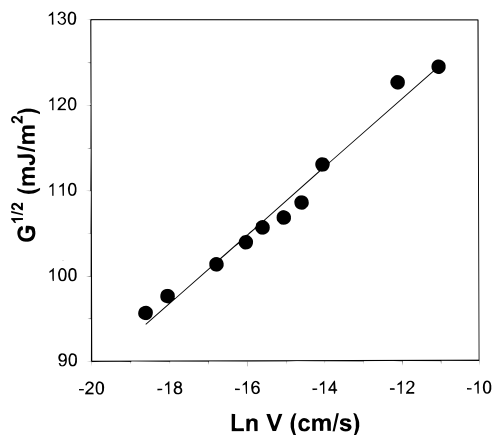


**Figure 2.** Schematic of a PDMS film ( $\sim 20 \mu\text{m}$ ) bonded to glass. The glass slide was primed with a silane (undecenyltrichlorosilane) before the elastomer was applied on it as a liquid. The elastomer cross-links by hydrosilation reaction. During the process of cross-linking, it also reacts with the olefin groups of the silane, thus adhering strongly to glass.



**Figure 3.** Schematic of a method used to measure the adhesion energy between the thin silicone film and glass. The PDMS film and a large PDMS hemispherical lens were first oxidized in an oxygen plasma. Part of the film is masked in order to prevent it from oxidation (A). When the oxidized hemisphere is pressed against the oxidized PDMS film, strong adhesion develops where the oxidized surfaces come into contact (B). The oxidized lens peels off easily from the region of the PDMS film that was not oxidized. Finally, the hemisphere peels the PDMS film off the glass plate (C). The typical size of the PDMS hemisphere was about 1 cm. These large hemispherical PDMS elastomers were prepared under water on a polystyrene Petri dish by modifying a method described in ref 30. Because of the similarity of the density of PDMS and water, no significant gravitational flattening occurred during the cross-linking of the polymer.

cross-linked PDMS film was first masked with a tape but exposing a small area ( $9 \text{ mm} \times 9 \text{ mm}$ ) for plasma oxidation. After plasma oxidation, the adhesive mask was removed and subsequently a large ( $R = 1 \text{ cm}$ ) plasma oxidized silicone lens was pressed against the elastomeric film by covering the oxidized area for 2 min. Plasma oxidation renders the surface of the silicone elastomer highly reactive. When two such surfaces are brought into contact with each other, the interface welds almost instantaneously,<sup>30</sup> presumably due to the condensation of surface silanol groups. The oxidized PDMS lens adheres strongly to the oxidized PDMS film; thus, when the PDMS lens is unloaded, the tensile stress produced at the contact



**Figure 4.** A plot of  $G^{1/2}$  versus  $\ln(V)$ , where  $G$  is the fracture energy and  $V$  is the velocity at which the surfaces are separated in the direction perpendicular to the crack. From the slope  $(\Sigma/2M)^{1/2}$  and intercept  $[(\Sigma/2M)^{1/2}(\ln(M\lambda\tau/kT))]$  of this plot, the spring constant ( $M$ ) and the dissociation time ( $\tau$ ) of the siloxane bond can be estimated.

periphery partially peels off the PDMS film from the glass slide. As a result, a circular contact area develops at the PDMS film/glass interface, which decreases slowly with time. From this time dependent evolution of the contact area, the crack growth velocity could be determined. The fracture energy was obtained using the classical theory of Johnson, Kendall, and Roberts<sup>32</sup> (eq 16).

$$G = \frac{\left(\frac{4E^*a^3}{3R} - P\right)^2}{8E^*a^3} \quad (16)$$

$P$  is the external load, which, in the present case, is the weight of the lens;  $a$  is the radius of the contact circle; and  $R$  is the radius of the hemisphere. The elastic modulus  $E^*$  was determined in a separate calibration experiment following the methodologies described in ref 29. This method of peeling an already deposited thin film from a flat surface is somewhat similar to a method reported earlier by Knarr et al.,<sup>33</sup> who used it to form smooth gold films on mica surfaces.

## Results and Discussion

For a PDMS lens of  $R = 1$  cm, the contact diameter decreased by about 20% over a period of 20 h—corresponding to a 50% decrease of the fracture energy ( $G$ ). After 20 h, the interfacial area changed extremely slowly ( $< 1 \text{ \AA/s}$ ). Although the glass slide from which the PDMS film was delaminated appeared clean by visual inspection, atomic force microscopy before and after the fracture revealed that the surface was covered with a thin polymer film. Evidently, significant scission of polymer chains occurred near the interface. Consequently, the fracture energy ( $9\text{--}17 \text{ J/m}^2$ ) for this system is orders of magnitude higher than the van der Waals energy ( $0.1 \text{ J/m}^2$ ) of adhesion but is in the range of the tearing energy of the polymer.

Figure 4 shows that  $G^{1/2}$  varies logarithmically with the velocity<sup>34</sup> as expected from eq 9. We next estimate the values of the spring constant of the polymer chain and the natural dissociation time of the siloxane bond from Figure 4 using some approximate values of  $\Sigma$  and  $\lambda$ . Using the method of Lake and Thomas,<sup>1</sup> the number density of polymer chain crossing a fracture plane in the bulk of the polymer is estimated to be about  $2.5 \times 10^{18}$  chains/ $\text{m}^2$ , which is a reasonable upper-limit estimate of  $\Sigma$ .  $\lambda$  is taken to be  $0.1 \text{ nm}$ —on the order of a bond length. The values of  $M$  and  $\tau_-$  are, thus, estimated to be  $0.14 \text{ N/m}$

and  $3 \times 10^{13} \text{ s}$ , respectively. The magnitude ( $140 \text{ mN/m}$ ) of  $M$  obtained here is higher than that ( $0.3 \text{ mN/m}$ ) of a PDMS chain in a Gaussian coil, but much less than the spring constant ( $\sim 10^4 \text{ mN/m}$ ) of the chain due to bond distortion obtained from vibrational spectroscopy.<sup>35</sup> According to Eyring, the natural relaxation time of a chemical bond is  $\tau_- = (h/kT) \exp(E_a/kT)$ . Since the bond relaxation time ( $\tau_-$ ) is about  $3 \times 10^{13} \text{ s}$ , the activation energy of siloxane bond dissociation is estimated to be about  $151 \text{ kJ/mol}$ . This energy is higher than the activation energy of the hydrolysis<sup>36</sup> ( $67\text{--}76 \text{ kJ/mol}$ ) of a siloxane bond but is close to that obtained in the thermal de-polymerization<sup>37</sup> ( $180 \text{ kJ/mol}$ ) of PDMS in a vacuum and the value ( $147 \text{ kJ/mol}$ ) obtained from stress-relaxation measurements<sup>38</sup> on a PDMS elastomer under inert conditions. The estimated activation energy of bond dissociation is remarkably smaller than the dissociation energy ( $454 \text{ kJ/mol}$ ) of the siloxane bond.

Thomas and Kendrick<sup>37</sup> proposed that the siloxane bond scission and rearrangement occur via a transition state involving d-orbitals, which lowers the energy barrier relative to that which would, otherwise, be required for direct rupture of the bond. It is possible that the siloxane bond cleavage is autocatalysed by the backbiting of the siloxane bonds in the chain by the terminal  $\text{Si}^+$  and  $\text{SiO}^-$  groups and subsequently forming new  $\text{Si}^+$  and  $\text{SiO}^-$  terminated chains. Another plausible explanation for the low activation energy may be that the siloxane bond cleavage is catalyzed by impurities or other chemical agents (such as water) present either in the polymer or in the atmosphere. Systematic experiments under different environmental conditions are needed in order to shed more light on the problem in future.

Based on the above values of  $M$ ,  $\lambda$ , and  $E_a$ , the force ( $F = MV\dot{\gamma}$ ) to break a siloxane chain ( $D_p = 150$ ) is estimated to be about  $1$  to  $1.6 \text{ nN}$  for a velocity range of  $10^{-3}$  to  $10^3 \text{ \mu m/s}$ . Forces of this magnitude have been observed by Senden et al.<sup>39</sup> in the force–distance scans of a silica AFM tip on an adsorbed PDMS layer. It is however not clear if those forces represent siloxane bond breaking or multiple H-bonding interactions between silyl ethers and silica. Covalent forces of comparable magnitudes have however been reported for other systems recently.<sup>40</sup>

**General Comments.** The thermally activated bond-cleavage theory of Eyring seems to be adequate for the studies of fracture. The particular method of estimating the bond survival time and thus bond strength, as pioneered by Schallamach, provides an useful means to estimate fracture energy as a function of the rate of separation. Our analysis shows that the equilibrium threshold toughness of an interface is simply the product of the number of chains and the dissociation energy of a single bond, which is incompatible with the notion of Lake and Thomas. The well-known Lake–Thomas amplification of fracture energy by the molecular weight of the polymers can be understood only on the basis of the nonequilibrium nature of the bond dissociation kinetics.

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