Effect of a polystyrene–polyisoprene diblock layer on the adhesion between polystyrene and polyisoprene

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The adhesion between polystyrene and crosslinked polyisoprene homopolymers was found to be increased by the presence of a thin layer of polystyrene–polyisoprene block copolymer at the interface. The interfacial toughness was a function of both the layer thickness and molecular weight of the copolymer. If the homopolyisoprene was crosslinked before the joint was made, the joint failed at a relatively low toughness by the polyisoprene of the diblock pulling out of the polyisoprene homopolymer. Joints that failed by pull-out could be reformed by contact at room temperature. A high degree of interfacial toughness was found when the homopolymer and copolymer polyisoprene were crosslinked together.

(Keywords: polyisoprene; polystyrene; adhesion)

INTRODUCTION

Crack propagation in polymers requires that the polymer chains crossing the crack plane either break or pull-out from one side. Recent work on glassy polymers has begun to delineate the situations in which chain breakage occurs and find the relationships between the microscopic failure processes and the macroscopic toughness[1–4]. The basic experimental tool in this recent work has been the use of controlled amounts of diblock copolymers at the interface between immiscible polymers. The interface toughness is examined as a function of the number and length of the interlinking chains while information on the fracture process is obtained from a study of the location of the diblock molecules on the fracture surfaces. The relationship between the microscopic crack tip processes and the macroscopic toughness is based on the fact that the majority of fracture energy is dissipated in a craze located close to the crack tip[5].

The situation in elastomers is different from that in glassy polymers in a number of ways. For crosslinked elastomers and at very low crack speeds (threshold conditions), the relation between the fracture energy and the number and length of the broken network chains was developed by Lake and Thomas some years ago[6]. The change of fracture energy with crack speed is known to be described by time–temperature superposition and so is a viscoelastic property in both adhesive and cohesive failure[7,8]. The mechanism of bulk energy loss has been considered recently in a model proposed by de Gennes[9]. If the elastomer on the crack plane is not crosslinked, a situation that might often occur in adhesion, then the failure process is liable to be one of chain pull-out. Models have been proposed that estimate the energy involved in the pull-out processes[10,11] but there is little direct experimental evidence that these pull-out processes contribute significantly to the failure energy. The indirect evidence that exists on the effects of chain pull-out comes from some elegant experiments of Ellul and Gent[12] where the adhesion of crosslinked elastomer blocks was studied as a function of the fraction of uncrosslinkable material present.

The aim of the present work is to extend the diblock experiments from purely glassy systems to systems where one component is a crosslinkable elastomer. A known amount of the diblock is placed between the glassy polymer and the crosslinked elastomer. It is then possible to study the failure energy as a function of the areal density and length of the elastomer chains and to examine directly the relationship between interfacial failure energy and pull-out. It is also possible to crosslink the diblock elastomer chains into the elastomeric homopolymer so that failure requires either chain breakage or pull-out on the glassy polymer side. Such processes might be expected to cause a significantly higher failure energy than that seen in the elastomeric pull-out case.

EXPERIMENTAL

Materials

The polystyrene (PS) used in this work was of a commercial moulding grade (Styron 685, Dow Chemical Company, $M_w = 355 \times 10^3$). Mixtures of polyisoprene (PI) and dicumyl peroxide (DCP) crosslinking agent were prepared on an open two-roll mill. Crosslinked and uncrosslinked rubber sheets were made by using a range of DCP contents (0, 0.27, 1.00 and 2.70 wt%). A range of hydrogenated and partially deuterated polystyrene-*b*-polyisoprene copolymers (PS-*b*-PI) with

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Table 1 Specifications of copolymers

		M_w ($\times 10^3$)		
Diblock code	M_w ($\times 10^3$)	PS	PI	M_w/M_n
hPS-*b*-hPI 150K	150	40	110	1.05
hPS-*b*-hPI 100K	100	50	50	1.05
hPS-*b*-hPI 24K	24	9	14	1.06
dPS-*b*-hPI 65K	65	25	40	1.07

different molecular weights were used in these experiments. The diblocks used for mechanical tests were fully hydrogenated materials provided by Dexco Polymers. Secondary ion mass spectrometry (SIMS) experiments were done using a copolymer whose PS side was deuterated (dPS-*b*-hPI). This copolymer was synthesized by Lou Fetters of Exxon Corporation. The specification of each copolymer is listed in *Table 1*.

Experimental techniques and preparation

Peel tests. Polystyrene strips with dimensions 55 mm × 15 mm were cut from compression-moulded sheets. The strips were wiped with a clean tissue and compressed nitrogen was then used to remove dust from the surface. The PS-*b*-PI copolymer films were spin coated on sodium chloride substrates and the films floated off on deionized water, picked up on the PS strips and dried for 24 h at room temperature. Films of the PS-*b*-PI copolymer were also spin coated under the same conditions onto silicon wafer and their thicknesses measured by ellipsometry. It was assumed that the film thicknesses on both substrates would be the same.

In the next step the diblock-coated PS strips were annealed to permit the diblock to organize so that its PS part could diffuse into the PS homopolymer. The specimens were held for a fixed period in a vacuum oven at a temperature above the glass transition temperature of PS. Specific annealing parameters are attached to each set of experimental results. After this high-temperature annealing a PI strip (5 mm wide and 1 mm thick) was brought into 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 homopolyisoprene with the PI of the diblock were 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 h to interdiffuse and crosslink the isoprene. Before peel testing, all the samples were glued with a cyanoacrylate adhesive onto an aluminium plate to improve handling. A diagram of a completed sample is displayed in *Figure 1*.

The peel test is a common way to determine the strength of an adhesive joint. This test method has two distinct advantages: bond failure proceeds at a controlled rate and the peel force is sometimes a direct measurement of the work of detachment G_a (ref. 13). The peel tests (with an approximately 90° peel angle) were carried out at room temperature (23°C) using an Instron mechanical testing machine and a peel rate of 10 mm min^{-1}. No special jig was used to translate the sample as the strip was peeled but a long rod was used between the load cell and the peeled strip so that the peel angle changed little during the test. The peel load fluctuated a little during peeling and was recorded to give four to six measurements of the work of detachment per sample. In addition, if the second annealing had been performed at room temperature so that the PI of the homopolymer and the diblock were not crosslinked together, the samples could be rejoined. Therefore one sample could provide many values for the work of detachment.

SIMS experiments. The aim of the SIMS experiments was to learn about the location and organization of the diblock and particularly to find if the diblock stayed at or near the inferface. The partially deuterated diblock was used in these experiments. The preparation of the SIMS samples was the same as the preparation of the samples for the mechanical tests except that no PI strip was applied. Instead, after annealing the diblock layer with the PS homopolymer, a 46 nm film of homopolystyrene was floated onto the sample to provide a buffer layer to stabilize the SIMS etch rate before reaching the interface.

The SIMS experiments were done on a Perkin–Elmer 6300 secondary ion mass spectrometer using oxygen as a primary ion source. Detailed information on the instrument can be found elsewhere[14]. The experimental parameters used are listed in *Table 2*. The raw data were converted to secondary ion count as a function of depth by assuming that the etching rate was equal to that of PS, an assumption made on the grounds that there was very little PI in the sample.

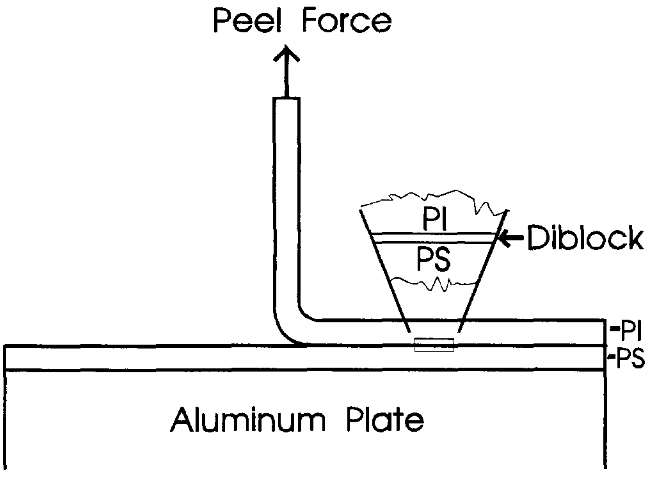

Figure 1 Diagram of sample preparation and peel test

Table 2 Analytical conditions of the Perkin Elmer 6300 secondary ion mass spectrometer

Primary bombarding species	Ox$_+$
Impact angle	60°
Primary ion energy	2 keV
Beam current	210 nA
Raster size	400 × 400 μm
Detected area	240 × 240 μm
Secondary ion polarity	(−)

Transmission electron microscopy (TEM) studies. Copolymer films were floated onto small (2 mm x 5 mm) pieces of PS homopolymer. After the annealing process, which was the same as that described above for the samples for mechanical tests, two different techniques were used for the preparation of the TEM samples. In the first technique, a gold layer was evaporated onto the diblock–air interface to act as a marker. In the second technique the samples were stained for 2 h with osmium tetroxide (a selective staining agent for PI). Both sets of samples were then embedded using Lowicryl KM4, a highly crosslinked acrylate and methacrylate based embedding medium. The embedded samples were trimmed and then ultramicrotomed at room temperature into thin sections of thickness 50–70 nm. The diamond knife of the microtome was set so that the cutting direction was normal to the interface. All the thin sections were floated off on a deionized water surface and picked up with a copper grid of mesh size 200. The thin sections with the gold layer (the first technique) were stained by osmium tetroxide vapour on a microscope grid before the TEM studies. Staining polymer samples with osmium tetroxide is a common method to achieve electron scattering contrast between two phases, particularly when one phase contains double bonds and stains rapidly. The staining is also useful in crosslinking and fixing the elastomer prior to microtomy to reduce cutting distortion and artifacts. There was no obvious evidence of cutting artifacts in the elastomer even without prior staining, perhaps because there was very little elastomer in these embedded samples.

The micrographs of the samples were taken with a Phillips EM400T TEM with the acceleration voltage set to 100 kV.

RESULTS AND DISCUSSION

Mechanical results

The adhesion between PS and PI is expected to be weak because PS and PI are immiscible polymers and the interface between them is narrow[15]. In addition, the sample preparation techniques used, where a PI strip was applied and annealed at room temperature, would ensure a weak interface even if the polymers were miscible as the annealing temperature is so far below the glass transition temperature T_g of PS that interdiffusion would be very unlikely. The measured work of detachment results from Van der Waals forces together with surface contamination and surface roughness effects. *Figure 2* shows the work of detachment as a function of the crosslinking (or network density) of the applied PI strip. As expected, the less crosslinked the rubber, the stronger the adhesion to the PS. Decreasing the crosslink density of the rubber increases the measured adhesion in two ways. First, the increased mobility and decreased elastic modulus of the rubber improves the ability of the PI to make good contact with and wet the PS; inevitably neither of the PS or PI sheets were entirely smooth so molecular contact required some elastic distortion of the PI. (No attempt was made to find if regions of poor contact existed between the two materials.) Second, the increased mobility increases the viscoelastic losses in the rubber on crack propagation and so increases the measured adhesion energy at constant thermodynamic work of adhesion. This trend is consistent with previous results of Chang and Gent[16].

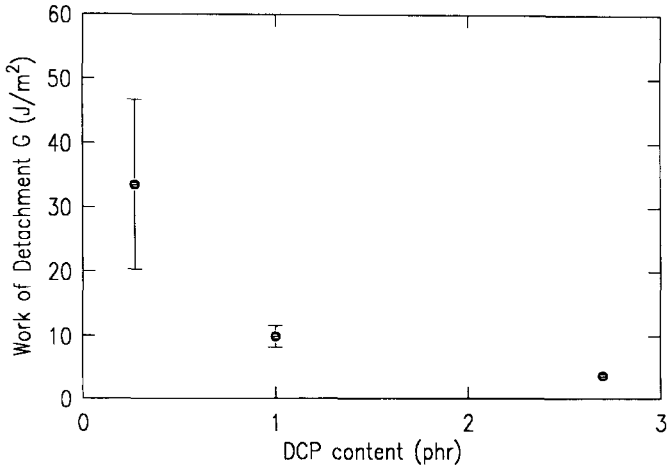

Figure 2 Work of detachment *versus* the dicumyl peroxide (DCP) content of the homopolyisoprene strip

The experiments were initiated on the assumption that the block copolymer layer would enhance the adhesion between the homopolymers. Pure PS-*b*-PI block copolymer organizes in bulk so that a layer of PI is adjacent to a free surface[17,18]. This is quite reasonable because such organization minimizes the surface free energy. The values of critical surface tension for PI, 30–32 mN m^{-1} (ref. 19), are smaller than those for PS, 33–36 mN m^{-1} (ref. 19) (however, smaller values have also been found for the latter). 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 10–170 nm thick layers of the three PS-*b*-PI diblocks with differing molecular weights. *Figure 3* displays the work of detachment after 1 and 8 days annealing time, respectively, at room temperature of the complete sample. The data obtained from peel tests for the 1-day anneal show the block copolymer causing no remarkable improvement in the adhesion. A small increase in the work of detachment compared with a pure PS–PI interface is seen with the 24K and 100K diblocks for some intermediate diblock thicknesses. The 8-day room temperature anneal obviously increased the adhesion in the presence of the 100K diblock. However, the work of detachment remained almost unaffected by longer annealing times for the other diblocks.

There is some evidence from previous work[1] that a diblock layer of thickness equal to half the repeat unit of the lamellar structure of the pure diblock produces the toughest interface between two immiscible polymers. Such an effect would be expected as half a long period is a reasonable estimate of the amount of diblock that would saturate an interface. In *Figure 3* the half long period is marked with an arrow for each diblock. However, only the 100K diblock shows any evidence of a maximum in the work of detachment for a diblock thickness corresponding to the half long period.

Further experiments and variation of the annealing parameters were designed to gain an understanding of the behaviour, function and organization of the diblocks at the interface.

Two major differences between the experiments described here and in previous work on the effect of a PS-*b*-PMMA diblock at glassy homopolymer interfaces

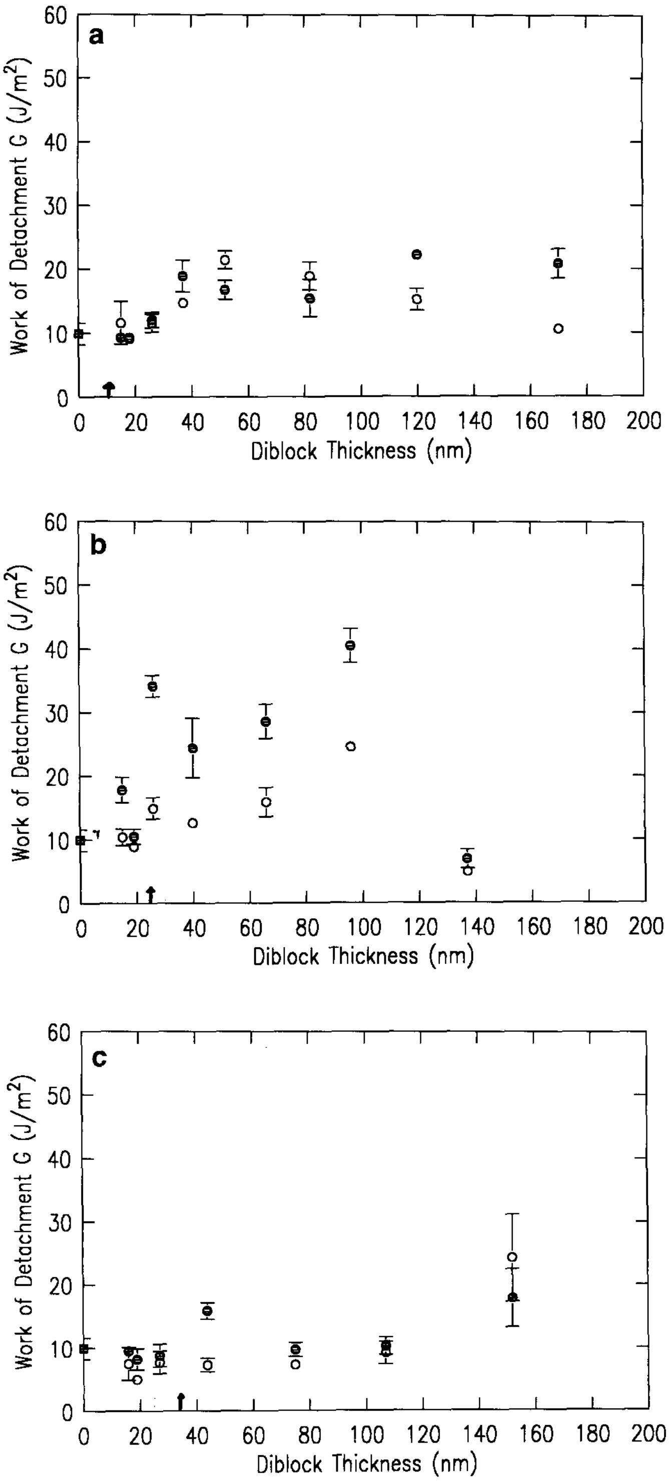

Figure 3 Work of detachment *versus* diblock layer thickness. The PI strip has been annealed for 1 day (○) or 8 days (○) with the PS surface. Diblocks of different molecular weight were used: (a) 24K; (b) 100K; (c) 150K

are that the annealing here was done in two steps and that the PI homopolymer was normally crosslinked. 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 diblock chains have to diffuse into the PI homopolymer during the second, room temperature, anneal and entangle with the network chains of the crosslinked rubber. This diffusion of the PI chains may be considered as diffusion of tethered chains into a crosslinked network because the PS side of the diblock is fixed in the glassy PS homopolymer. The diffusion of such tethered chains has some similarities to the process of the diffusion of star molecules in a very high-molecular-weight or crosslinked 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 4* displays the work of detachment, G_a, 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 (considering the T_g of PI is 200 K) and the adhesion saturates after about 100 h. It should not be assumed from this figure that the diffusion of tethered chains is 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 $s \sim t^{1/4}$.

For the 24K and the 150K diblocks an increase of the time of room temperature annealing had no significant

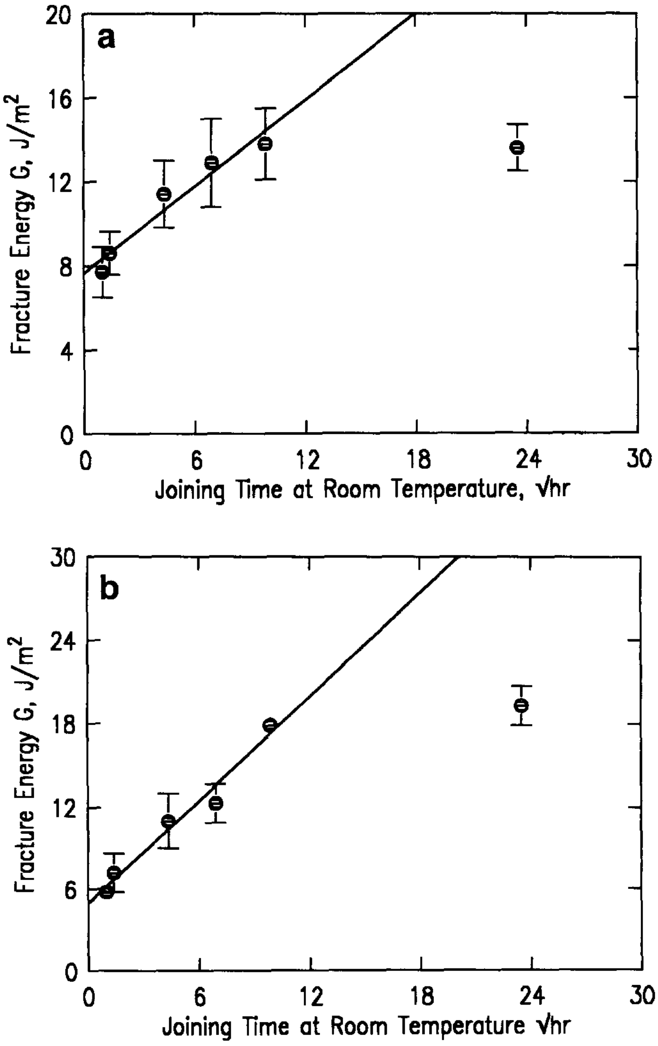

Figure 4 Work of detachment *versus* $t^{1/2}$ where t is the annealing time at room temperature. The diblock PS-*b*-PI 100K layer thicknesses were (a) 32 nm and (b) 64 nm. The PI strip was crosslinked with 1 wt% DCP

Table 3 Work of detachment as a result of two different annealing times at 115°C

Copolymer	Thickness (nm)	Annealing time 15 min	24 h
PS-*b*-PI 100K	11	17.8±2.0	13.4±1.1
PS-*b*-PI 100K	26	34.1±1.7	16.6±1.4
PS-*b*-PI 100K	66	28.6±2.7	29.7±1.1
PS-*b*-PI 150K	27	9.7±1.3	19.7±0.6
PS-*b*-PI 150K	108	9.0±1.4	28.1±4.0

Values given are work of detachment (G_a) (J m^{-2})±s.d.

effect on the strength of adhesion. The explanations for this effect are probably different for the two polymers. The PI part of the 24K polymer is not long compared with the entanglement length of PI which is 6.5 x 10^3 (ref. 20). The diffusion process is therefore expected to be rapid but little energy is required to pull out a length of not more than two entanglements. Hence these low-molecular-weight diblocks are not very effective in toughening a PS–PI interface. On the other hand the 150K diblock (110K PI side) probably diffuses much too slowly to form significant entanglements with the crosslinked homopolymer in the experimental time scale; however, if left long enough it would perhaps be very effective. If these arguments are correct there is an optimum length of the PI chain for maximum adhesive strength in any given time scale. If the chain is too short it pulls out easily and if it is too long it cannot interdiffuse within the time scale. In the case studied here, in only the 100K diblock could the PI chains diffuse in a reasonable time and form sufficient entanglement to obtain a tough interface.

The results presented in *Table 3* show that the annealing time of the diblock with the PS homopolymer (the first annealing time) affects the adhesion. For the thinner layers of the 100K symmetric diblock and especially the 27 nm (half long period) layer, a short annealing time (15 min) gave a stronger interface than the 24 h anneal. In contrast, the 150K diblock layer required the 24 h anneal to give any amount of interface toughening. These results will be discussed later after consideration of the morphological information on the diblock.

Diffusion of the PI chains of the diblock into the crosslinked rubber network is clearly necessary to toughen the interface between PS and PI. The diffusion can be altered by changing the annealing temperature and also, possibly, by altering the network density of the homopolymer PI. To examine the effect of annealing temperature, samples were prepared by annealing the PS homopolymer, the PS-*b*-PI diblock layer and PI strip at the same time. Using the 26K diblock, all three layers were joined at 115°C for 15 min. As *Figure 5a* shows, the adhesion was similar to the values obtained after joining the PI strip at room temperature for 8 days (or 1 day as there was not much difference for this copolymer). A similar experiment (*Figure 5b*) was done using the 100K diblock layer but here the annealing parameters were 125°C for 4.5 h. Again, the results from the high-temperature joined polymer were similar to the 8-day room temperature anneal results. However, in this case the joint toughness did depend on the annealing time at room temperature but, as seen in *Figure 4*, the toughness had saturated after annealing for 8 days at room temperature. The results of *Figure 5* are consistent with the idea that the diffusion saturated rapidly at room temperature for the 24K diblock and was saturated after 8 days at room temperature and 4.5 h at 125°C.

A second possible way to increase the mobility of the network chains is to decrease the crosslink density of the applied PI strip, assuming of course that the crosslink density remains greater than the entanglement density. However, the results of any such experiments would be complicated by the fact that changing crosslink density also changes the relationship between the measured toughness and the actual local fracture energy, as discussed earlier when considering the results of *Figure 2*.

In all 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 6*. 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. (The results of *Figure 5* show that just heating the system above the T_g of the polystyrene to permit the PS and PI to interdiffuse had no significant effect on adhesion.) Presence of the diblock, particularly a 90 nm layer of

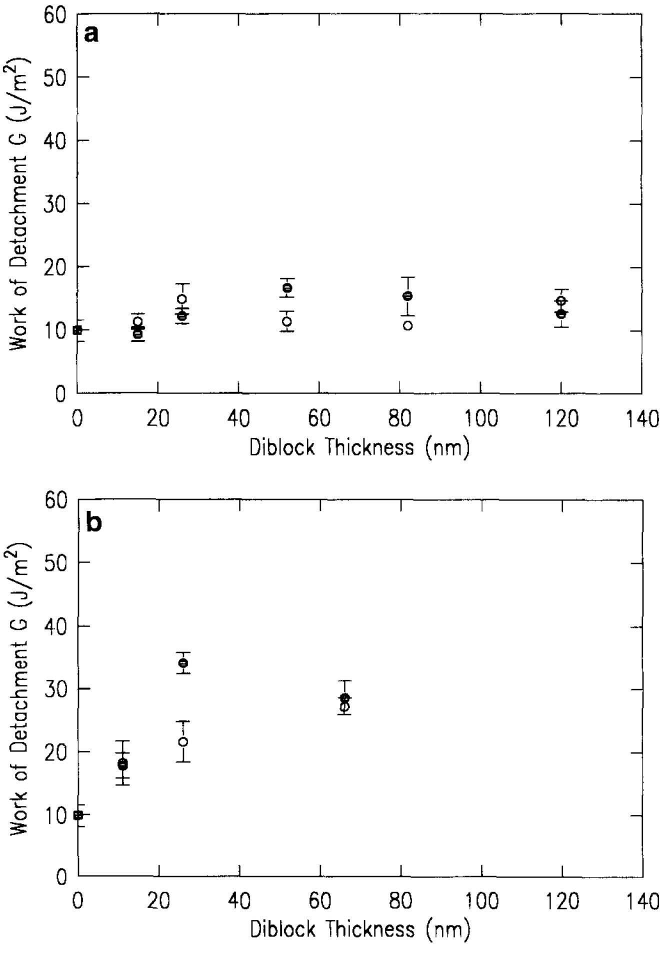

Figure 5 Work of detachment *versus* diblock thickness: (a) PS-*b*-PI 26K; (b) PS-*b*-PI 100K. G_a is displayed after a high temperature (○) and a room temperature (⊖) second anneal

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. A similar experiment using the 25K copolymer showed the same sort of enhancement of toughness with no diblock but in this case the diblock layer had no effect on the toughness. The most likely explanation for the difference in the results obtained with the two diblocks is that, in the case of the 100K diblock, the PI of the diblock did co-crosslink with the PI homopolymer. However, for the 24K 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.

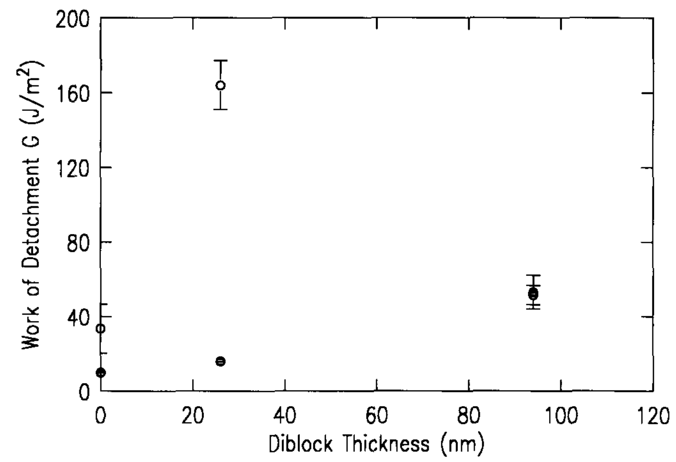

Figure 6 Work of detachment *versus* diblock thickness where the copolymer and homopolymer were crosslinked together. ○, 0.27 phr dicumyl peroxide (DCP); ⊖, 1 phr DCP

SIMS results

SIMS experiments were carried out to provide information on the location of the diblock copolymer after the first (high temperature) anneal. These experiments were inspired by the observation, discussed above when considering the results of *Table 3*, that, for the 100K diblock, increasing annealing time decreased the toughness. A possible explanation of this decrease in toughness would be that diblock was being lost from the interface and diffusing into the polystyrene during the annealing, unlikely though this might seem on thermodynamic grounds. Two samples were made using 26 nm and 84 nm thick layers of dPS-*b*-hPI copolymer. The layers were annealed at 115°C for 15 min, 1 h and 24 h. *Figure 7* shows deuterium depth profiles from these samples. The main conclusion from these results is that, for all annealing times, the copolymer stayed mainly at the surface though, after 24 h, some diffusion into the bulk probably occurred. As the 65K partially deuterated copolymer did not diffuse into the bulk very much it would seem unlikely that loss of diblock from the interface was the explanation for the decrease in toughness with increased annealing time observed with the 100K copolymer.

The SIMS experiments do not provide any information about the organization of the copolymer layers at the interface. Such information could, however, be obtained by studies using TEM.

TEM studies

The TEM studies were carried out to provide information about the morphology of the microdomains and the block copolymer microphase separation at or near the free surface. Here we are interested in the morphology of a

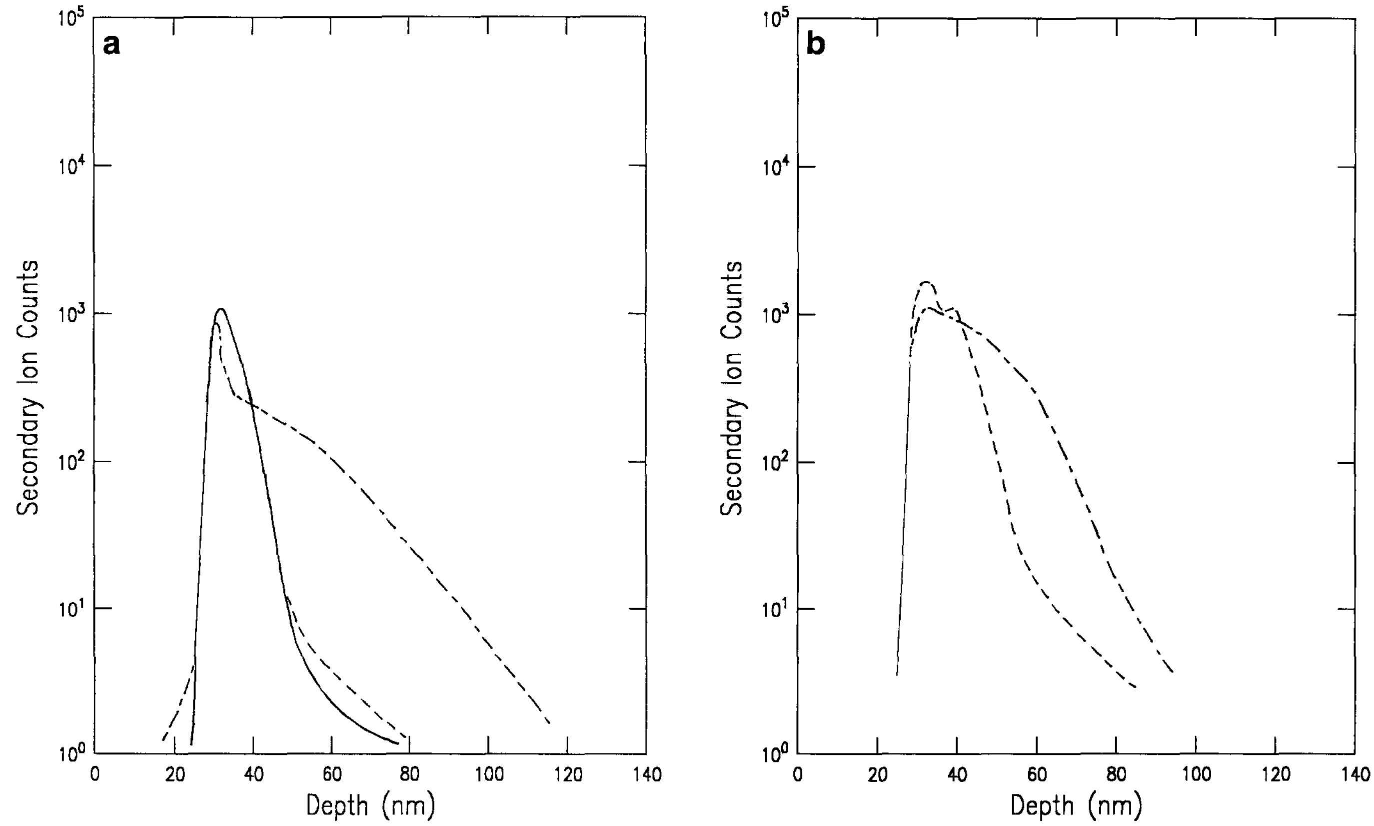

Figure 7 SIMS deuterium depth profiles for three different annealing times (——, 15 min; --, 1 h; ·-·, 24 h) of the diblock with the bulk material. Two copolymer layer thicknesses were investigated, (a) 26 nm and (b) 83 nm

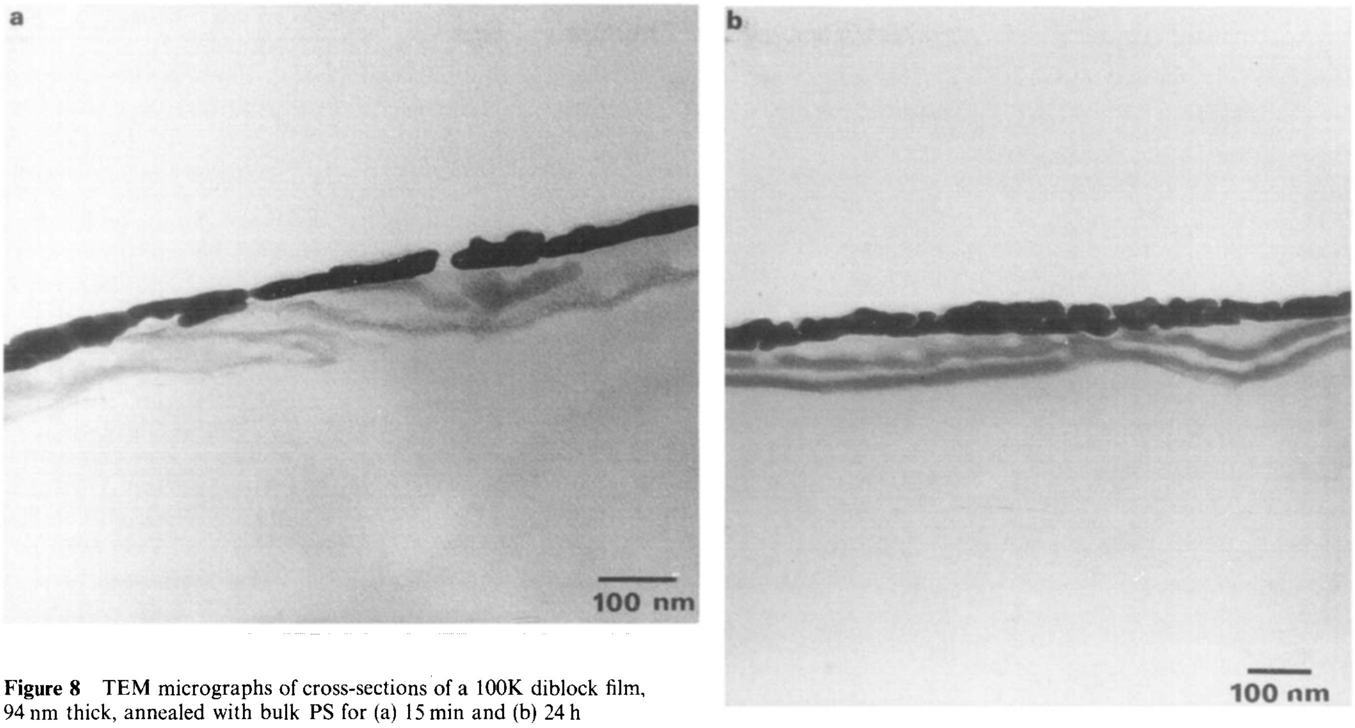

Figure 8 TEM micrographs of cross-sections of a 100K diblock film, 94 nm thick, annealed with bulk PS for (a) 15 min and (b) 24 h

thin PS-*b*-PI diblock film annealed with PS bulk material. The results of these studies are of substantial importance for the understanding of the mechanical tests.

Figure 8 compares the morphology of a 94 nm thick 100K copolymer film that was annealed for 15 min (*Figure 8a*) with one annealed for 24 h (*Figure 8b*) at 115°C. The evaporated gold layer, used to mark the surface, appears as a completely black line on the micrographs. The dark phases correspond to the polyisoprene microdomains selectively stained by osmium tetroxide while the bright areas on the micrograph are unstained polystyrene. A change in morphology on annealing is immediately evident on comparing the micrographs. During the short-time annealing the copolymer just begins to organize, but can reach only a cloud-like structure in which the formation of lamellas has started. After a 24 h anneal the diblock shows a very well ordered structure. As expected, for this molecular weight, the lamellar repeat unit is in the range 20–30 nm.

A second interesting result from these micrographs is that the free surface is not completely covered by PI. In the case of a short-time anneal, PS and PI are not completely phase-separated so a mixture of PS and PI at the surface is to be expected. The micrograph of the 24 h annealed diblock shows that some surface areas are completely covered with a material that is not stained by osmium tetroxide. It is not possible to tell by TEM if this unstained layer is PS or some surface contaminant. From the surface energies one would expect the free surface to be covered with a PI layer.

To make sure that the results presented above were not caused by the TEM sample preparation techniques, one sample was prepared using a different technique. A 94 nm thick copolymer film was annealed with the bulk material at 115°C for 24 h. Before embedding, the sample was stained with osmium tetroxide vapour. The fixation of the structure by osmium tetroxide prevented the sample from possible interaction with the epoxy embedding resin. *Figure 9* shows a micrograph of the sample prepared this second way. We find almost the same lamellar organization of the copolymer as before. In addition, there are again areas where unstained material is at the interface.

The TEM studies are consistent with the results obtained by mechanical measurements. Using the 100K diblock, the work of detachment is lower for a 24 h first anneal than for a 15 min or 1 h first anneal. PI chains at the free surface are essential for the generation of interfacial strength. With a short annealing time more PI chains are at the free surface than after a 24 h anneal as the latter shows areas where unstained material is at the free surface.

The 150K PS-*b*-PI diblock (110K PI side) behaves in an entirely different way. A long-time anneal of the diblock with the PS homopolymer gives a much tougher interface than a 15 min anneal (*Table 3*). The micrograph of a 150K diblock, annealed for 24 h, shows a completely

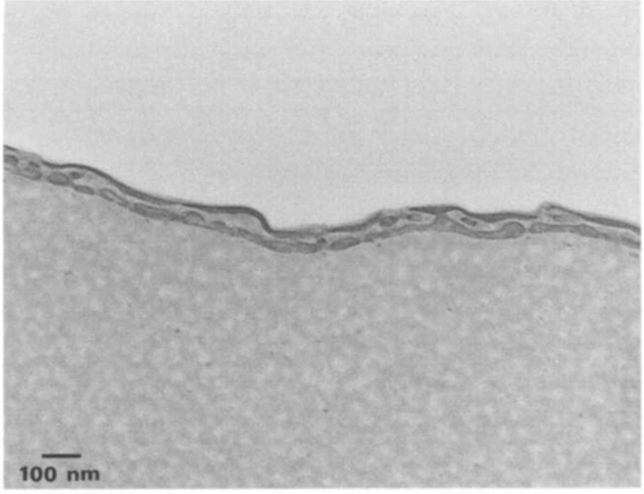

Figure 9 TEM micrograph of a cross-section of a 100K diblock film, 94 nm thick, annealed for 24 h and stained before embedding

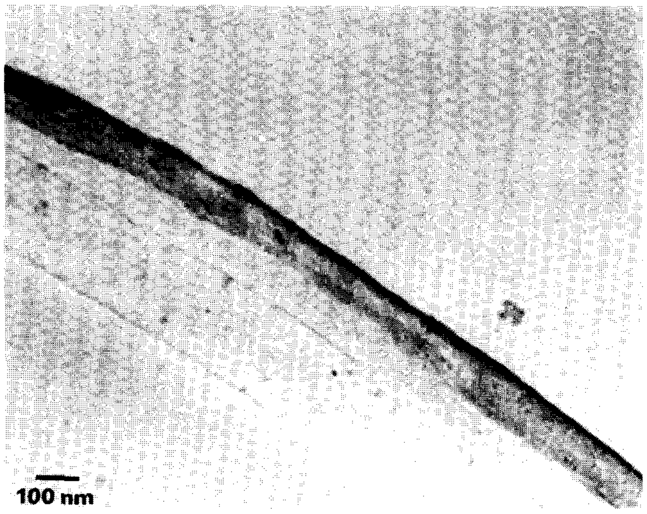

Figure 10 TEM micrograph of a 150K diblock annealed for 24 h with the PS homopolymer. The thickness of the floated diblock film was 108 nm

different morphology at the interface (*Figure 10*) from the 100K material. This sample was stained before embedding and no gold layer was evaporated onto the surface. We find a 60–80 nm thick PI rich layer (dark in the micrograph) at the interface which is covered with a 8 nm thick almost black layer. It would seem likely that this 8 nm layer is pure PI. Hence for this polymer long-time anneal causes the surface to be covered by pure PI causing the adhesion to be greater for the 24 h rather than the 15 min first anneal.

CONCLUSIONS

We have shown that a thin layer of a PS–PI diblock copolymer can increase the adhesion between PS and crosslinked PI homopolymers. The joint toughness was found to be 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. There was therefore no possibility of incorporating the copolymer PI into the PI network and so 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 copolymer PI into the network. If the copolymer was large enough this co-crosslinking could produce very strong adhesion.

The samples were made by placing the copolymer layer on the PS homopolymer and then annealing at a temperature above the T_g of the PS to permit the copolymer to organize so that the PS part of the copolymer diffused into the PS homopolymer. For the 100K diblock the adhesion was found to decrease with long annealing times. This decrease was found by TEM and SIMS to be caused, not by loss of diblock from the interface, but by the formation of a layer of material other than PI at the air surface. The nature of the material in this layer is not known but is presumed to be a contaminant. The 150K copolymer showed neither the adhesion decrease with long annealing times nor the presence of the contaminating layer.

REFERENCES

1 Brown, H. R. *Macromolecules* 1989, **22**, 2859
2 Brown, H. R., Deline, V. R. and Green, P. F. *Nature* 1989, **341**, 221
3 Creton, C., Kramer, E. J. and Hadziioannou, G. *Macromolecules* 1991, **24**, 1846
4 Brown, H. R. *Macromolecules* 1991, **24**, 2752
5 Doell, W. *Adv. Polym. Sci.* 1983, **52/3**, 105
6 Lake, G. J. and Thomas, A. G. *Proc. R. Soc. London (Ser. A)* 1967, **A300**, 108
7 Greensmith, H. W., Mullins, L. and Thomas, A. G. *Trans. Soc. Rheol.* 1960, **4**, 179
8 Andrews, E. H. and Kinloch, A. J. *Proc. R. Soc. London* 1973, **A332**, 385
9 de Gennes, P. G. *C. R. Acad. Sci. II* 1988, **307**, 1949
10 de Gennes, P. G. and Troian, S. M. *C. R. Acad. Sci. II* 1990, **311**, 389
11 Xu, D.-B., Hui, C.-Y., Kramer, E. J. and Creton, C. F. *Mech. Mater.* 1991, **11**, 257
12 Ellul, M. D. and Gent, A. N. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1953
13 Gent, A. N. and Kaang, S. Y. *J. Adhesion* 1987, **24**, 173
14 Benninghoven, A., Rudenauer, F. G. and Werner, H. W. 'Secondary Ion Mass Spectrometry', Wiley, New York, 1987
15 Annighofer, F. and Gronski, W. *Makromol. Chem.* 1984, **185**, 2213
16 Chang, R.-J. and Gent, A. N. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 1619
17 Ishizu, K., Yamada, Y. and Fukutomi, T. *Polymer* 1990, **31**, 2047
18 Hasegawa, H. and Hashimoto, T. *Macromolecules* 1985, **18**, 589
19 Brandrup, J. and Immergut, E. J. 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975
20 Sanders, J. F., Ferry, J. D. and Valentine, R. H. *J. Polym. Sci. A-2* 1968, **6**, 967