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MECHANICAL EFFECTS OF DIBLOCK COPOLYMER AT INTERFACES

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ABSTRACT

The effects of a thin layer of diblock copolymer on the adhesion between a glassy polymer and two different materials, an elastomer and a silicon wafer, have been examined. The glassy polymer was polystyrene and the elastomer was polyisoprene. A polystyrene–b–polyisoprene copolymer was employed at the polyisoprene–polystyrene interface whilst a polystyrene–b–polymethylmethacrylate copolymer was used at the polystyrene–silicon interface. The toughness of the glassy–rubbery interface depended on the length of time at room temperature the polyisoprene of the copolymer diffused into the crosslinked polyisoprene homopolymer, when the two were not crosslinked together, but reached a maximum toughness enhancement of a factor of 4. The diffusion process was very slow because the block polyisoprene was tethered to the polystyrene and the polyisoprene homopolymer was crosslinked. Much greater joint toughnesses were found when the block and homopolymer polyisoprene were crosslinked together. The toughness of an interface between polystyrene and a silicon wafer (SiO_2) was increased from about 1 J/m^2 with no diblock present to about 40 J/m^2 with an organized diblock layer at the interface.

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INTRODUCTION

The interfaces between immiscible polymers are frequently weak because there is little chain entanglement between the materials. Diblock copolymers, selected so that one block mixes with each of the homopolymers, can be used as coupling agents between the immiscible polymers. In recent work it has been shown that the toughness of interfaces between pairs of glassy polymers can be enhanced by orders of magnitude by the presence of an optimally selected diblock copolymers. When the interface fractures the diblock copolymer chains crossing the interface either break, if high molecular weight, or pull out from one side, if low molecular weight [1–4].

The situation in elastomer–glassy polymer interfaces may be expected to be different from that at glassy–glassy polymer interfaces. It is assumed here that the elastomer homopolymer is crosslinked. If the copolymer elastomer is not crosslinked into the

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homopolymer elastomer then the diblock copolymer might be expected to be anchored relatively firmly in the glass and liable to pull out from the elastomer. Alternatively, if the copolymer and homopolymer elastomer are crosslinked together then relatively high failure energies are to be expected but with the copolymer molecules either breaking or pulling out from the glassy side.

The adhesion between polystyrene (PS) and silicon wafers (with a silicon dioxide surface) is known to be very low in contrast to the high adhesion that is observed between polymethylmethacrylate (PMMA) and silicon wafers. It would therefore seem likely that a thin layer of a PS–b–PMMA diblock at the interface would increase the adhesion between PS and silicon wafers. One of the aims of the work described here was to test this hypothesis.

EXPERIMENTAL PROCEDURES

Materials

The homopolymers used were a commercial molding grade of polystyrene (PS) (Styron 685, Dow Chemical Company, M_w 355,000), and a polyisoprene (PI) that was crosslinked using dicumyl peroxide. The diblock copolymers were two symmetric polystyrene–b–polyisoprene (PS–b–PI) materials of molecular weights 24K and 100K and one symmetric PS–b–PMMA copolymer of molecular weight 282K.

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Experimental Techniques and Preparation

Polystyrene–Polyisoprene Samples

The polystyrene–polyisoprene samples were made by first molding polystyrene strips with dimensions 5.5 cm in length and 1.5 cm in width. Thin films of PS–b–PI copolymer were spin coated on sodium chloride substrates and then floated off in deionized water, picked up on the PS strips and then dried for 24 hours at room temperature. In the next step, in the samples that used a precrosslinked PI homopolymer, the diblock coated PS strips were annealed to permit diblock organization and interdiffusion of the PS part of the diblock with the PS homopolymer. The specimens were held for 15 minutes in a vacuum oven at 115° C, a temperature above the glass transition temperature of PS. After this high temperature annealing a PI strip (5 mm width and 1 mm thick) was brought in contact with the diblock coated PS sample. The PI strip was pressed slightly against the PS to aid wetting and held there for a fixed period. If not explicitly specified, this second annealing, whose aim was to permit the PI part of the diblock to interdiffuse with the PI homopolymer, was carried out at ambient temperature and without significant external pressure. The effects of crosslinking the PI homopolymer with the PI of the diblock was examined in a series of experiments where an uncrosslinked PI strip was laminated with the diblock coated PS. The total sample was then annealed at 115° C for 2.5 hours to interdiffuse and crosslink the PI. Before peel testing the samples were glued with a cyanoacrylate adhesive onto an aluminum plate to improve handling.

The adhesion of the glassy–elastomer interfaces were measured by peel tests (with a 90° peel angle) that were carried out at room temperature (23°C) using an Instron

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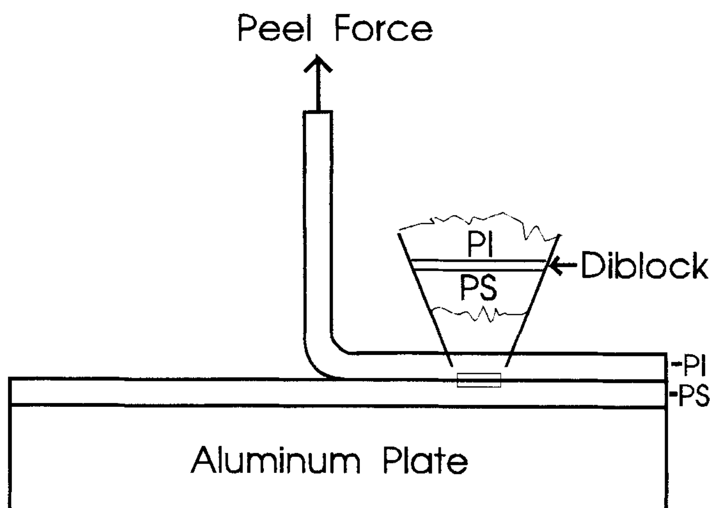

Figure 1 Peel test on a completed glassy–elastomer specimen

mechanical testing machine and a peel rate of 10 mm/min. Each sample provided 4 to 6 measurements of the work of detachment. In addition, if the second annealing had been performed at room temperature so that the PI of the homopolymer and the diblock were not cross–linked together, the samples could be rejoined. Therefore one sample could provide many values for the work of detachment. A sketch of a peel test on a completed sample is displayed in figure 1.

Polystyrene–Silicon Samples

The polystyrene–silicon wafer samples were made by first spinning a thin (0–70nm) layer of PS–b–PMMA diblock onto the silicon wafer. A thicker (500nm) layer of PS was floated onto the diblock and then the sample was annealed at high temperature in a vacuum oven. For mechanical testing it was necessary to increase the stiffness and hence thickness of the polystyrene side of the sample but without heating the sample above room temperature and hence causing differential thermal contraction stresses. This reinforcement was done by oxidizing the PS surface and then using an epoxy resin to attach a thin glass coverslip to the PS. Details of this procedure will be published later. The adhesion was measured using an asymmetric wedge opened double cantilever beam technique [5]. The light reflection properties of the silicon wafer made it easy to check that the failure had occurred on the polymer to wafer interface.

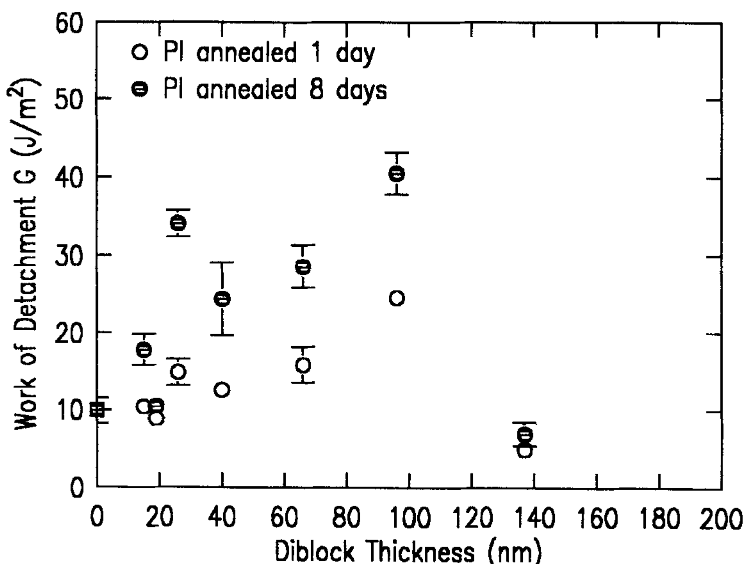

Figure 2. Variation of the interfacial toughness with the thickness of the PS–PI layer for two annealing times.

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EXPERIMENTAL RESULTS AND DISCUSSION

The Polystyrene–Polyisoprene System

The sample preparation technique was designed on the hope that it would produce an organized diblock layer between the two homopolymers. Pure PS–b–PI block copolymer organizes in bulk in such a way that a layer of PI is adjacent to a free surface PI [6,7]. One would expect a similar result, namely a PI layer adjacent to the free surface, in the situation considered here where a PS–sheet was annealed when covered with a PS–b–PI film.

Mechanical tests were done using 10 nm to 170 nm layers of the two PS–b–PI diblocks. Figure 2 shows the work of detachment after one day and eight days annealing time at room temperature for the 100K diblock. It is evident that, after just one day anneal, the block copolymer caused no great increase in the adhesion. The eight day room temperature anneal caused the adhesion to increase considerably. The 24 K diblock showed similar results to the 100K for the 1 day anneal (a toughness increase of about a factor of 2) but no significant change after 8 days.

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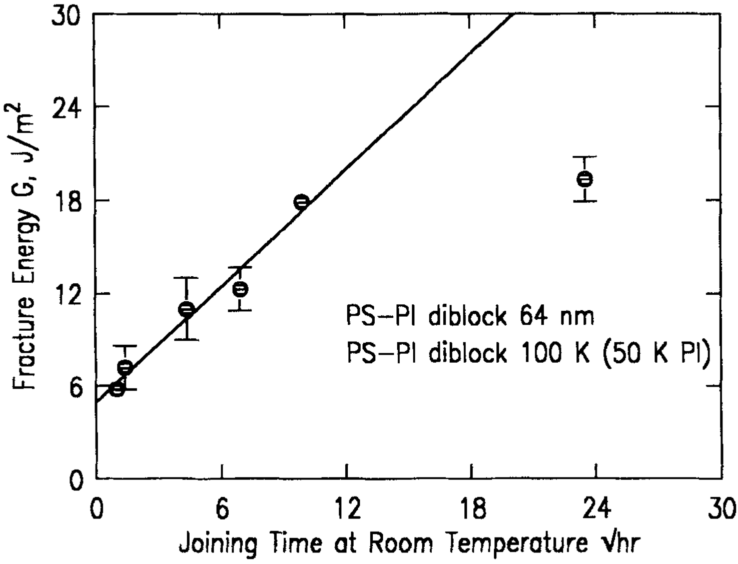

Figure 3a. Variation of interfacial toughness with joining time at room temperature, 64 nm thick diblock layer.

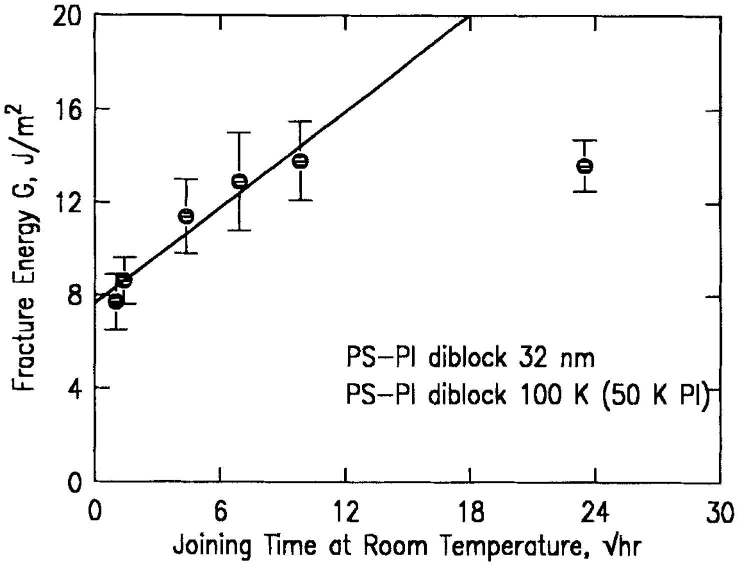

Figure 3b. As above but using a 32 nm diblock layer

Two major differences between the experiments described here and previous work on the effect of a PS–b–PMMA diblock at glassy homopolymer interfaces are (a) the annealing here was done in two steps and (b) the PI homopolymer was normally cross–linked. The diblock was annealed with the PS homopolymer in the hope that the diblock would organize at the interface and the PS part of the diblock and the PS homopolymer would interdiffuse. To form a toughened interface, the PI parts of the PS–b–PI diblock chains have to diffuse across the interface into the PI homopolymer and entangle with the network chains of the crosslinked rubber during the second, room temperature, anneal. This process may be considered as diffusion of tethered chains into a crosslinked network because the PS side of the PS–b–PI diblock is fixed in the glassy PS homopolymer. The diffusion of such tethered chains has some similarities to the process to the diffusion of star molecules in a very high molecular weight or cross–linked matrix and so is expected to be very slow. Star diffusion is controlled by the rate at which a tethered chain (or network arm) can contract out of (or retrace) all of its entanglements, a very slow process for long arms, and hence the diffusion constant decreases exponentially with the length of the arms. Figure 3 displays the work of detachment for two thicknesses of the 100K diblock as a function of $t^{1/2}$ where t is the annealing time of the whole sample at room temperature. Clearly the growth in adhesion is very slow and the adhesion saturates after about 100 hours. It should not be assumed from this figure that the diffusion of tethered chains in Fickian, even in the early stages. There is no a priori reason to assume that G_a varies linearly with the diffusion distance, or even with the diffusion contour length, s (which varies as $t^{1/2}$ in normal reptation). From pull–out models it would seem more likely that G_a varies with the work of pull–out, hence with s^2 implying that, if $G_a \sim t^{1/2}$, then $s \sim t^{1/4}$.

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For the 24 K diblocks an increase of the time of room temperature annealing above 1 day had no significant effect on the strength of the adhesion. This is because the PI part of the 24K polymer is not long compared with the entanglement length of PI (6.5 K [8]). The diffusion process is therefore expected to be rapid but little energy is required to pull–out a length of not more than 2 entanglements. Hence these low molecular weight diblocks are not very effective in toughening a PS–PI interface.

In the results discussed so far the polyisoprene homopolymer was crosslinked before lamination with the diblock coated polystyrene sheet. Experiments were also done where the PI strip was crosslinked after lamination thereby permitting the PI homopolymer and the PI of the copolymer to be crosslinked together. Results of such co–crosslinking experiments using the 100K diblock are shown in Figure 4. The interface toughness was very much enhanced by the co–crosslinking, even when there was no diblock present, so the crosslinking process must have caused some grafting between PS and PI. Presence of the diblock, particularly a 90nm layer of diblock, increased the joint toughness by a factor of 4 to about 200 J/m^2, which is by far the highest value observed in this work. Similar experiment using the 25K copolymer showed the same grafting effect but in this case the diblock layer had no effect on the toughness. The most likely explanation of these results is that, in the case of the 100K diblock, the PI of the diblock did co–crosslink with the PI homopolymer. For the 25K

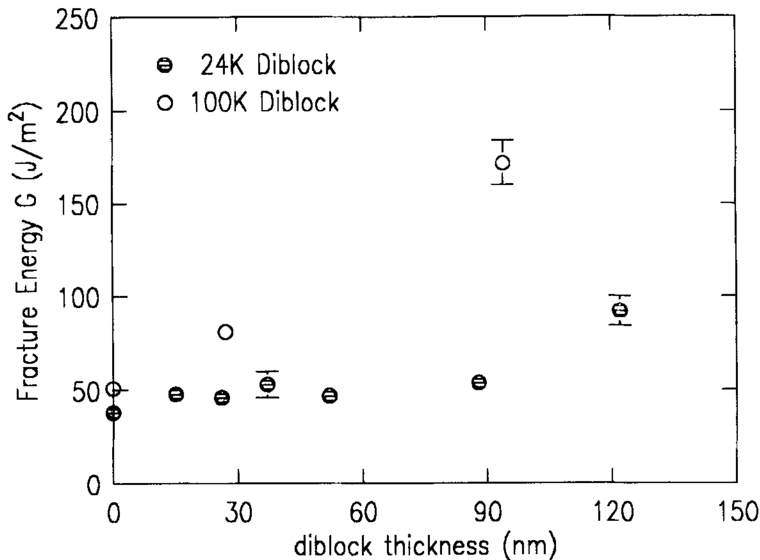

Figure 4. Interfacial toughness when the diblock and homopolymer PI are cross-linked together.

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copolymer no co–crosslinking occurred, either because the copolymer PI was too short or because the copolymer did not remain at the interface during the crosslinking process.

Polystyrene–Silicon System

Figure 5 shows the variation of interface toughness with thickness of the PS–PMMA layer between PS and a silicon wafer. Results are shown for two different annealing treatments, 115°C for 15 minutes and 170°C for 8 hours. The bare interface (no diblock) had a toughness of about 1 J/m^2 in both cases. For the low temperature anneal this toughness increased significantly for an 8nm thick diblock layer but then decreased again for thicker layers. The results from the samples annealed at high temperature were very similar to those from the low temperature anneal for the 8 nm thick layer but the toughness continued to increase with increasing layer thickness up to 44J/m^2 at the maximum layer thickness used, 40nm. Thicker layers were not used as 40 nm is about half the long period of the diblock and hence the maximum thickness that might be expected to organize in a single layer.

These results show that the PS–PMMA diblock can be very effective in coupling the PS homopolymer to a silicon wafer. The differences between the results obtained

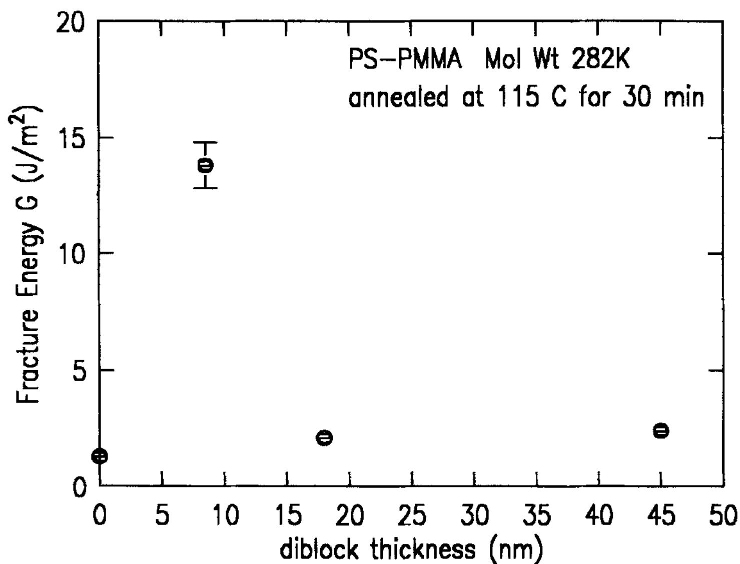

Figure 5a. Variation of interfacial toughness of a PS–Si joint with thickness of a PS–PMMA diblock layer at the interface. Sample annealed at 115°C for 30 minutes.

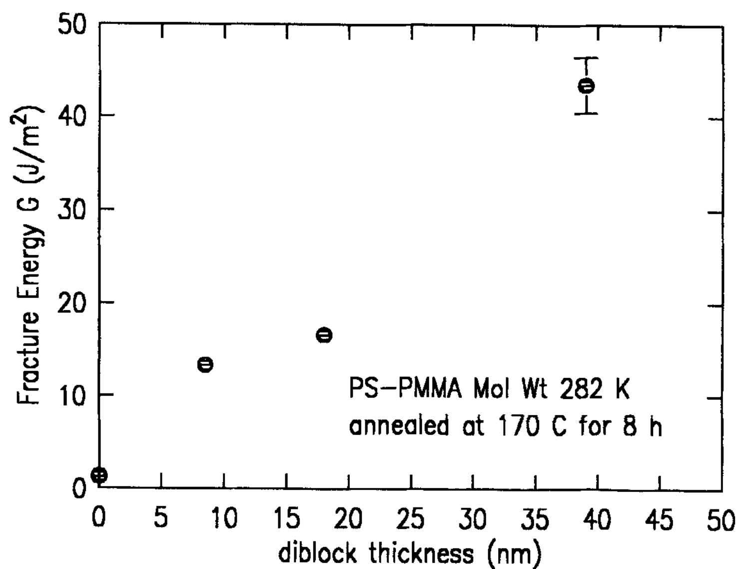

Figure 5b. As Fig 5a but annealed at 170°C for 8 hours.

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using the two annealing treatments are probably caused by differences in the state of organization of the diblock layer. When a thin layer of a diblock is placed between homopolymers, its organization rate is known to decrease rapidly with increasing layer thickness [9] so it is reasonable to assume that the 8nm layer of the diblock can organize and interdiffuse with the PS homopolymer during the low temperature anneal while the thicker layer remains unorganized. This explanation of the results is based on the assumption that a high interface toughness requires that the silicon wafer is entirely coated by the PMMA layer. However it is not clear why such complete coating could not be obtained using a layer thinner than 40nm.

CONCLUSIONS

We have shown that a thin layer of a PS–b–PI diblock copolymer can increase the adhesion between PS and crosslinked PI homopolymers. The joint toughness was a function of both the molecular weight and layer thickness of the copolymer. In addition, for the 100K copolymer, the toughness of the joint was found to increase slowly with the time the copolymer coated PS strip was in contact with the PI, probably because the diffusion of the tethered copolymer PI chains into the crosslinked bulk PI was very slow. In all these cases the PI was crosslinked before it was put into contact with the copolymer coated PS and so there was no possibility of incorporating the copolymer PI into the PI network. Therefore the basic failure mechanism was one of pull–out of the PI copolymer from the homopolymer. In other experiments the homopolymer PI strip was crosslinked when in contact with the copolymer hence allowing the possibility of incorporating the latter into the network. If the copolymer was large enough this co–crosslinking could produce very strong adhesion.

A thin layer of a PS–PMMA copolymer can cause a large increase in the adhesion between PS homopolymer and a silicon wafer. The adhesion depended on both the amount of diblock used and the annealing conditions. It is likely that the largest adhesion is obtained when the copolymer organizes at the interface.

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