Effects of Chain Pull-out on Adhesion of Elastomers

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ABSTRACT: The effect of chain pull-out processes on adhesion has been examined for the case of an elastomer. A thin layer of polystrene–polyisoprene diblock copolymer was placed at the interface between a polystyrene-coated substrate and a lens-shaped block of cross-linked polyisoprene. The interface toughness was found to vary with the crack growth rate and the areal density of copolymer present at the interface. At high crack growth rates (0.05 mm/h) the toughness was increased by about a factor of 10 by the presence of 0.1 chain/nm^2 at the interface. At lower rates the toughness varied linearly with crack velocity and showed a threshold toughness, as the velocity tended to zero, that increased with the areal density of copolymer. The experimental results are compared with the predictions of a number of recent models of chain pull-out.

Introduction

The adhesion between polymers can be caused, at a molecular level, by any of three possible means by which the interface can sustain a stress. The stress can be held by (i) van der Waals or other secondary bonds across the interface, (ii) chains that cross the interface and are coupled by entanglement with the bulk polymer, and (iii) chains that cross the interface and are chemically coupled to the materials on both sides of the interface. The ability of mechanisms i and ii to give significant adhesion depends on the nature of the materials and the time scale of the experiment. However, a sufficient number of chemical links across an interface (mechanism iii) always gives significant adhesion.[1]

In glassy polymers, van der Waals forces alone give insignificant adhesion as they cannot sustain sufficient stress to initiate the main crack tip energy dissipation processes that occur in these materials. Experiments using diblock copolymers at the interface have shown that high adhesion can be obtained in glassy polymers by the use of chains that entangle on both sides of the interface.[2] When the interface is broken these coupling chains can either pull-out or break depending on their length and the fracture mechanism.[3,4] There is now some understanding of the relation between the number of chains per unit area of the interface and the toughness they cause.[5,6]

In elastomeric polymers the interface toughness is a very strong function of the rate of crack propagation and, at relatively high crack growth rates, van der Waals forces alone across the interface (mechanism i) have been shown to give significant adhesion.[7,8] The main aim of the current work was to measure the contribution of coupling chains that can pull-out (mechanism ii) to the adhesion between a cross-linked elastomer and a more rigid substrate. There is currently good evidence that such chains do contribute to adhesion. Incorporation of un-cross-linked chains into a cross-linked network enabled Ellul and Gent to show that pull-out processes can contribute to the toughness of interfaces between cross-linked elastomers at finite crack growth rates.[9,10] However they had no way of knowing the areal density or pulled-out length of the chains that toughen the interface. Reichert and Brown placed known amounts of diblock copolymer at an interface between cross-linked polyisoprene and polystyrene and then measured the interface toughness using a peel test.[11] They found that the pull-out of the polyisoprene chains of the diblock from the bulk cross-linked polyisoprene increased the interface toughness by a factor of up to 5 at the single crack propagation rate they used. Chain pull-out in an elastomer is expected to be very dependent on the crack propagation rate, as it is thought to be a viscous process. One of the aims of the models of the process is to obtain the relation between crack propagation rate and the speed at which the chains are extracted. Hence it would be valuable to extend crack pull-out experiments to a range of crack speeds.

Peel tests have a number of problems for the study of pull-out processes in elastomers. Firstly, they require the preparation of large areas of interface and it is difficult to ensure smooth surfaces on the samples to be joined over such areas. Hence there is always uncertainty about the quality of the contact over the whole tested area. Secondly, a large volume of the sample is loaded during a peel test so it would seem likely that a considerable amount of energy could be lost in viscoelastic deformation in the bulk sample in such tests. An alternative test that can alleviate both these problems is the JKR test[12] in which an elastic spherical cap is pushed into contact with a second spherical cap or a flat. The contact radius is a function of the radii of curvature and elastic moduli of the materials with spherical surfaces (as in Hertzian contact) and, in the original version of the model, the work of adhesion between the two spheres. If the two spheres are pushed into contact and then the load is released, the contact radius decreases with time with the "work of adhesion" interpreted as a strain energy release rate G.[13-15] The advantages of the JKR test are that the volume of material that is under significant strain is very small and, as the contact area is small, it is possible to use very smooth surfaces. This test has recently been used by Chaudhury and co-workers[16,17] who made spherical caps of a smooth silicone elastomer by cross-linking drops of low molecular weight end-linkable polymer that were placed on a low surface energy substrate.

A number of models have been proposed to describe the process of chain pull-out and the relation between chain pull-out and interface toughness.[18-24] The differences between all but the most recent of these models have been reviewed recently.[1] The models all assume that a threshold stress exists below which pull-out does not occur and that the pull-out rate increases as the interface stress is increased above the threshold. The models differ in the assumptions that are made of the state of the pulled-out chains (are they stretched or do they condense on the crack faces) and in the techniques that are used to solve the elasticity problem. In the most recent models[23,24] the threshold stress and hence threshold toughness G_0, is related to the extra surface and elastic energy of the individual chains as they are pulled-out. G_0 is hence

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predicted to increase with the length and areal density of the connector chains.

Experimental Techniques

Preparation of the Semispherical Lenses. The polyisoprene (PI) lenses were made from a narrow molecular weight distribution standard PI of M_w equal to 31 000 and a polydispersity of 1.05 that was obtained from Polymer Laboratories. The PI was dissolved in decalin to form a 50% solution, and then 6 wt % (based on the PI) of dicumyl peroxide (DCP) cross-linking agent was added. The PI was used as a solution because the high viscosity of the neat polymer made it hard to dissolve the DCP in the polymer and to deposit the polymer in the form of drops on a surface. A low surface energy surface was made by immersing a glass slide in a hexane solution of (tridecafluoro-1,1,2,2-tetrahydrooctyl-1)trichlorosilane. About 15 separate drops of the polymer solution were placed on the slide and then cross-linked to form 15 lenses. To cross-link the PI, the slide was then put in a 50-mL flask, the air in the flask was exchanged a few times for nitrogen, and then the flask was evacuated for 3 min, sealed, and placed in an oven at 155 °C for 2 h. It is assumed that a certain amount of both the decalin and the DCP evaporate into the flask during the heating and so the concentration of both decalin and DCP in the polymer during cross-linking are less than the original concentrations. The cross-link densities obtained are therefore expected to be less than those obtained by using 6% DCP in bulk polymer.

After cross-linking, a lens was weighed straight after removal from the slide, again after swelling to equilibrium in octane, and finally after drying in air. The molecular weight between cross-links, M_c, and modulus E was obtained from the swelling data using the relations given by Queslel and Mark for a network cross-linked in solution.[25]

$$(\ln(1 - \nu_{2m}) + \nu_{2m} + \chi\nu_{2m}) = (\rho V_1/M_c)(\nu_{2m}/2 - \nu_{2m}^{1/3}/\nu_{2x}^{2/3})$$

$$E = 3\rho RT\nu_{2x}^{2/3}/M_c$$

The volume fractions of polymer in the solutions at the time of cross-linking and at equilibrium swelling are given by ν_{2x} and ν_{2m}, V_1 is the molar volume of the solvent whose Flory–Huggins interaction parameter with the polymer is χ, and ρ is the density of the polymer. Chain end corrections were ignored as they enter both relations in the same manner. The values of M_c obtained were 3500 and 1800, respectively, for the lenses used in the first and second set of experiments.

Lenses were also made using UV cross-linking[26] as it appeared to be a simpler technique than peroxide cross-linking. Well-cross-linked clear lenses could be obtained as long as oxygen was excluded during the cross-linking. However the outer surface of these lenses seemed to be very sensitive to atmospheric degredation and they never gave consistent results.

Preparation of Substrates. As the aim of the work was to examine pull-out processes, it was necessary to make substrates on which there were a known number of end-attached polyisoprene chains. To this end, 19-nm layers of symmetric polystyrene–poly(methyl methacrylate) copolymer of molecular weight about 300 000 were spin coated from a toluene solution onto silicon wafers and then annealed in a vacuum at 170 °C overnight. Such annealing is known to give an organized layer with the PMMA adhering to the silicon surface and a PS layer on top. A thin layer of symmetric PS–PI block copolymer of molecular weight 120 000 was spun from a cyclohexane solution on top of the PS–PMMA layer, and then the substrate was annealed at 120 °C in a vacuum oven for 2 h. Subsidiary experiments showed that spinning cyclohexane onto the annealed PS–PMMA layer did not remove any of the polymer. It is assumed that the second anneal organized the PS–PI layer so that its PS part mixed with the PS of the PS–PMMA leaving a PI layer on the top surface. No morphological experiments were done to test this assumption; however it is consistent with previous TEM observation.[11] Layer thicknesses were all measured using ellipsometry.

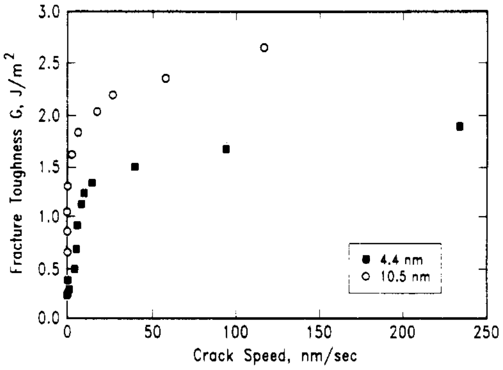

Figure 1. Variations of toughness with crack speed for two different thicknesses of PS–PI diblock copolymer.

JKR Measurements. The JKR technique was used to measure the interface toughness. An unused lens was placed on the substrate and then loaded overnight with a weight of approximately 10 g. A thin piece of polystyrene film was placed between the lens and the weight to stop the lens sticking to the weight. The weight was removed to start the crack propagation and the diameter of the contact patch was measured using a ficullar eyepiece in an optical microscope. Measurements were made for periods of up to 1 week. There is evidence that peroxide cross-linked PI is prone to degredation in light[27] so the samples were stored in the dark between mesurements.

The fracture toughness was obtained from the relation[13,14]

$$G = \frac{1}{6\pi Ka^3}\left[\frac{Ka^3}{R} - P\right]^2$$

where a is the radius of the contact zone, $K = 16E/9$ (E is Young's modulus), and P is the load on the lens while the crack propagates (just its weight). Plots were obtained of G as a function of time and crack speed.

Results

Two series of experiments were undertaken, in the first series the main aim was to examine the crack growth at relatively high speeds, 10^{-7} to 10^{-8} m/s (0.5 to 0.05 mm/h), as this is a speed region where preliminary experiments had shown that the presence of the PS–PI diblock copolymer had considerable effects on the crack growth. In this first series a relatively large number of diblock layer thicknesses were used, but just one lens per thickness. The thickness of the PS–PI diblock layer was always less than half a long period of the neat diblock, so it is unlikely that the interface was ever saturated or that multilayers were formed. The aim of the second series of experiments was to examine the effect of diblock on the crack growth rate at lower rates, 10^{-8} to 10^{-10} m/s, where the effect of the diblock is smaller. A second aim was to find if a threshold toughness greater than the work of adhesion could be observed and, if it was seen, examine how its magnitude depends on the presence of the tethered PI chains from the PS–PI diblock. In the second series of experiments only four diblock layer thicknesses were used but three lenses were used for each layer thickness.

Figure 1 shows two examples obtained in the first series of experiments of how of the toughness varied with crack speed. The results are all presented with crack speed as the abscissa and toughness as the ordinate, as fracture results are conventionally plotted this way. It might seem more logical to plot the data the other way round since, in these experiments, it is easier to think of the applied G as the driving force and the crack speed as the result. It is evident that the toughness increases rapidly with crack speed in the low crack speed region and then, at the higher crack speeds, above about 10^{-8} m/s, tends more toward saturation. The main effect of the amount of PI on the substrate was to change the "saturation" level, that is to say the toughness at high speeds. This variation is

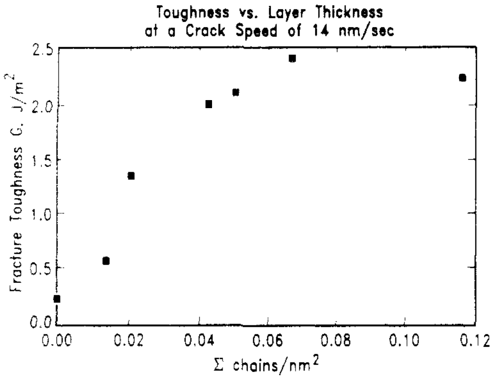

Figure 2. Variation of the interface toughness with the copolymer chain density at a single high crack speed.

shown in Figure 2 where the toughness at an arbitrary 1.4 × 10^{-8} m/s is plotted against the areal density of PS–PI on the substrate. Clearly, the presence of the diblock has a profound effect on the interface toughness at these "high" crack speeds.

Typical results of G as a function of crack speed, V, obtained in the second series of experiments are shown in Figure 3 for two different amounts of PS–PI diblock. It appears that, for low crack growth rates, the crack growth rate increases linearly as the toughness is increased above a threshold value, G_0. It was not possible to obtain results as a function of crack speed for the samples with no diblock since the crack stopped rapidly during the test. This rapid arrest implies that the crack growth rate increased very rapidly as G increased above G_0 (or decreased rapidly as G was decreased toward G_0). Figures 4 and 5 show that both G_0 and the gradient, dG/dV, increased with areal density of tethered PI chains, Σ.

Discussion

It is immediately evident from the results presented in Figures 1–5 that the presence of a thin layer of PS–PI diblock between a PS layer and a cross-linked PI bulk had a considerable effect on the fracture toughness of the interface. It would seem most likely that the PI chains of the diblock were anchored by the PS chains and that the toughness increase is caused by the process of chain pull-out. The magnitude of the toughness increase caused by the PS–PI diblock, a factor of about 10, is larger than the toughness increase observed by Reichert and Brown[11] and similar to the largest amount seen by Ellul and Gent.[9,10] The values of G_0 obtained using no diblock, 0.12 J/m² are a little larger than the expected work of adhesion between PS and PI, which is about 0.065 J/m², but the difference is not very large and is consistent with what has been seen previously with almost all JKR experiments on elastomers.[12-15] The one case where good agreement was found between the JKR experiment and other techniques to measure the work of adhesion is some recent work using an end-linkable silicone elastomer.[16] The origin of the difference between JKR results and other techniques is not clear but has been ascribed to viscoelastic effects and to chain end effects.[13,14]

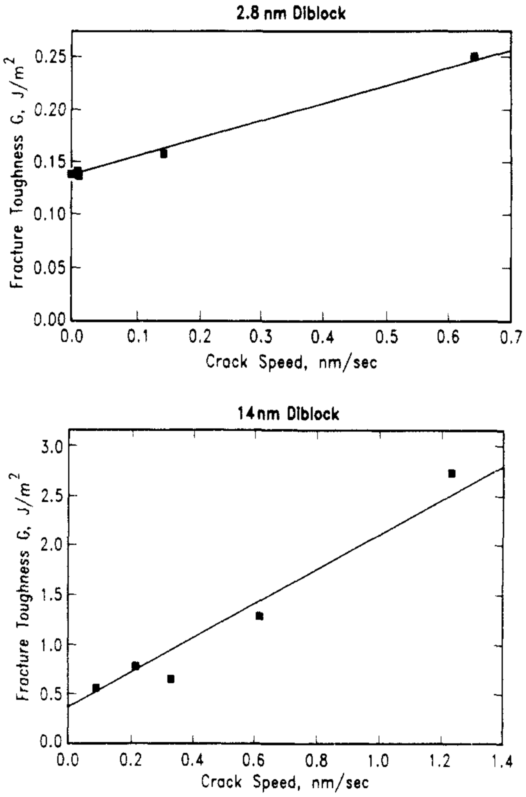

Figure 3. Linear variation of interface toughness with crack speed at low crack speeds for (a, top) a 2.8-nm layer of diblock and (b, bottom) a 14-nm layer of diblock.

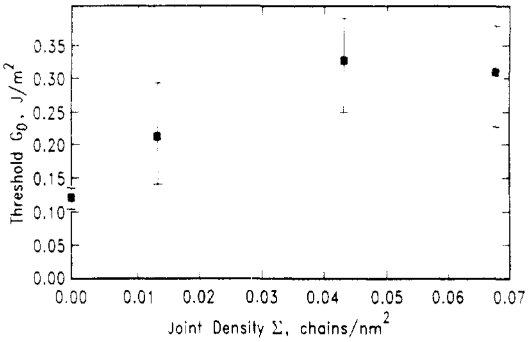

Figure 4. Increase in the threshold toughness with areal copolymer chain density.

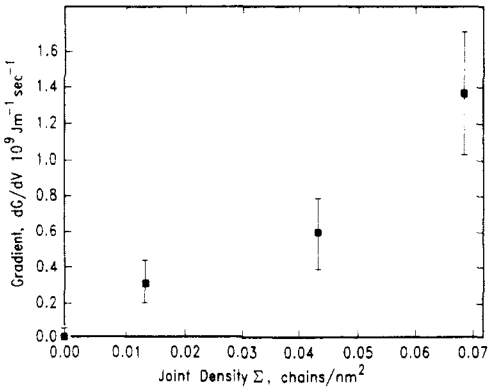

Figure 5. Variation of the gradient, dG/dV with amount of copolymer at the interface.

It is worth noting that there is no direct evidence that the tethered PI chains had diffused into and swollen the cross-linked PI. The equilibrium swelling of a cross-linked polymer by a chain of identical chemical composition tends to be rather small if the free chain has a molecular weight much greater than the molecular weight between cross-links of the network, M_x.[28,29] The situation at interfaces between cross-linked material and tethered chains is not clear, but one would certainly expect loops of the tethered chains with a size at least equal to M_x to cross the interface into the network. It is quite possible that the tethered chains were entangled both with each other and with the network and so crossed the interface a number of times. As it is clear from the results that the tethered PI chains had a considerable effect on the toughness even at very low crack growth rates, it would seem most reasonable to assume that some interdiffusion had occurred.

It is always necessary to consider bulk viscoelastic losses when the measured fracture energy of an elastomer is interpreted. There is good experimental evidence that, in large samples, the essential, crack-tip fracture energy is multiplied by a temperature- and rate-dependent factor $\Phi(V,T)$ that describes the viscoelastic losses in the bulk material.[7,8,30-32] The loss function Φ is controlled just by the properties of the bulk material and so should be the same for all the samples in a series. In the JKR experiments considered here, the volume of loaded material is small, the crack growth rates are low, and the adhesion is relatively weak so it is worth considering if viscoelastic losses are significant. In the low crack speed region examined in the second series of experiments, for the samples with no diblock, the increase in toughness with rate was too small to be observed. The observation limit was perhaps 10% so the increase in G was less than 10% over the crack speed range. Therfore the viscoelastic amplification factor, which tends to 1 at zero crack speed, must be less than 1.1 at the maximum speed of these experiments. The toughness increase that was observed over the crack speed range with the diblock present was at least a factor of 3. As Φ is at most 1.1 at the maximum speed, this increase must come mainly from effects other than bulk viscoelastic loss. Turning now to the first series of experiments, the increase in toughness with rate in the high crack speed region was relatively small and it is not possible to tell how much of it was caused by bulk viscoelastic effects.

The crack was observed to move from the interface into the bulk PI when a large amount of diblock was present at the interface. It is tempting, but incorrect, to interpret this result as showing that the interface was tougher than the bulk cross-linked polymer. The direction of crack propagation at an interface is controlled by detailed mechanics at the crack tip, particularly the mixity (the ratio of opening to shear mode stresses at the crack tip)[33] and the variation of crack resistance of the bulk materials with mixity. The situation is particularly complicated when one of the materials is an elastomer and so can undergo finite deformation. It is known that cracks in elastomers can be expected to open at their tips even if the external loading pattern is one of shear parallel to the crack faces.[34] It has been argued that, for an elastomer, the geometry of the JKR experiment ensures that the crack is in pure opening mode (mode I), but it is not clear that this argument is valid when finite deformations (which can cause finite rotations) are taken into account. Little can be concluded from the direction of crack propagation without more knowledge of the mechanics at the crack tip.

It is valuable to compare the experimental results with the predictions of the current models of chain pull-out. Such a comparison is best presented after a detailed discussion of the predictions of the models.

The models of chain pull-out have a number of common features. One of these features is that the models all predict that the toughness will increase linearly with crack speed when the speed is above a critical value, V^*. When the speed is below a critical value, $G \sim G_0$. The critical speed is the speed at which the viscous, or rate-dependent, work of pull-out of the chains becomes comparable to the threshold toughness and so is related to the number of chains per unit interface area, Σ, the number of repeat units in the chain being pulled-out chain, N, and the monomer friction coefficient, ζ_0. The models differ in the relation that is derived between the rate of pull-out of the individual chains and the crack velocity. This relation depends on the assumptions that are made on the nature of the partially pulled-out chains. If the chains in the cohesive zone (the pull-out zone) are assumed to be straight[18,23,24] so that the volume fraction of polymer in this zone is small, then the cohesive zone is relatively long, as its opening at the crack tip must equal the chain length. A long cohesive zone means that the pull-out rate for any given crack speed is slow and V^* is large. Alternatively, the chains in the pull-out zone may be assumed to collapse and form fully dense polymer.[19,20,22] The pull-out zone will then be relatively short, and hence the pull-out rate for a given crack speed will be high and V^* will be small.

A second important difference between the pull-out models is connected with the interpretation of the threshold stress and hence G_0. The model proposed by Xu et al.[18] is aimed mainly at the pull-out process in glassy polymers, and so a threshold pull-out force enters naturally as a type of yield at the molecular level. In the early de Gennes models[19,20,22] it was assumed that the connector models were chemically attached at their ends to the network so that a threshold force was required to break this attachment. In de Gennes' recent models[23,24] the partially pulled-out chains are assumed to form single chain fibrils and minimization of the sum of the surface and stretching energies of these chains shows that there is a minimum force required for a fibril to exist even at zero pull-out rate. The energy involved in forming a fibril is assumed to be lost when the chain is finally pulled out and the fibril collapses. As the force on a chain that is being pulled out remains finite as the pull-out rate goes to zero, the existence of a threshold toughness G_0 that is larger than the work of adhesion is predicted by these models.

It has recently been shown[24] that V^* is expected to be considerably different when the connector chain crosses the interface just once from when it forms multiple stitches. G_0 is not altered, but the "block and tackel effect"[35] ensures that viscous processes dominate at lower velocities and V^* is reduced by a factor of N from the value obtained in the single crossing case.

When comparing the results of the chain pull-out models with experiment, it is valuable to have some numerical estimates of the predicted values of the parameters G_0, V^*, and $\mathrm{d}G/\mathrm{d}V$. I shall assume that $\Sigma = 10^{17}$ chains/m^2, $N = 10^3$, $\zeta_0 = 4 \times 10^{-10}$ (N s)/m,[36] and the monomer length $a = 5 \times 10^{-10}$ m. From the model of Raphaël and de Gennes[23] G_0 is given by

$$G_0 - W \approx \gamma N \Sigma a^2 \approx kTN\Sigma$$

where γ is the surface energy of the chains. With the numerical values and the two approximations given above, $G_0 - W$ is given as 0.75 or 0.4 J/m^2. For fully straight chains[18,23] V^* is given by

$$V^* \approx \frac{E}{3\Sigma\zeta_0 N}$$

which gives a value of $V^* = 10^{-5}$ m/s. If the chains collapse, V^* is multiplied by a factor of $\Sigma^2 a^4 = 6 \times 10^{-4}$.

From Raphaël and de Gennes[23]

$$\frac{\mathrm{d}G}{\mathrm{d}V} \approx \frac{G_0}{V^*} = \frac{3\gamma\zeta_0(\Sigma N a)^2}{E}$$

and so $\mathrm{d}G/\mathrm{d}V$ is about 2×10^5 J m^{-3} s. It is interesting to note that G_0 varies linearly with Σ while the gradient, $\mathrm{d}G/\mathrm{d}V$, varies as Σ^2.

All the pull-out models predict that the crack growth rate increases linearly with $(G - G_0)$ as long as the velocity is above V^*. It should be emphasized that the results shown in Figure 7 of Xu et al.[18] demonstrate that there is no sharp transition at $V = V^*$. It would be reasonable to consider V^* as the velocity at which G is about 20% greater than G_0. The results presented here agree with the predicted linear dependence of G on V for crack speed less than 10^{-9} m/s but only if V^* is at the lower end of the experimental velocity range.

The absolute values of G_0 are in reasonable agreement with the predictions of the chain pull-out model (assuming straight pulled-out chains), and the data are not inconsistent with the idea that G_0 varies linearly with Σ. There is too much scatter to be more positive about the variation of G_0 with Σ. In the same way, the data are consistent with the suggestion that $\mathrm{d}G/\mathrm{d}V$ varies with Σ^2. It is clear from a comparison of Figures 4 and 5 that $\mathrm{d}G/\mathrm{d}V$ changes more rapidly than does G_0 with Σ.

As G_0 agrees reasonably with the pull-out models, V^* can be estimated from the measured value of $\mathrm{d}G/\mathrm{d}V$. For $\Sigma \sim 10^{17}$, $\mathrm{d}G/\mathrm{d}V$ was found to be about 1.5×10^9, by assuming G_0 is 0.5 J/m^2, giving V^* of 3×10^{-10} m/s. Such a low value of V^* is not consistent with the assumptions of Raphaël and de Gennes that the partially pulled-out chains are straight and only cross the interface once in the pull-out zone. It would seem likely that the PI block copolymer chains are entangled both with themselves and with the cross-linked network and so both form multiple stitches and also collapse on themselves in the pull-out zone to form multichain fibrils.

At high crack speeds the toughness saturates, or at least increases, only slowly with V. Such a transition is not predicted by the current chain pull-out models. It has been suggested that, at high rates, chain scission may begin to occur.[24] However the predicted rates and toughnesses for scission are much higher than the rates and toughnesses seen here, so scission is unlikely to be the explanation for this saturation. A more plausible explanation for the saturation is that, at high rates and chain loads, the multichain fibrils break up into single chain fibrils, decreasing the pull-out rate for any given crack velocity and hence increasing V^*. As V^* increases with V, there would be a region of crack velocities over which G is nearly constant.

Conclusions

We have shown that placing a thin layer of a PS–PI diblock at the interface causes a considerable increase in the adhesion between a cross-linked PI lens and a PS surface. The extent of the increase is dependent on both the crack speed and the amount of PS–PI present. There is good reason to believe that the main cause of this adhesion increase is the energy involved in the pull-out of the PI diblock chains from the cross-linked PI lens. It is likely that these PI chains are tethered by their PS ends to the PS-coated substrate.

At low crack speeds the toughness was found to increase linearly with the crack speed from a threshold value, G_0, which obtained as the crack speed tended to zero. At higher crack speeds a transition occurred to a situation where the toughness increased more slowly with increasing crack speed. The toughness at constant crack speed above this transition increased with the areal density of tethered chains at the interface. The threshold toughness G_0 also increased with the areal density of tethered chains.

The results were compared with predictions of a number of models of chain pull-out. The linear dependence of G with crack speed agrees with the models. The values of G_0 are in reasonable agreement with one model, but the rate of increase of G with V is consistent only with the assumption that the tethered chains crossed the interface a number of times and also tended to form many chain fibrils in the pull-out zone.

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