Molecular Weight Effects in Chain Pullout

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Received September 8, 1993; Revised Manuscript Received February 22, 1994[⊛]

ABSTRACT: We have shown that the addition of polyisoprene (PI) tethered chains to a polystyrene (PS) substrate produces a large increase in its adhesion to a PI cross-linked lens over the whole range of crack speeds (10^{-10}–10^{-7} m/s) that we have investigated. Such an increase cannot be explained by the rate dependence of bulk viscoelastic losses and is believed to be due to the viscous pullout of the PI chains from the network. At low crack speeds the fracture toughness of the interface G_c was found to increase linearly with velocity from a threshold value G_0. At higher crack speeds a transition occurred, after which the fracture toughness increased at a much lower rate which could be attributed to viscoelastic bulk losses. The threshold toughness G_0 increased monotonically with both the areal density of tethered chains and their degree of polymerization. The results are compared with existing models of interfacial failure by chain pullout. The measured rate of increase of G_c with V implies there is a very high effective friction at very low pullout rates. This high friction is probably related to the very long time constant for a chain within a network.

Introduction

Adhesion between elastomers is a technologically important field and has therefore been the subject of continuing study for several decades. However, compared to glassy polymers, little is known about the relation between the molecular processes controlling failure and the macroscopic fracture properties. Two main difficulties face the investigator: (i) The plastic or viscoelastic deformation taking place during fracture is generally not localized at the crack tip but is spread over a large volume, and (ii) the molecular structure of the cross-linked network is very hard to characterize and to control precisely. It is therefore very difficult to determine which molecular mechanisms are responsible for the observed macroscopic behavior.[1,2]

At the molecular level, adhesion between two polymers depends on the ability of the interface to sustain stress. This can be achieved by any of the following means: (1) van der Waals bonds between the polymer chains on either side of the interface; (2) bridging chains coupled on each side of the interface by physical entanglements; (3) bridging chains coupled on each side of the interface by chemical bonds.

At the macroscopic level, on the other hand, the energy required per unit area to fracture the interface, G_c, depends on the ability of the interface and its surrounding volume to dissipate energy by plastic or viscoelastic deformation. An understanding of the relationship between sustainable stress and fracture energy is critical to the molecular approach to fracture mechanics.

Although mechanism 3 is always effective in increasing the sustainable stress, mechanisms 1 and 2 are effective only in specific conditions which will now be reviewed briefly. In elastomers, the dissipative mechanisms are viscoelastic in nature and are a very strong function of the rate of crack propagation.[3-6] The adhesion of an elastomer to a rigid, nonreactive substrate (where no chain interpenetration is possible and only mechanism 1 can operate) can be quite high at a sufficiently high crack growth rate, while a value close to the thermodynamic work of adhesion is recovered when the crack propagation rate is very low. It has been argued that viscoelastic losses act as a rate-dependent factor that multiplies the Dupré work of adhesion.[3-6] In contrast, for glassy polymers, significant adhesion is obtained only if the interface can sustain a high enough stress to activate the main dissipative plastic deformation mechanisms, causing a considerable increase in fracture toughness. van der Waals forces are too weak to cause such an activation but recent experiments with block copolymers have shown that well-entangled chains, hence mechanism 2, can give high adhesion.[7-10]

The effect of chain interdiffusion and subsequent pullout on the measured energy of adhesion of elastomers is still somewhat under debate. In the case of self-adhesion between networks, where some chain interpretation is possible, there is little conclusive evidence that the chain interpenetration has any effect as in some cases[11] no difference was found at low rates between self-adhesion and adhesion to rigid substrates while at high rates the difference could be attributed to different bulk viscoelastic dissipation processes. However, the effect of chain interdiffusion on the work of adhesion was clearly seen in Ellul and Gent's experiments on blends of cross-linked and un-cross-linked material.[11,12] An addition of free chains greatly increased G_c at high rates but had no effect on the toughness at very low rates. It should be pointed out that in those experiments there was no control on the areal density of chains being pulled out or on the pulled-out length so that it was impossible to relate the measured toughnesses to molecular parameters. More recently, Reichert and Brown[13] placed a known amount of block copolymer at the interface between sheets of polystyrene and polyisoprene and found that, at the pullout rate that they used, the presence of block copolymer increased G_c by up to a factor of 5. In his preliminary results obtained using the JKR technique discussed here, Brown[14] showed that this increase in G_c caused by chain pullout is, as expected, greatly dependent on the crack propagation rate and subsists even when the crack velocity tends to zero.

On the theoretical side, the traditional view has been that, if no chemical bonds are being broken during the separation process, all energy losses are due either to viscoelastic losses around the crack tip or to viscous friction due to the extraction of chains from the bulk polymer.[2] Both of those contributions should vanish when the crack propagation rate goes to zero, giving therefore a zero-rate toughness equal to the thermodynamic work of adhesion

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[⊛] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

0024-9297/94/2227-3174$04.50/0

W which is twice the surfac energy γ for adhesion between two blocks of the same material. More recently, Raphaël and de Gennes[15] argued that, in the case of chain extraction, a finite force due to a combination of the surface energy of the chains exposed to air and their elastic stretching energy was necessary to keep an opening displacement even at zero velocity. Hence the zero-rate toughness G_0 should be greater than W.

Until very recently it has been assumed that the friction involved in chain pullout is just the Rouse friction that controls the mobility of a chain in its tube in diffusion processes. However, Rubinstein et al.,[16] in considering the problem of slip between a hard wall with attached grafted chains and a network, have argued that chain pullout should have similar, very slow, dynamics to those of a star molecule. If this argument is correct, it should have a profound effect on the understanding of the dynamics of chain pullout with ramifications in areas as diverse as rheology, adhesion, and polymer crystallization. Adhesion experiments are a direct way to measure the dynamics of chain pullout.

It is clear that an investigation of these outstanding issues requires the use of a test where G_c can be measured for a range of crack velocities including specifically very low velocities. The test also must minimize the volume of the sample which is under stress to reduce the contribution of bulk viscoelastic losses to G_c to a negligible amount. Traditionally, adhesion between elastomes and rigid substrates has been measured by peel tests.[5,6] This technique is relatively simple and allows the experimenter to control crack velocity over a broad range of values. Its recognized disadvantages are however that, although viscoelastic losses can be minimized by careful experimental design and use of very low peel rates, they remain relatively large compared to the thermodynamic work of adhesion W. Blister tests have alternatively been used but, in measurements of threshold adhesion, values approximately 1–2 orders of magnitude larger than W are typically found, indicating a still substantial contribution of bulk viscoelastic losses to the measured energy of adhesion even near zero crack velocity.[17-19] At room temperature, practical growth rate for these techniques are of the order of 10^{-1}–10^{-6} m/s and to further lower viscoelastic losses, experiments must be carried out at higher temperature. Furthermore, the reproducibility of the contact surface between the adherends is problematic for both techniques.

Alternatively, a technique first developed by Johnson, Kendall, and Roberts[20] can be used. In this technique, a spherical cap is pushed against a flat plate so that their contact area depends on the applied load, the elastic properties of the cap, and the work of adhesion between the two materials. If a load is applied and then released, the area of contact will decrease slowly with time and the measured work of adhesion can be interpreted as a strain energy release rate G_c. The practical range of crack growth rates is typically very low and in our case was 10^{-7}–10^{-10} m/s. These low rates and the small volume of material under stress make this experimental technique ideally suited for measurements of rate-dependent very weak adhesion. Recently, Chaudhury et al.[21,22] have developed a procedure to make hemispherical caps with very reproducible surfaces, and it is this technique which we chose to use for our experiments.

Experimental Procedure

Preparation of the Substrates. Our goal was to control both the areal density and the length of the chains being pulled out. To that end, we chose to use a flat surface covered with a controlled number of anchored polyisoprene (PI) chains. These anchored polyisoprene chains were in fact the polyisoprene blocks of an ordered layer of polyisoprene–polystyrene block copolymer. The silicon substrates were first "primed" with a polymeric brush made of end-grafted polystyrene (PS) chains. The end-functionalized PS had a number-average molecular weight M_n = 160000 and a polydispersity M_w/M_n = 1.05 and was prepared by terminating a living polystyryl anion with (*p*-(chloromethyl)-phenyl)trimethoxysilane.[23] A thin film of the resulting polymer with spin-coated on a silicon substrate from a solution in toluene and subsequently annealed in vacuum at 175 °C for 1 h to allow the sililation grafting reaction to proceed. The surplus polymer was then washed off with toluene, leaving a PS film of ~13-nm thickness. A thin film of PS–PI block copolymer was spun cast onto these modified silicon substrates from a solution in cyclohexane or in toluene. The characteristics of the block copolymers are given in Table 1 and will be referred to by the degree of polymerization of the polyisoprene block, N.

Table 1. Properties of the Diblock Copolymers[a]

N	M_{PS}	M_{PI}	v (nm^3)	R_g (nm)	v/R_g (nm^2)
588	25,000	40,000	73	6.3	7.9
882	60,000	66,000	110	7.7	14.3
2205	100,000	150,000	274	12.1	22.6

[a] N is the degree of polymerization of the PI block, M_{PS} and M_{PI} are the molecular weights of the PS and PI blocks, and v is the molecular volume and R_g the radius of gyration of the PI block.

In the final preparation step the spun film of diblock, which was in a nonequilibrium, relatively homogeneous state, was annealed at a temperature above the T_g of both blocks so that it organized with the PS block mixing with the PS underlayer and the PI block at the air surface. In previous work[14] the substrates were heated to 120 °C for 1 h to permit this organization but in this work, to alleviate concerns about thermal degradation, the annealing was done at room temperature in the presence of solvent vapor. The substrate was exposed for 15–45 min to toluene vapor with reduced activity (a 50 wt % solution of PS in toluene). Diblock layers on flat substrates are known to organize by forming terraces of uniform thickness that are observable by optical microscopy as areas of constant interference color.[24] Terraces only form in layers with thicknesses considerably greater than those used in this work. However, even for thin layers of copolymer the spinning process leaves a thick copolymer rim round the edge of each wafer and terraces can form in this rim. Hence annealing times were chosen to be long enough that terraces formed in the thick copolymer rim at the edges of the substrates. We assumed here that, after the vapor anneal, the PS block was mixed with the PS in the brush and the PI block was at the air surface. Unfortunately, we do not have any direct evidence that the diblock organizes in this way; however, the assumption is consistent with previous TEM and nuclear reaction analysis observations.[13,25-27]

It should be noted that, if the sample is left too long in toluene vapor, patches in the diblock layer will increase in thickness and form islands of copolymer and areas that are free of copolymer, thereby reducing the area of interface between PS and PI.[28] However, the kinetics of this islanding process is much slower than the kinetics of organization of the block copolymer, allowing us to choose an annealing time that is long enough to organize the copolymer but short enough that the copolymer layer is still of uniform thickness. Thereby we can obtain substrates with a controlled areal density of grafted PI chains.

The areal density of copolymer chains was calculated by measuring the film thickness before and after spin casting the copolymer with a Rudolph AutoEl ellipsometer.

Preparation of Lenses. The polyisoprene lenses were made from a nearly monodisperse PI standard with M_n = 28300 and a polydispersity of 1.05 purchased from Polymer Laboratories. A solution of 50 wt % of the PI was made in decalin, to which 6 wt % (based on the PI) of dicumyl peroxide was added as a cross-linking agent. About 15–20 drops of the solution were then deposited on a glass slide, the surface of which had been previously treated to reduce its surface energy. The low surface energy surface was obtained by dipping a glass slide in a dilute solution in hexane of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane purchased from PCR Inc.

The glass slide covered with drops of isoprene solution was then sealed in a 50-mL flask under reduced pressure of argon and put in an oven at 155 °C for 3 h to cross-link the lenses. Special care was taken to prevent light from entering the oven during the cross-linking process.

After cross-linking, the lenses were dried by leaving them overnight in a vacuum oven. The modulus of the lenses was determined by a direct mechanical measurement for each individual lens as described in the next section. From these modulus values we obtained the average molecular weight between cross-links, which varied somewhat from lens to lens, probably due to uneven heating conditions, and was typically between 2400 and 4200. In a previous paper,[14] the moduli were obtained by swelling measurements. Because of the very small weight of the lenses (2–3 mg), an accurate measurement of the swelling ratio was difficult and hence we changed to the present method of measuring modulus. The sol fraction after cross-linking (probably <1%) was not normally extracted from the lenses. Lenses where the sol fraction had been extracted in cyclohexane gave results which were not significantly different from those obtained using the unextracted lenses except that the extracted lenses gave a higher experimental scatter, probably because they had a less reproducible surface due to the greater amount of handling required. The effect of the sol fraction was therefore assumed to be small and accepted as an inevitable result of the experimental method.

Measurement of the Modulus and the JKR Experiment. When a spherical cap is loaded in contact with a plane, the equilibrium contact area is influenced by both the loading and the surface forces that operate in the contact area. The first solution to this problem was proposed by Hertz, who neglected surface forces all together. When surfaces forces are considered, the problem is no longer amenable to an analytical solution. However, two limiting cases have been solved analytically: when the modulus of the spherical cap is high and its radius small relative to the interfacial work of adhesion, the Derjaguin–Muller–Toporov[29] (DMT) approximation is valid, while in the opposite limiting case, the Johnson–Kendall–Roberts[20] (JKR) approximation is valid. The transition between the two solutions has been discussed recently.[30,31] In our case the JKR approximation is appropriate and will be used to calculate the results. The situation with equilibrium surface forces can be extended directly to the situation of crack propagation as long as the apparent work of adhesion, W, is interpreted as a fracture toughness[32] (really critical strain energy release rate) G_c. This extension, which is discussed in more detail in the Appendix, is entirely equivalent to the extension of the Griffith theory of brittle fracture (essentially an equilibrium theory) to form the basis of fracture mechanics.

The modulus of the hemispherical lenses are obtained using the JKR analysis by measuring the diameter of the contact area between the lens and a PS surface as a function of the applied load P. The measurement of the load was obtained from the deflection of a three-point bending beam outfitted with a strain gauge, while the diameter of the contact area was obtained by direct observation through a reflected-light optical microscope.

Following Chaudhury's procedure,[22] the modulus was then obtained by fitting the data to the expression

$$a^3 = (R/K)\{P + 3\pi WR + [6\pi WRP + (3\pi WR)^2]^{0.5}\} \qquad (1)$$

where $K = 16E/9$ is the efective modulus, E is the Young's modulus of the lens, a is the radius of the contact area, R is the radius of the lens, and W is the work of adhesion. It should be pointed out here that we measured the area of contact using loads of up to 0.2 N, a value which is much larger than Chaudhury's maximum load.[22] In this regime, surface forces have a negligible effect on the area of contact and $a^3 \approx RP/K$. As can be seen in Figure 1, our data fit eq 1 very well and give a value of K that is accurate within 3–5%. The radius of curvature of the lens was obtained by photographing the lens from the side after the experiment was finished.

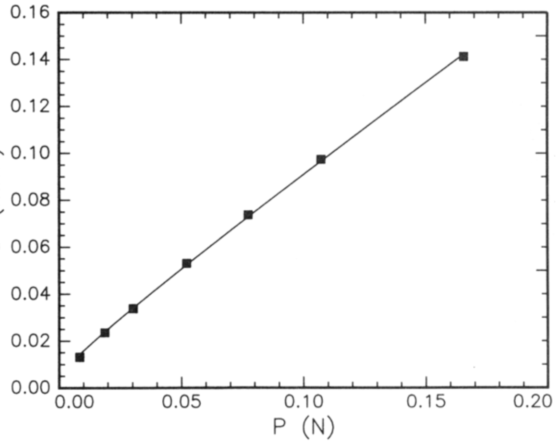

Figure 1. Variation of the cube of the contact radius with the applied load. The solid curve is calculated from the JKR model.

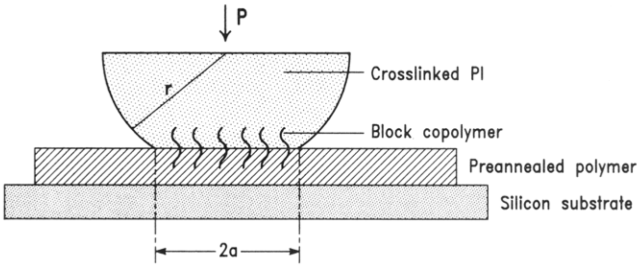

Figure 2. Sketch of the JKR specimen geometry. The cross-linked PI lens is first loaded in contact with the substrate with a load P to join the interface. The load is then removed and the diameter of the contact patch slowly decreases with time.

The fracture experiment itself was done by gently placing the lens upside down in contact with the substrate, as sketched in Figure 2 and then applying a load of ~0.1 N for a fixed amount of time t_c. The load was then removed rapidly and the contact radius was measured using an optical microscope as a function of time. In between measurements the sample was kept in the dark in a nitrogen atmosphere to minimize oxidation. For the same reason the light level in the microscope was kept low. The contact radius is related to the work of adhesion from the JKR analysis by

$$W = \frac{1}{6\pi K a^3}\left[\frac{Ka^3}{R} - P\right]^2 \qquad (2)$$

W obtained from the JKR analysis can be interpreted as a critical energy release rate G_c so from the variation of a with time we obtain the variation of G_c with time. The crack velocity V in this geometry is just $-\mathrm{d}a/\mathrm{d}t$ and is obtained by taking for each data point the derivative of the experimentally measured a vs time curve so we finally obtain the variation of G_c with V. Because of our experimental setup, the minimum interval between measurements of the contact areas was 1 min. This limited our measurable velocities to a maximum of 10^{-7} m/s. However, the sensitivity of the technique, which could resolve a crack advance of 0.3 μm, permitted measurement of V down to 10^{-10} m/s, making it ideally suited for the investigation of adhesion at near-threshold conditions.

Results

The primary goal in this investigation was to obtain quantitative data on the effects of chain pullout on interface toughness that could be compared with existing models. Such models assume that the tethered chains were fully mixed with the bulk elastomer before the start of the pullout process. Diffusion of the tethered polyisoprene chains into the cross-linked lens is expected to be slow, so we chose a long loading time, t_c, to permit the system to come to equilibrium. In our first set of experiments we chose, based on previous experience, to set t_c to 16 h as had been done before.[14] With t_c kept constant, we varied the areal density of chains (Σ) and the degree of polymerization of the tethered chains (N).

The preliminary experiments[14] had shown that the presence of tethered chains at the interface caused a

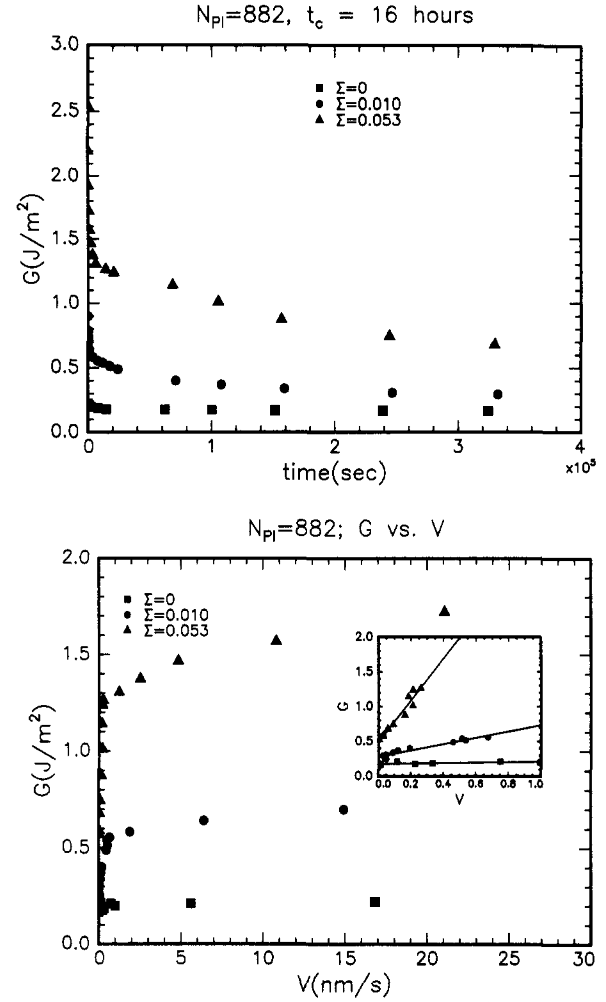

Figure 3. (a, Top) Variation of G_c with time after unloading for three coverages of the medium molecular weight copolymer. This form of presentation emphases the low-speed regime. (b, Bottom) The results of (a) shown as G_c vs crack speed. The lower crack speed region is emphasized in the inset. The existence of two distinct speed regimes is evident in this figure.

significant increase in the interface toughness and that the toughness was dependent on crack speed. Figure 3 shows the variation of G_c vs t and G_c vs V for a polymer with $N = 882$ and three values of Σ. Note that $\Sigma = 0$ corresponds to the situation where the PI lens is pushed up against the 13-nm PS layer grafted on the silicon wafer with no copolymer present. It is clear that these data that an increase in the areal density of chains has a profound effect, increasing the measured G_c up to a factor of 10 at high velocity and giving a significant increase even at zero velocity. When the block copolymer is present on the substrate, two regimes of crack propagation can be distinguished. At high speeds, when $10^{-7} < V < \approx 5 \times 10^{-10}$ m/s, G_c varies approximately linearly with V with a relatively small slope, indicating that a small variation of the crack energy release rate causes a large variation in crack speed. At low speeds, when $V < \approx 5 \times 10^{-10}$ m/s, G_c generally varies linearly with V but at a much higher rate. The transition between the two regimes is relatively sharp, as shown in Figure 3b, and appears to be controlled by V rather than by G_c. This transition was always observed at high Σ for $t_c = 16$ h. However, at low Σ or on pure PS, this slow regime was sometimes never observed and the crack would stop abruptly. To characterize the effect of Σ and N on the measured G_c vs V curve, we measured for each sample the slope of the slow regime, its intercept at $V = 0$, which we will call G_0, the slope in the high regime, and the value of G_c at $V = 15$ nm/s, which is directly comparable to the results obtained previously.[14]

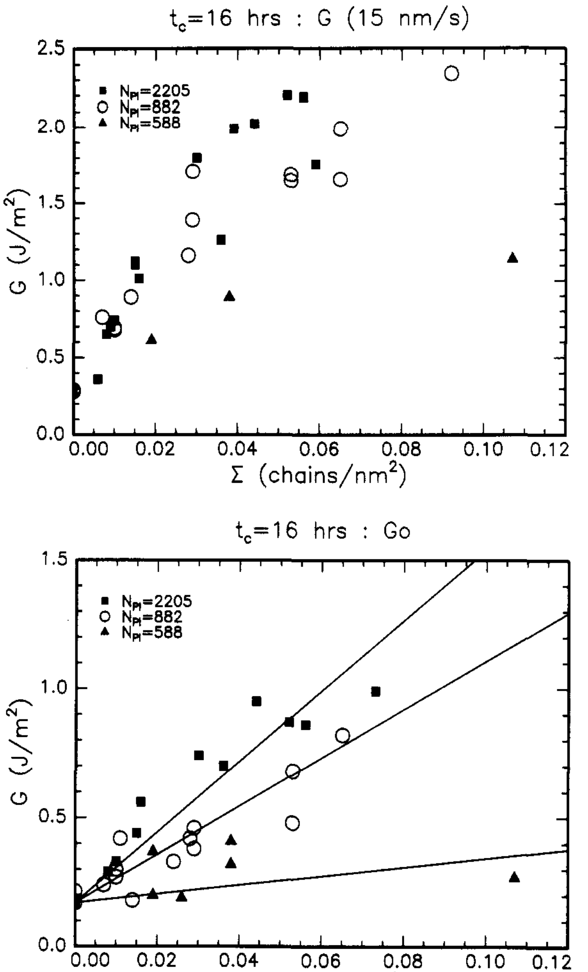

Figure 4. Dependence of the high-speed toughness G_c (15 nm/s) (a, top) and the threshold toughness G_0 (b, bottom) with copolymer degree of polymerization and coverage.

The results for G_c (at $V = 15$ nm/s) vs Σ are shown in Figure 4a for the three values of N which we used. In all cases the measured G_c increases monotonically from a value of 0.3 J/m^2 for $\Sigma = 0$ up to $\sim$1 J/m^2 for $N = 588$ and up to 2.5 J/m^2 for $N = 882$ and 2205. As was previously pointed out,[14] this increase of G_c with Σ is very good evidence that the tethered chains do influence the fracture energy. However, while the $N = 882$ polymer proved to be clearly more effective than the $N = 588$ polymer, it was somewhat surprising to us that increasing N from 882 to 2205 produced only a very marginal increase, if any, in G_c. This latter result stresses the need for more information on the conformation of the tethered chains in the network.

Similar qualitative behavior to that discussed above for G_c at $V = 15$ nm/s is apparent in Figure 4b for the threshold toughness. G_0 increases monotonically with Σ and with N. It is important to note that, for the longer polymers, the increases in G_0 with Σ are clearly significant as the maximum observed value of G_0 was $\sim$1 J/m^2, which is a factor of 6 larger than the value of PS, demonstrating that the tethered chains cause a significant increase in the threshold adhesion. As far as we know, it is the first time that such a correlation has been established so clearly. However, it is worth noting that there was no significant difference in the low-velocity regime, which defines G_0, between the results obtained with a pure PS substrate and those obtained using the $N = 588$ polymer, suggesting that existence of a critical molecular weight above which threshold adhesion increases significantly.

Additional information can be obtained from the analysis of the gradient dG_c/dV at low velocity. This

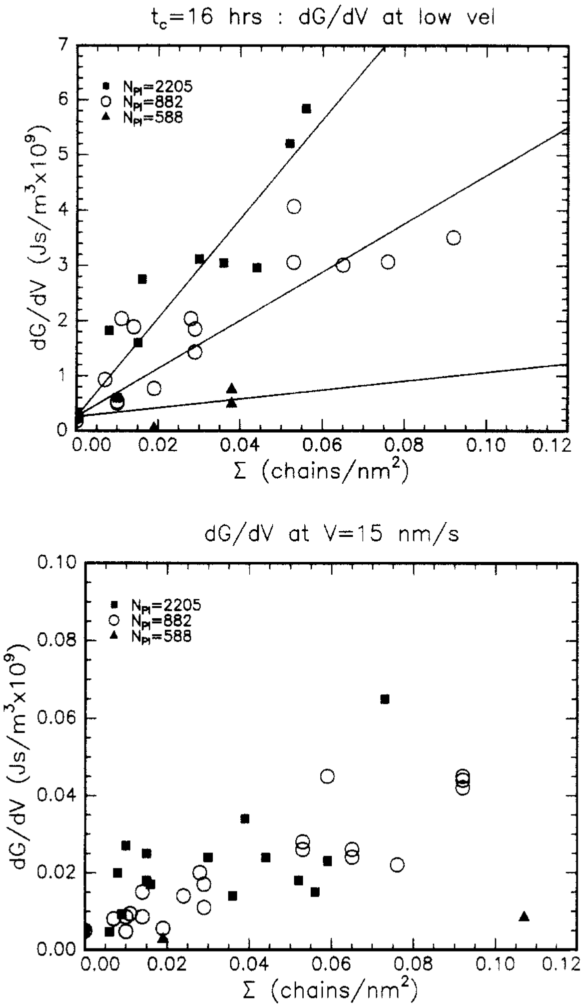

Figure 5. Dependence of the gradient at low speed (a, top) and high speed (b, bottom) with copolymer degree of polymerization and coverage.

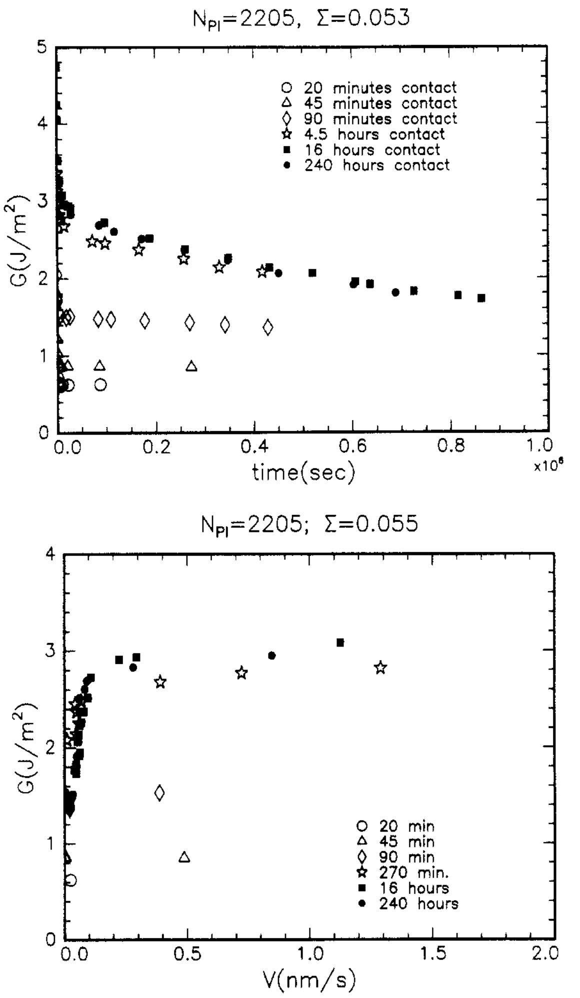

Figure 6. Effect of time of contact before unloading is shown as G_c vs time in (a, top) to emphasize the low-speed regime and as G_c vs crack speed in (b, bottom).

gradient may be a measure of the importance of the viscous losses in the material where a high gradient is indicative of a very high friction process. As can be seen from Figure 5a, dG_c/dV increases from a value of $\sim 0.3 \times 10^9$ J s/m^3 for pure PS up to 6×10^9 J s/m^3 at the highest value of Σ and N, indicating again a very large influence of the presence of the tethered chains on the energetics of the fracture process. Although our experimental data show a very large amount of scatter, dG/dV appears to increase monotonically with Σ and with N. One should note that such a behavior could possibly be the result of the viscoelastic and rate-dependent bulk losses in the lens. This possibility will be considered in the Discussion.

It is interesting to compare the gradient of the G_c vs V curve in the high-velocity regime, as shown in Figure 5b, with the low-velocity gradient, Figure 5a. Although the shapes of the two plots are very similar, it is clear that the absolute values of the gradients at high velocity are much smaller than at low velocity. This difference implies that the mechanism of energy loss may be different in the two regimes.

Effect of the Time of Contact. As discussed above, the time under load, t_c, was normally held constant at 16 h. One series of experiments were done to test the assumption that a t_c of 16 h was long enough to permit the chains to diffuse in and come to equilibrium. In this latter series t_c was varied while Σ and N were kept constant. To maximize the observed effects, we chose a situation where G_c at t_c = 16 h was high, namely, a coverage Σ of 0.053 chains/nm^2 with the high molecular weight copolymer. From the observed results shown Figures 6a and 6b, it is immediately clear that, in the time scales we examined, the time under load has a very profound effect on the measured fracture toughness. Both threshold and high-speed toughness increase significantly with t_c before leveling off at a loading time between 4.5 and 16 h. Clearly, for N = 2205, the measured fracture toughness did not vary much when t_c was increased above 16 h indicating that our assumptions of equilibrated chains was valid. The N = 882 polymer gave similar results to those from the N = 2205 material. We do not have any data on the effects of time under load for the lower molecular weight chains with N = 558 but it is reasonable to assume that diffusion for this polymer would not be slower than for the N = 2205 polymer so we assume that a t_c of 16 h will give an equilibrium situation for all the materials.

It is worth noting that, while the time under load can be easily controlled, the actual time of contact is determined by the time during which the experiment is run, which can be significantly longer than t_c. High-speed toughness is typically measured just a few minutes after releasing the load and therefore reflects much more accurately the effect of t_c. Low-speed toughness and G_0, on the other hand, are often measured a long time after load release and so might be expected to only show the effects of t_c for very small loading times when the high-speed toughness is low and the velocity drops rapidly after load release.

The Reweld Experiment. It has been suggested that, at high crack speeds, tethered chains may break rather than pull out from an elastomer.[33] While the very low crack speeds used in these experiments make chain scission

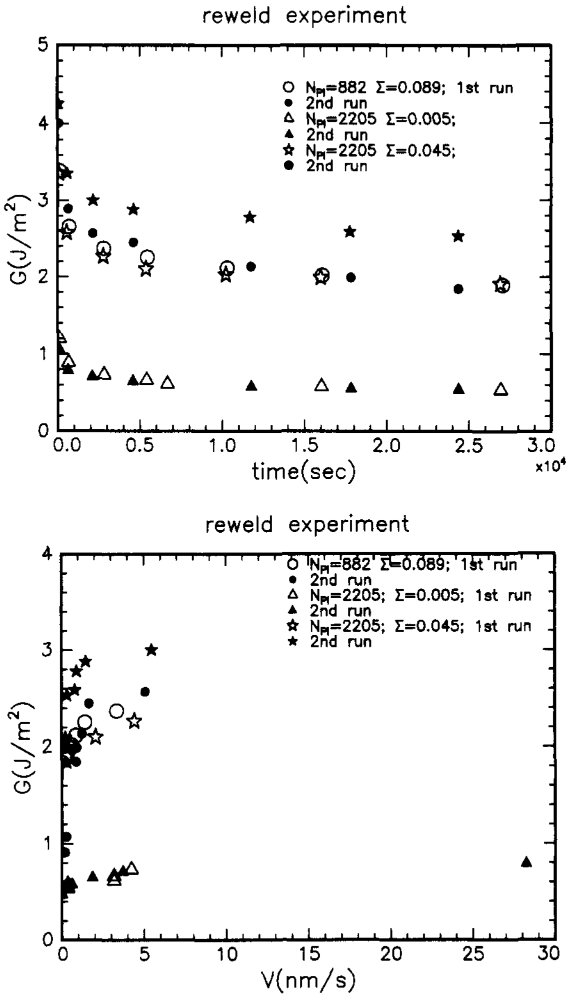

Figure 7. Comparison for three different conditions of a normal first run with the results of a second run where the sample was reloaded in the same spot on the substrate and then unloaded. The similarity between the results of the two runs shows that chains were not broken during the interface failure.

unlikely, we felt that experimental information on the reversibility of the fracture process would be useful. To that end we tested three samples in the following conditions: the substrate was loaded for $t_c = 16$ h and then unloaded and the contact diameter $2a$ was monitored for 8 h. At this point the samples were reloaded on the same spot on the substrate for $t_c = 16$ h so that the contact surface was exactly the same as for the first loading. After removal of the load, the contact diameter was then monitored in the standard way.

The results are shown in Figure 7 and it is clearly apparent that the measured G_c for the second loading was either exactly the same as or higher than (in one case) that of the first loading. Clearly, no significant chain scission could have occurred during the first fracture process as it would have reduced the value of G_c measured after reloading.

Discussion

It is clear from the results presented here, in agreement with the preliminary study,[14] that the presence of tethered chains on the substrate caused a considerable increase in the fracture toughness of the PI–PS interface over the whole range of velocities that we measured. At high velocity we observe an increase of toughness of up to 10 times the value for the bare substrate. Such an increase is larger than that seen by Reichert and Brown[13] and as large as the maximum increase observed by Ellul and Gent.[11,12] At zero velocity, we observed an increase of toughness with Σ of up to a factor of 6, a considerably larger factor than was found by Brown in the preliminary experiments. The reason for this difference is not clear but presumably is caused by the different experimental procedures of which the most significant may be the extra precautions taken to suppress oxidation of the isoprene during the measurements. For the bare substrate, we obtain a G_0 of 0.17 ± 0.03 J/m^2 after applying a load and 0.035 J/m^2 when G_0 is measured by mounting the sample on a soft spring and lowering it slowly toward the substrate until it jumped into contact. This hysteresis has been observed in a variety of JKR experiments on elastomers and may be related to chain end effects[34–36] or roughness effects. These values of G_0 should be compared with the thermodynamic work of adhesion of a PS–PI interface which is ~0.065 J/m^2. The value measured by just contact is somewhat low but within the range of values observed in the JKR experiment done on elastomers. The most important point about these values of G_0 obtained on PS is that the uncertainty in the value, caused by the hysteresis, is very much less than the changes in G_0 caused by loading for significant periods on tethered chains.

An important concern of any tests of elastomer adhesion or failure is the amount of the measured fracture toughness which is due to viscoelastic losses in the bulk materials rather than loss processes close to the crack tip. Experimental evidence shows[4–6,37] that these viscoelastic losses appear as a rate- and temperature-dependent multiplicative factor Φ of the microscopic losses at the crack tip, G_1.

$$G_c = G_1\Phi(V,T,d) \tag{3}$$

In eq 3 it is recognized that Φ is a function of the specimen dimensions represented by d.[38,39] G_1 and Φ are both functions of V and T. G_1 depends on the local properties at the interface while Φ is only dependent on the bulk mechanical properties and should not therefore vary from sample to sample provided the lenses have similar bulk viscoelastic properties. As one reason to use the JKR experiment was to minimize such viscoelastic losses, it is interesting to examine the importance of the bulk viscoelastic loss in both the fast and the slow regimes. Such information can be obtained from a comparison of the measured value of the gradient $\mathrm{d}G_c/\mathrm{d}V$ with that expected from bulk viscoelastic losses alone. We assume that G_1 on PS is constant, independent of V and so that the variation of G_c and V comes only from Φ. Also we assume that there are a slow regime and a fast regime and that $\mathrm{d}\Phi/\mathrm{d}V$ is constant in each regime; then, from the $\Sigma = 0$ results, for $0 \le V \le 0.3$ nm/s, $\mathrm{d}\Phi/\mathrm{d}V = 0.6$ s/nm and for $0.3 \le V \le 15$ nm/s, $\mathrm{d}\Phi/\mathrm{d}V = 0.032$ s/nm. When tethered PI chains are present, the gradient in the fast regime expected from bulk losses alone is obtained by assuming that $G_1 = G_c/\Phi$ is constant; hence

$$\left(\frac{\mathrm{d}G_c}{\mathrm{d}V}\right)_{\text{fast}}^{\text{bulk}} = \frac{G_c(V)}{\Phi(V)}\left(\frac{\mathrm{d}\Phi}{\mathrm{d}V}\right)_{\text{fast}} \tag{4}$$

with an equivalent relation for the slow regime.

The measured gradient $\mathrm{d}G_c/\mathrm{d}V$ and the corresponding "bulk" gradient are shown in Figure 8 for the copolymer with $N = 2205$. It is immediately apparent that, in the fast regime, all the increase in toughness with crack speed could be attributed to the increase in bulk viscoelastic losses. However, in the slow regime, the measured gradient is much larger than the value expected just from bulk losses and also clearly dependent on Σ, demonstrating that, in this regime, there is a clear increase with Σ and V in the energy dissipated near the crack tip.

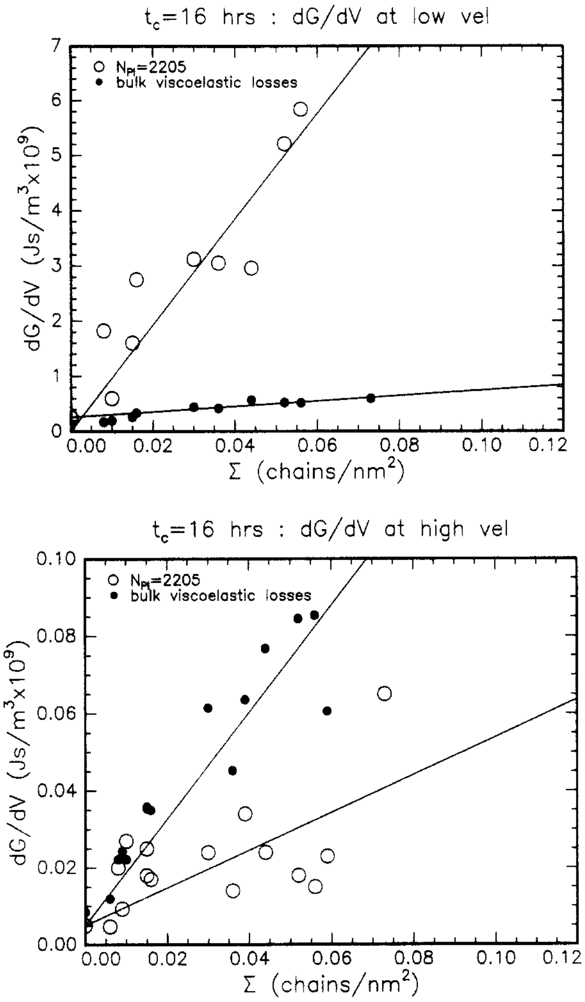

Figure 8. Comparison of the gradient dG/dV in both the low-speed (a, top) and high-speed (b, bottom) regimes with the value expected from just bulk viscoelastic losses. See the text for details.

To continue our analysis further, it is useful to review the predictions of models of crack propagation controlled by chain pullout. Microscopically, the models have in common the fundamental feature that the chain being pulled out experiences a pullout force proportional to its length and to the pullout rate. This common feature leads to the models predicting similar limiting behavior at high rates where G_c is predicted to increase linearly with crack speed. At zero crack speed, all models assume the existence of a threshold stress below which no pullout can take place, giving rise to a threshold toughness G_0. When V is increased from zero, the energy dissipated in viscous losses increases and becomes dominant at a critical velocity V^* above which G_c increases linearly with crack speed. The value of V^* is related therefore to the molecular origin of both the threshold toughness and the viscous losses and can be expressed as a function of the areal density of chains Σ, the degree of polymerization of the chain being pulled out N, and the monomer friction coefficient ζ_1. One important feature where the models differ is in the relationship between the crack velocity and the chain pullout rate. This relationship is crucial to the understanding of the differences between the models and depends on the microscopic assumptions made on the nature of the partially pulled out chains.

In de Gennes' earlier model[40] and Xu et al.'s exact mathematical solution,[41] the chains being pulled out are assumed to be straight, forming molecular fibrils and creating a considerable amount of void in the pullout zone. This assumption results in a long pullout zone and an opening at the crack tip equal to the chain length, the highest final opening that is physically reasonable. Consequently, at a given crack speed, chain pullout rate is the slowest and the predicted V^* is the highest of any of the models. V^* given in molecular terms as

$$V^* = \frac{E}{3\Sigma\zeta_1 N} \tag{5}$$

where E is Young's modulus.

In a later model,[42] de Gennes suggested that the chains being extracted are actually collapsed and there are no voids in the pullout zone. This assumption results in a much smaller pullout zone and a larger pullout rate for a given crack speed, thereby reducing V^* by a factor of $\Sigma^2 b^4$, where b is a monomer size. Very recently, Hong Ji and de Gennes[33] have argued that, if the chain crosses the interface several times, a much increased viscous effect can be expected. In this model the length of the pullout zone is similar to that for the straight-chain model. Most of the viscous work occurs close to the crack tip where because of the multiple crossings, the pullout rate is much larger than the movement apart of the cohesive zone faces and hence much larger than the "average" pullout rate for the straight-chain, single-stitch model. This increase in the pullout rate has the effect of decreasing V^* by a factor of N.

The second important feature of the models pertains to the origin of the threshold toughness. Xu's model was developed originally to explain pullout in glassy polymers and therefore relates G_0 to a yield stress at the molecular level. In the earlier de Gennes models, the chains were assumed to be chemically bound into the network so that a critical force to break the bond had to be reached before the pullout could start. More recently, Raphaël and de Gennes[15] reconsidered the straight-chain pullout model, arguing that there is a cost in elastic energy and surface energy to hold a chain that is being pulled out from the bulk in the form of a single chain fibril. Thus a force exists on the fibril which remains finite even at $V = 0$. From their arguments one obtains

$$G_0 - W \approx \gamma b^2 N\sigma = kTN\sigma \tag{6}$$

where W is the thermodynamic work of adhesion. From this approach one can also obtain the predicted gradient dG_c/dV, which is given by

$$\frac{dG_c}{dV} \cong \frac{G_0}{V^*} = \frac{3\gamma\zeta_1(\Sigma Nb)^2}{E} \tag{7}$$

where E is the Young's modulus of the material.

We are now in a position to make a more quantitative comparison of our experimental results with the predictions of the models. If one uses reasonable numerical values of $\gamma = 30$ mJ/m^2, $\Sigma = 10^{17}$ chains/m^2, $N = 1000$, and $b = 5 \times 10^{-10}$ m, G_0 from the Raphaël and de Gennes model is predicted to be $\sim$0.75 J/m^2, in good agreement with our experimental values. Furthermore, our results are consistent with G_0 increasing linearly with Σ in accordance with all models except the collapsing-chain model (where $G_0 = W$ in our situation where there is no covalent bonding across the interface). From the same numerical values together with the Rouse value of $\zeta_1 = 4 \times 10^{-10}$ N s/m,[43] one can predict a value for V^* which, for the straight-chain model and with $E = 2$ MPa, gives $V^* \cong 10^{-5}$ m/s. If the chains are collapsed, V^* is lowered to $\sim 6 \times 10^{-9}$ m/s.

Experimentally, we do not observe a transition to a rate-independent G_c even at the lowest velocities that we measured, implying that V^* should be below 10^{-10} m/s.

We can estimate V^* from the measured value of the gradient dG_c/dV at $V = 0$ and the above equation. With an average value of dG_c/dV of 3×10^9 Js/m^3 and $G_0 = 0.5$ J/m^2, we obtain $V^* \cong 1.7 \times 10^{-10}$ m/s. There seems little doubt that V^* is much lower than the predictions of the straight-chain models when the Rouse monomer friction coefficient is used. If one were to interpret our data using the straight-chain model, the effective monomer friction coefficient must be higher by 6 orders of magnitude than the Rouse value assumed above.

It is important to consider the physical meaning of the friction coefficient in these pullout models. Indeed what is experimentally measured is the work to pullout a chain, an integral of the pullout force with the change in extracted length of the chain. The pullout force is assumed proportional to the pullout rate, and this coefficient is called the chain friction coefficient. If the chain friction coefficient increases linearly with the length of the embedded chain, then it is possible to define a monomer friction coefficient. Using a constant monomer friction coefficient in the calculations therefore implies that the pullout force increases linearly with rate throughout the spectrum of velocities considered. However, Rubinstein et al.[16] have recently considered the dynamics of pulling a chain out of a cross-linked rubber. In their model the chain friction coefficient is dependent on pullout speed and varies in a complex way with the chain length. They were concerned with the problem of wall slip between a network and chains that were grafted on a wall but their analysis should apply equally well to the pullout process considered here.

The important physical idea in their argument is that an entangled grafted chain which is being dragged through a network by its grafting point will first be partially extended. The degree of extension will be controlled by the ratio between the relaxation time of the chain and the time necessary to extend the segments of length N_x (the number of units between cross-links). In particular, at very low speeds (in a regime where the time to pull out a chain is much longer than the relaxation time of the chain), only the first chain section of length N_x can be partially extended. In these conditions, an increase in velocity causes an increase in the degree of extension of that first section and is directly related to an entropic force. Such an analysis leads to the prediction of a "friction" coefficient of $kT\tau_z/d_e^2$, where d_e is the mesh size of the network and τ_z is the (very large) relaxation time of an end-tethered chain in the network. An estimate of τ_z of 1600 s can be obtained from Pearson and Helfand's rheological experiments on polyisoprene stars[44] with an arm molecular weight of 100 000. The value of τ_z in the network is likely to be considerably larger than this estimate because the molecular weight between cross-links ($\sim$3000) is less than the entanglement molecular weight (5000) of polyisoprene and also because relaxation in stars can occur partly by tube renewal. With Pearson and Helfand's relaxation time, the arm friction is given by 0.4 N s/m, a value that is 10^6 larger than Rouse friction.

The low-speed, high-friction regime exists until the first chain section is completely extended, level at which the force is approximately equal to kT/d_e. When V is further increased, the rest of the chain is progressively extended. In this regime the relationship between F and V is given by the sum of the contribution of the extended part which is being pulled out (Rouse friction which is very small) and the contribution of the entropic force which is now constantly extending a section of length N_x (no longer the first segment but the following ones). This causes the force to be relatively constant with V in that regime. When the chain is fully extended, the only contribution to the force is now given by the Rouse friction, and the classical expression is recovered.

It is interesting to note that Raphaël and de Gennes predict a force per chain of kT/b just to hold a single chain in air with no pullout. This static force should be added to the frictional force at finite pullout rates as the static force is essentially a surface tension and does not exist within the network. The static and frictional forces are not grossly different in size, considering the assumptions made in their derivations, as $d_e \sim 7b$. A combination of Raphaël and de Gennes' pullout model with Rubinstein et al.'s model for friction would predict that there should be a high chain friction coefficient regime at very low crack velocity followed by a regime over which G_c is approximately constant. It is immediately evident that such a prediction does give a good qualitative description of the experimental results.

An estimate of V^* can also be obtained from the model of Rubinstein et al. As mentioned above, the effective chain friction is 0.4 N s/m, from which one obtains a V^* of 1.7×10^{-11} m/s, a value that is only 1 order of magnitude less than the experimental estimate. Considering the uncertainties in the friction estimates, it is reasonable to interpret the low observed value of V^* as evidence for Rubinstein et al.'s model of pullout friction.

In the discussion so far it has been assumed that, at equilibrium, the tethered chains are entirely dissolved in the network. However, such a situation is unlikely as there is an elastic free energy cost in swelling the network by tethered chains. The main driving force for the chains to swell the network is the release of the free energy (again mainly entropy) of a sharp interface that must exist between the tethered chain layer and the network if no swelling occurs. The tethered chains are hence likely to form loops and pass in and out of the network a number of times. The length of the loops can be estimated from the assumption that the swelling energy of the network for each loop is likely to be about kT. For small strains the network can be considered to have an internal pressure equal to its shear modulus and so equal to kT/N_xb^3, where N_x is the number of monomer units between cross-links. Hence the loops will on average be the same length as chains between cross-link points. There may also be an unswollen layer of tethered chains next to the substrate where the tethered chains are entangled just with themselves. Because the elastic energy of a network increases with extension, the volume fraction of network chains in this mixed layer will not decrease to lower than a finite amount. One still expects an interface that is sharp on the scale of the distance between cross-links where the network volume fraction drops from this finite limit to zero. There is to our knowledge no experimental information on the swelling of a network by tethered chains but it is known that free polymer chains do not swell networks much if their molecular weight is much larger than the average molecular weight between cross-links.[45–47]

The total time that a chain takes to pull out depends on the crack speed and the length of the cohesive zone. In the high-speed regime it is reasonable to assume that the pullout force is approximately constant along the cohesive zone and so the zone length can easily be estimated from the Dugdale model. Assuming a Σ of 0.05 chains/nm^2, a pullout force of 1.5 times the static pullout force, and a G_c of 1 J/m^2, one obtains a cohesive zone of length $\sim$2 μm. The transition from low- to high-speed failure typically occured at a crack speed of $\sim$0.1 nm/s and so at a pullout time of $\sim$20 000 s. This pullout time is in the correct range to represent the relaxation time of a chain.

The dependence of G_0 and G_c on the degree of polymerization of the chains N and on Σ deserves more discussion. While G_0 always increased significantly with Σ, its increase with N did not show the linear relationship that would be expected from the models. The $N = 588$ polymer was found to be much less mechanically effective than the two higher molecular weight ($N = 882$ and $N = 2205$) polymers. Considering that the average degree of polymerization between cross-links N_x was ~50 for the network and so much smaller than 588, this result is somewhat surprising and suggests that N needs to be much greater than N_x for mechanically effective entanglements to form. It would appear from the results obtained with the two higher molecular weight polymers that increasing chain length above the critical value did not have a very large effect. This result is reminiscent of the situation in glassy polymers where the fracture toughness increases rapidly when the molecular weight becomes high enough for crazes to form.

As discussed above, the equilibrium length of the chain in the lens is probably not equal to Nb or even directly proportional to N as it is likely that the degree of swelling of the network is fairly limited. Hence one might expect that the total length of the tethered chain might penetrate the network when Σ is low but saturation of the penetrated length will start to occur as Σ is increased. There is evidence of saturation with increasing Σ in the results of Figure 4 for G_c at a crack velocity of 15 nm/s and perhaps also for G_0. The similarity between the results for the two longer polymers implies that there is little change in the length of penetration per chain when the degree of polymerization is increased from 882 to 2205.

It is interesting to note that there is only about a factor of 2 increase in the gradient, dG_c/dV, on increasing N from 882 to 2205 and also that the gradient increased approximately linearly with Σ. Within a Rouse type friction model one expects the gradient to increase by N^2 and also as Σ^2. If the high, starlike, friction process is operative, one expects the friction and hence the gradient to increase exponentially with N. It would seem likely again that the penetrated length is less than Nb and does not increase rapidly with N.

The experiments with variable loading time t_c can be used to obtain more information on the molecular weight dependence of G_c. Assuming that tethered chains diffuse in the network in a similar way as the arms of a star polymer,[48] one can reason as follows: the retraction time of the arm of a star varies with e^N, implying therefore that the length of the chain which is free to diffuse in the network varies with log t_c. (It is assumed here that the tethered chains are entangled with each other before they are put in contact with the gel.) Hence the length of the tethered chain that is in the network, represented by its degree of polymerization n ($n \leq N$), is now a time-dependent quantity due to the diffusion process. If the length of chain in the network is short, then its relaxation time is small and we will see just a threshold G_0 that varies linearly with n and so with log t_c. For long penetrated lengths, from the viscous pullout model including the star friction assumptions, one expects G_c at high crack speeds to again depend linearly on n, and hence log t_c, as the pullout force at high speeds is a constant, independent of n, but the maximum cohesive zone opening varies linearly with n. At very long contact times, as the chain penetration reaches a constant, G_c will saturate. Hence, in summary, one might expect two regimes where G_c increases linearly with log t_c with a region of higher gradient between them. Figure 9, which shows the variation of G_c with log t_c, is consistent with these arguments.

The time constant for diffusing in of these chains was ~4 h or ~10^4 s. This is considerably faster than the value found in previous work where the joint was found to continue to strengthen for periods of ~10 days.[13] The reason for this difference is probably connected with the fact that the earlier work was done using peel tests. It was not possible to get very smooth and clean surfaces to be joined for the peel test, so it was possible that the long time constant observed with peel test was connected with slow surface flattening and diffusion away of contaminants.

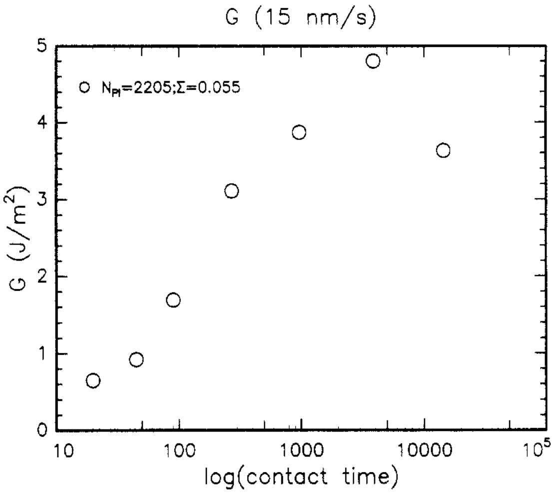

Figure 9. Variation of G_c measured at 15 nm/s with contact time t_c showing a regime where G_c varied approximately with log t_c.

This work has demonstrated that chain pullout processes can have a significant effect on the adhesion and by implication also cohersion of elastomers. The existence of the threshold G_0, which can be considerably greater than W, and also a high-friction regime at low velocity help to explain why un-cross-linked elastomers can be useful as long-term adhesives. Joints made with such materials often last for times that exceed the terminal relaxation time of the un-cross-linked chains by many orders of magnitude.

Conclusion

We have clearly demonstrated that the addition of PI tethered chains at the interface between a PI cross-linked lens and a PS substrate produces a large increase in the work of adhesion over the whole range of crack speeds (10^{-10}–10^{-7} m/s) that we have investigated. Such an increase cannot be explained by the rate dependence of bulk viscoelastic losses and is believed to due to the viscous pullout of the PI chains from the network.

At low crack speeds the fracture toughness G_c was found to increase linearly with velocity from a threshold value G_0. At higher crack speed a transition occurred, after which the fracture toughness increased at a much lower rate which could be attributed to viscoelastic bulk losses. The threshold toughness G_0 and the toughness at a crack speed of 15 nm/s increased monotonically with Σ and with N.

The results were compared with existing models of interfacial fracture by chain pullout. The linear dependence of G_0 with Σ agrees well with the models and the absolute values that we measured are consistent with a threshold stress controlled by the interfacial energy necessary to form a single chain fibril. The measured rate of increase of G_c with V implies there is a very high effective friction at very low crack speeds. This high friction is probably caused by the very long time constant for pullout of a chain without a network. The dependence of G_c on the degree of polymerization N was found to be nonlinear, suggesting that the length of the chain that penetrated in the network was not simply proportional to N. The experiments where the loading time was varied showed that the process of diffusing into the network was slow and that the penetrated length varied as log t_c.

Acknowledgment. We have benefited from discussions with M. Rubinstein and A. Adjari on chain pullout and with M. Chaudhury and E. J. Kramer on JKR techniques.

Appendix

The equilibrium situation where the thermodynamic energy of adhesion due to surface forces W and the elastic stored energy are balanced has been extended to the dynamic case where the contact surfaces varies with time by the elegant analysis of Maugis and Barquins. Consider the edge of the contact surface is a propagating crack. The system tends to minimize its free energy. For a variation in contact surface dA (a reversible and isothermal transformation), the variation of the free energy can be written as the variation of internal energy:

$$\mathrm{d}F = \mathrm{d}U_\mathrm{T} = \mathrm{d}U_\mathrm{E} + \mathrm{d}U_\mathrm{P} + \mathrm{d}U_\mathrm{S} \leq 0$$

where U_E is the elastic energy stored in the sphere, U_P is the potential energy of the applied load P, and U_S is defined as

$$\mathrm{d}U_\mathrm{S} = -(\gamma_1 + \gamma_2 - \gamma_{12})\,\mathrm{d}A = -W\,\mathrm{d}A$$

where W is the Dupré energy of adhesion. One can also define the strain energy release rate G as

$$G = (\mathrm{d}U_\mathrm{E}/\mathrm{d}A) + (\mathrm{d}U_\mathrm{P}/\mathrm{d}A)$$

so that the variation in free energy dF becomes

$$\mathrm{d}F = \mathrm{d}U_\mathrm{T} = (G - w)\,\mathrm{d}A \qquad \text{(A1)}$$

Let us come back to our experimental configuration. The sample is first maintained in an equilibrium where P is imposed. Then the load is removed and the stored elastic energy is released at a certain rate to reach the new equilibrium (at $P = 0$). In our case $G = (\mathrm{d}U_\mathrm{E}/\mathrm{d}A)$. If $G > w$, equation A1 shows that the contact area must decrease to reduce the free energy and the crack extends.

G is called the strain energy release rate. G dA is the mechanical energy released when the crack extends by dA. The breaking of bonds requires an amount of energy w dA and the excess $(G - w)$ dA is changed in kinetic energy and in dissipative processes.

The approximations made by the authors of this paper are (a) that $(G - w)$ is entirely changed in dissipative processes (these dissipation processes are dependent on crack velocity and are interpreted in molecular terms and (2) that at any given time during the dynamic process, the JKR approximation relating the elastic stored energy to the area of contact is valid. Both of these approximations cannot be strictly valid but are justified in the authors' opinion, considering the very slow crack velocities investigated here.

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