

Measurement of the fracture toughness of polymer–non-polymer interfaces

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One of the primary factors limiting the development of a better understanding of polymer–non-polymer adhesion is the lack of a good testing method for the measurement of the strength of the interface. In this paper polymer–non-polymer adhesion is evaluated in terms of the fracture toughness of the interface using an asymmetric double cantilever beam testing geometry. The test is applied to the measurement of polystyrene (PS)–glass and PS–silicon (native oxide) interfaces modified by PS–poly(2 vinylpyridine) (PVP) and PS–poly methyl methacrylate (PMMA) diblock copolymers. The importance of mixed mode crack propagation is demonstrated and it is shown that through an appropriate choice of sample geometry, the crack-tip trajectory can be controlled so that the crack is forced to propagate along the interface. The PS–glass test, in particular, is shown to overcome many of the traditional problems of adhesion measurements, such as failure, away from the interface and effects of far-field deformation in the polymer. The interfacial fracture toughness of the PS–glass and PS–silicon interfaces without copolymer modification are approximately the same and weak with values of 1 J m^{-2} . The addition of the block copolymers results in significant (>40-fold) increases in the interfacial fracture energies. The increase in fracture toughness is dependent on the quantity and degree of organization of the block copolymer at the interface.

1. Introduction

Common tests for measuring polymer–non-polymer adhesion have problems which are intrinsic to the types of materials being measured and are thus difficult to circumvent. Engineering tests such as the peel and blister tests are often hyper-sensitive to the global non-elastic deformation occurring in the polymer away from the crack tip. Standard fracture mechanics tests such as the single-edge notch test are often limited in their applicability because the introduction of bi-material interfaces often results in cohesive failure of one of the substrate materials as cracks tend to deflect into the more compliant substrate. While microscopic approaches, such as those using the surface force measurement apparatus, can provide a wealth of information about the molecular affinity between polymer and substrate, they may not allow the development of the local interfacial crack-tip plastic deformation mechanisms such as crazing which have significant effects on the magnitude of interfacial fracture toughness in glassy polymers. In the light of the importance of localized deformation mechanisms such as crazing in polymer fracture, we have adopted the fracture mechanics approach for our investigation. Our approach is to use an asymmetric double cantilever beam specimen which allows us to direct the crack along the desired interface.

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The interface chosen for study is that between polystyrene (PS) and a rigid non-polymer substrate. Two different substrates (silicon, covered with native oxide, and soda–lime glass) have been studied, necessitating two slightly different approaches to the problem. In experiments on silicon, the technique was applied to the measurement of the interfacial adhesion between PS and the native oxide on silicon wafers. The interface was reinforced by a thin (1–10 nm) layer of PS–poly methyl methacrylate (PMMA) diblock copolymer. The measured interfacial fracture toughness, G_c , was then correlated with the thickness of the PS–PMMA copolymer layer as measured by ellipsometry prior to specimen assembly. In the experiments using soda–lime glass substrates, a PS–glass interface was modified by the addition of dPS–poly(2 vinylpyridine) (PVP) block copolymer. By labelling the PS block of the block copolymer with deuterium (dPS), the areal density, Σ , of block copolymer at the interface after the fracture of the specimen was determined directly using forward recoil spectrometry (FRES). The interfacial fracture toughness was then correlated with Σ .

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1.1. Block copolymers at interfaces

It has been shown that small quantities of dPS–PVP block copolymers dissolved in PS homopolymer will segregate strongly to native oxide-covered silicon surfaces [1]. At the interface, the block copolymer chains align themselves as enthalpic forces drive the PVP block to the interface while entropic forces cause the dPS block to extend into the PS homopolymer forming a brush. If the PVP block adheres well to the glass substrate, and the PS block is sufficiently long to entangle in the PS homopolymer, then the PS–glass adhesion should be improved and the magnitude of the improvement should depend on the number of block copolymer chains bridging the interface. Indeed this phenomenon may be observed qualitatively, as a 1 μm film of PS spun cast on a silicon wafer can be easily peeled from the wafer by inserting a razor blade between the film and substrate. A similar film doped with dPS–PVP block copolymer cannot be peeled without the PS film breaking first. Similar reasoning applies for the PS–PMMA block copolymer at the PS/native oxide silicon interface with the PMMA block being attracted enthalpically to the SiO₂ interface [2].

The effect of adding diblock copolymers to homopolymer–homopolymer interfaces has been examined by Brown *et al.* [3–5] with PS/PMMA diblock copolymers and Creton *et al.* [6, 7] with PS/PVP diblocks. Using a double cantilever beam testing geometry they were able to show that the addition of diblock copolymers significantly increased the otherwise weak interfacial strength between these two incompatible homopolymers. The block copolymer chains acted as stitches across the interface which were able to transfer the stress from one homopolymer to the other. The extent of reinforcement was shown to be dependent upon the areal density of block copolymer chains, Σ , at the interface and the respective block lengths of the copolymer chains. Blocks shorter than the entanglement molecular weight of the respective homopolymer pulled out when stressed and provided only limited improvement in adhesion [4]. Longer blocks, on the other hand, entangled well with the homopolymers and resulted in large increases in G_c of the interface by allowing stresses high enough to cause a craze to form in the PS side of the interface. In the case of the polymer–non-polymer adhesion, as long as the PVP (or PMMA) block remains firmly attached to the glass (native oxide silicon) surface, we expect the same type of behaviour to be observed.

1.2. Mechanics

The double cantilever beam is shown schematically in Fig. 1. It consists of two beams attached together along the long axis, forming an interface. The interfacial adhesive strength is evaluated in terms of the fracture energy required to create an increment of new surface as a razor blade is propagated along the interface. It is assumed that all of the energy released during fracture is dissipated locally near the crack tip in an interface zone which is small compared to the

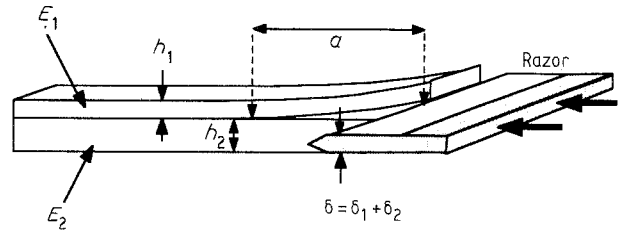


Figure 1 A schematic drawing of the asymmetric double cantilever beam geometry showing the labelling convention.

thickness of the outer glass beams. This assumption permits the fracture toughness, G_c , to be equated with the energy release rate, G , of the beam sample using a simple relationship derived from beam theory [8]

$$G = \frac{3\Delta^2}{8a^4} \left[\frac{E_1 E_2 h_1^3 h_2^3}{E_1 h_1^3 + E_2 h_2^3} \right] \quad (1)$$

where the subscripts 1 and 2 refer to the top and bottom glass beams and a is the crack length as shown in Fig. 1. E is Young's modulus of the glass, h is the thickness of the beam sections and Δ is the opening displacement which is assumed to be the thickness of the razor blade.

While the approximation given by Equation 1 is sufficient for weak interfaces with long cracks, for shorter cracks typical of the stronger interfaces measured in this investigation, this relationship overestimates G and thus G_c . A more accurate approximation for G was obtained by Creton *et al.* [6, 7], based on a model of a cantilever beam mounted on an elastic foundation developed by Kanninen [9]. This approximation is valid when the crack length to beam thickness ratio is large and the length of the unfractured interface ahead of the crack tip is also large when compared with the beam thickness. For this model G is found to be

$$G = \left(\frac{3E_1 E_2 h_1^3 h_2^3 \Delta^2}{8a^4} \right) \left[\frac{C_2^2 E_1 h_1^3 + C_1^2 E_2 h_2^3}{(C_2^3 E_1 h_1^3 + C_1^3 E_2 h_2^3)^2} \right] \quad (2)$$

where

$$C_1 = \left(1 + 0.64 \frac{h_1}{a} \right) \quad (3a)$$

$$C_2 = \left(1 + 0.64 \frac{h_2}{a} \right) \quad (3b)$$

Equation 2 was used to calculate the interfacial fracture energy for the PS–glass adhesion experiments.

1.3. Mixed mode fracture effects

In a homogeneous isotropic material, crack growth usually follows a trajectory in which only tensile stress acts on the plane of separation directly ahead of the crack tip (Mode I). For this reason, fracture toughness tests are carried out in these materials under Mode I loading conditions. However, at a bi-material interface, due to the asymmetry of the material properties, the shear component of the stress ahead of the crack tip does not vanish even when the specimen and loadings are symmetric with respect to the crack [10]. For example, under plane strain loading conditions, the traction in the interface at a distance x directly

ahead of the crack tip is given by

$$\sigma_{22} + i\sigma_{23} = \frac{K}{(2\pi x)^{1/2}} x^{i\epsilon} \quad (4)$$

where $K = K_1 + iK_2$ is the complex stress intensity factor [$i = (-1)^{1/2}$] and is related to the energy release rate, G , by

$$G = \frac{c_1 + c_2}{16 \cosh^2(\pi\epsilon)} |K|^2 \quad (5)$$

where the c_i and ϵ are material constants defined by

$$c_i = \frac{8(1 - \nu_i^2)}{E_i} \quad (6a)$$

$$\epsilon = \frac{1}{2\pi} \ln \left(\frac{1 - \beta}{1 + \beta} \right) \quad (6b)$$

$$\beta = \frac{1}{2} \left[\frac{\Gamma(1 - 2\nu_2) - (1 - 2\nu_1)}{\Gamma(1 - \nu_2) + (1 - \nu_1)} \right] \quad (6c)$$

$$\Gamma = \frac{E_1}{(1 + \nu_1)} \frac{(1 + \nu_2)}{E_2} \quad (6d)$$

where ν_i s are Poisson's ratios of the top and bottom glass beams and $|K|$ is the absolute value of the complex number K . The term $x^{i\epsilon}$ in Equation 4 gives rise to very rapid oscillations in the stress and displacement field as one approaches the crack tip which leads to interpenetration of the crack faces. The region of rapid oscillations, however, is extremely small and can be neglected as pointed out by Rice [10]. Suo and Hutchinson [11] show how to determine the relative proportion of tensile and shear loading at the crack tip from the phase angle, Ψ_c , defined by

$$Kt^{i\epsilon} = |K|e^{i\Psi_c} \quad (7)$$

where t is the thickness of the sandwiched layer between the glass plates. It should be noted that the definition of phase angle above differs from that of Cao *et al.* [12].

The asymmetric double cantilever beam specimen we have selected for the current experiments is a special case of the sandwich specimens discussed by Suo and Hutchinson [11]. The total thickness, t , of the polymer layer is relatively small compared with the thickness of the glass plates on either side. The crack length is also very large compared with the thickness of the polymer layer. The effect of the applied loading in a region surrounding the crack tip can be uniquely characterized by the classical Mode I and Mode II stress intensity factor, K_I and K_{II} (calculated by setting the thickness of the sandwiched polymer layer equal to zero) provided the region is small compared with the beam thickness but large compared with the sandwiched PS layer. Following Suo and Hutchinson [11], we let $K^\infty = K_I + iK_{II}$ such that the mixity

$$\Psi = \tan^{-1} \frac{K_{II}}{K_I} \quad (8)$$

of the applied K^∞ field can be controlled by adjusting the specimen dimensions such as h_1/h_2 and the crack length.

It is important to note that the mixity of the applied K^∞ field, Ψ , differs from the phase angle or mixity of the complex K near the crack tip and it is the local mixity that controls the crack trajectory. Because the crack-tip field, K^∞ , uniquely characterizes the far-field loading, the relationship between the two mixities is universal and is given elsewhere [11].

It should also be noted that the universal relation is obtained by assuming that the material behaviour everywhere in the specimen can be modelled as linearly elastic, which is a good approximation for ceramic materials. However, in our specimen, the length of the deformation zone along the interface is of the same order as the thickness of the PS layer so that it may not be possible to use the relation given by Suo and Hutchinson [11]. Indeed the mixity, Ψ_c , may not be well defined in our case because the material near the crack tip is no longer linear elastic in the sandwich layer and hence the stress field there can no longer be characterized by the complex K field. However, because the deformation zone ahead of the interface crack is small compared to the glass beam thickness, the applied K^∞ field still uniquely controls the local deformation experienced at the crack tip and hence, controls the relative amount of shear and tensile stress near the crack tip.

The effect of mixity on crack propagation and the interfacial fracture energy has been investigated experimentally by Cao *et al.* [12] and Evans *et al.* [13]. By choosing several test geometries they varied the mixity over a wide range and found that the interfacial fracture energy increased with increasing mixity. They also showed that the crack trajectory is dictated by the sign and magnitude of Ψ . For an asymmetric sample, the crack will deviate in the direction of the more compliant material.

Brown [14] has shown that a small amount of mixity due to modulus mismatch at a PS-PMMA homopolymer-homopolymer interface caused the interfacial crack to deviate away from the interface. The formation of a craze in the PS resulted in much higher fracture energies than that expected of the interface itself. By making the double cantilever specimen asymmetric with a PS beam that was thicker than the PMMA beam, it was possible to drive the crack in the direction of the PMMA. The PMMA has a higher crazing stress than PS and thus the crack remained at the interface giving much lower values of G_c . Creton *et al.* [6, 7] found similar results for a PS-PVP interface.

2. PS-glass adhesion

2.1. PS-glass specimen preparation

The double cantilever beam specimen used in the PS-glass experiments consists of two glass beams of different thicknesses with a thin polymer layer sandwiched between them as shown in Fig. 2. The exploded views of Fig. 2 illustrate the structure of the sample in more detail. The glass used came from standard laboratory microscope slides. Slides 0.97 and 1.27 mm thick (tolerance of $\pm 12.5 \mu\text{m}$) were hand picked from boxes of commercial microscope slides,

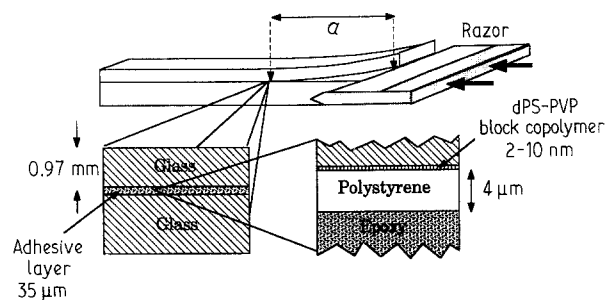


Figure 2 A schematic drawing of the PS-glass asymmetric double cantilever beam test sample showing details of the sandwich structure.

washed with soap and hot water, rinsed in deionized water and then dried in air. Each slide was rinsed in toluene and spun dry prior to application of the polymer.

The dPS-PVP block copolymer used in the PS-glass investigations was anionically polymerized, had a polydispersity of less than 1.1 and a degree of polymerization of 800–870 for the dPS and PVP blocks, respectively. Details of the polymerization are reported elsewhere [15]. The thin copolymer layer was spun cast (at 2500 r.p.m. for 20 s) on to the cleaned microscope slides. The lower concentration solutions of block copolymer were mixed with 0.5% PS ($N_{PS} = 6440$) in toluene to ensure a uniform distribution of the copolymer on the substrate. Ellipsometry measurements indicated these layers varied from 2–10 nm thick depending on the concentration of the copolymer solution. In order to form a weak starter crack, one-third of the glass slide surface area at one end was masked with tape prior to spin coating. The tape covering prevented the copolymer from depositing on one end of each specimen. The tape was then removed prior to deposition of the PS layer leaving a weaker PS-glass interface to start the crack. The thicker 4 μm PS films ($N_{PS} = 6440$) were spun on to glass plates, floated off on to water, dried in air and then transferred on to the copolymer-coated substrate. These coated slides were then annealed for 3 h at 160 $^{\circ}\text{C}$ in a vacuum oven.

Once annealed, the thicker glass was attached to the PS layer using an epoxy resin. The most suitable resin was a two-component epoxy resin from Reichhold Chemicals Inc. [16]. Without modification, the PS-epoxy adhesion was insufficient due to the lack of polar surface groups on the PS surface. To obtain acceptable PS-epoxy adhesion, the PS surface was subjected to an oxygen plasma using a barrel etcher prior to application of the epoxy. The exposure time for six to eight samples was 10 min at 300 W with an oxygen flow of 300 standard $\text{cm}^3 \text{min}^{-1}$. This etch is an almost purely chemical one resulting in a chemical alteration of the surface such as the formation of COOH groups. The glass-epoxy-PS-glass sandwiches were then cured for 2 h at 100 $^{\circ}\text{C}$.

The edges of each microscope slide sandwich were trimmed off using a water-lubricated diamond wafering saw leaving sufficient material to cut three 7.5 mm wide specimens from each slide. The width of the glass

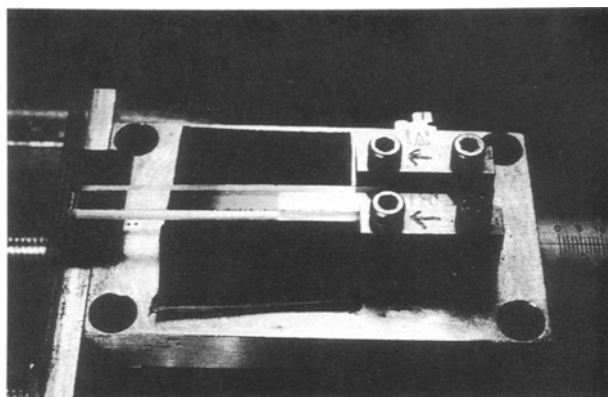


Figure 3 Photograph of the testing apparatus showing the servo-driven platen and the sandwich specimen. The crack front is clearly visible in the central portion of the specimen.

was then reduced by 200–300 μm by grinding on silicon carbide paper (240, 400, 600 grit) to remove defects from the cutting procedure. The specimens were then left in a vacuum desiccator overnight to remove moisture from the cutting and grinding procedure.

2.2. Testing procedure

The testing itself is simple in that a razor blade must be driven between the two beams forcing an interfacial crack the length of which may be measured by viewing through the glass from above. The testing jig, shown in Fig. 3, consists of a fixed table and platen and a moving platen attached to a servo-controlled motor. One-half of a standard double-edge safety razor blade (thickness 0.1 mm) is clamped firmly to the moving platform where it may be driven into the sample at a constant rate. A video camera is mounted above the testing apparatus and the crack length measurements are made from the video monitor. Steady state values of the crack length were measured and 15–20 measurements were made per specimen. Between three and six specimens were tested for each set of conditions. The interfacial fracture energy was calculated using Equation 2.

2.3. Numerical investigation of the mixity

To determine the mixity at the crack tip of the glass-PS-glass adhesion samples, a numerical model was developed using the boundary element method (BEM). The model assumes the polymer layer is very thin and thus the calculations are based only on the properties of the glass. Details of the numerical modelling can be found elsewhere [17, 18]. Several calculations were done for $h_1 = 0.97 \text{ mm}$ and $h_2 = 1.27 \text{ mm}$ which are the values used in the current experiments. Values of the strain energy release rate, G , from the BEM calculation for a series of crack lengths in the current experimental range are plotted in Fig. 4 along with curves from conventional beam theory and the elastic foundation approximation. The comparison illustrates the necessity of using the elastic foundation correction factor over simple beam theory. For

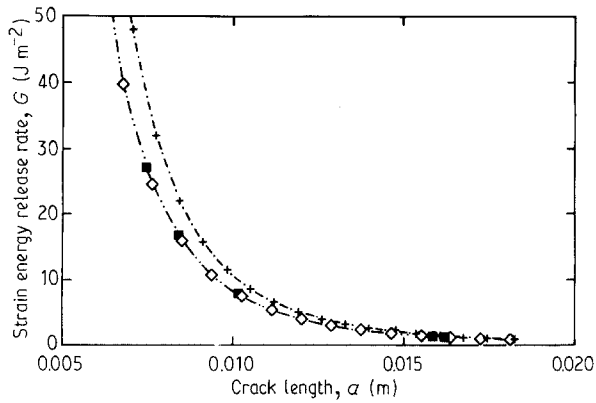


Figure 4 Comparison of the fracture toughness of the interface as determined by (■) the boundary element calculation, (◇) the Kanninen elastic foundation model and (+) simple beam theory.

a crack length of 8 mm the beam theory predicts G_c to be 40% higher than is found with the Kanninen's elastic foundation model. The G from the elastic foundation model, on the other hand, agrees well (within 2%) with G from the BEM; for the same crack length, the elastic foundation model is therefore a very reasonable approximation to the real system.

In the case of the PS-glass experiments, the mixity, as discussed in the introduction, is determined by the ratio of the thicknesses of the two beams and the crack length, a . Using the BEM programme, it was possible to calculate the classical K_I and K_{II} for the given specimen geometry and the results are shown in Table I with the accompanying values of mixity. The crack lengths illustrated include the entire range encountered in the current experiments and thus the range of mixities represent the mixities encountered as well. The values of mixity vary from -8.5° to -5.3° and are negative for all of the crack lengths investigated which confirms the existence of a force that is driving the crack in the direction of the PS-glass interface.

2.4. Control of crack trajectory

The purpose of these experiments was to determine the interfacial fracture toughness of the interface and thus the crack must be driven to the PS-glass interface. By making the glass backing for the epoxy thicker than the glass at the PS-glass interface, $\Psi < 0$ the crack should be driven to the PS-glass interface. To determine the value of mixity necessary to drive the crack into the interface, a series of fracture experiments were carried out. Ψ was varied from -9° to $+1.8^\circ$ by changing the thickness of the top glass beam in Fig. 2 from 0.91 mm to 1.35 mm while maintaining the bottom glass backing the epoxy constant at 1.27 mm. With the exception of the variation of the beam thicknesses, the samples were identical. The interface was modified by the addition of an 800–870 PS-PVP block copolymer with an areal density on the order of 0.01 chains nm^{-2} . The results are shown in Fig. 5 and the corresponding mixities calculated using the BEM are shown in Table II.

Specimens with aspect ratios of 0.86 and above failed at very high values of G_c and had a great deal of

TABLE I Stress intensity factor and mixity

Crack length (mm)	G_{BEM} (J m^{-2})	K_I ($10^4(\text{Pa m}^{1/2})$)	K_{II} ($10^4(\text{Pa m}^{1/2})$)	Mixity Ψ (deg)
7.8	32.4	148.0	-22.1	-8.5
8.9	20.1	117.0	-16.6	-8.1
10.8	9.4	80.0	-10.4	-7.4
12.0	6.5	67.0	-8.1	-6.9
15.0	2.6	42.0	-4.3	-5.9
17.4	1.4	31.0	-2.9	-5.4
17.8	1.3	30.0	-2.8	-5.3

scatter. These cases correspond to $\Psi > -5^\circ$ as shown in Table II. At these high aspect ratios, the crack does not stay on the PS-glass interface. Instead, it propagates into the PS layer and then along the weaker PS-epoxy interface. These specimens failed at higher fracture energies due to inelastic deformation occurring in the PS and at the PS-epoxy interface prior to fracture and are not representative of the PS-glass interface. The measured fracture energy is strongly dependent on the aspect ratio. As the aspect ratio is reduced from 1.05 to 0.71, the fracture energy appears to level off as lowering the aspect ratio increases the Mode II component of the crack-tip stress intensity factor, K_{II} , driving the crack into the glass-PS interface. For this reason G_c measured at lower values of Ψ is more representative of the PS-glass interface being tested as the crack is being forced to stay at that interface.

Further reduction of the aspect ratio will lead to smaller (more negative) Ψ . However, the thinner upper glass beam fractures typically 1–2 mm behind the crack tip for these aspect ratios as indicated in Fig. 5. The fracture of the upper glass beam depends not only on the upper beam thickness, h_1 , but on the interfacial toughness as well. In all of the experiments there appeared to be a maximum G for the given aspect ratio above which fracture of the glass beam occurred. The maximum tensile stress in the beam direction σ_{xx} occurs at the crack tip and can be calculated approximately using beam theory and Kanninen's approximation

$$\sigma_{\text{max}} = \left(\frac{G}{h_1}\right)^{1/2} \left(\frac{6E_1}{C_1^2 + C_2^2 \eta^3}\right)^{1/2} \quad (9)$$

where $\eta = h_1/h_2$, E_1 is Young's modulus of the glass and C_1 and C_2 are as in Equation 3. Note that this σ_{max} is proportional to $G^{1/2}$ and is a monotonically decreasing function of h_1 so that smaller h_1 for the same fracture toughness will lead to higher σ_{max} , thus facilitating fracture of the glass beam. Fracture of the glass beam can also occur when the aspect ratio is above 0.9 if large enough values of G can be reached (i.e. if G_c is large).

From the above analysis it is clear that the constraints imposed by the sample are such that at high aspect ratios, the mixity is insufficient to drive the crack to the interface, while at low aspect ratios, fracture of the glass beam precludes the measurement of high interfacial fracture energies. For our experiments, we selected the ratio of thicknesses to be 0.76 which

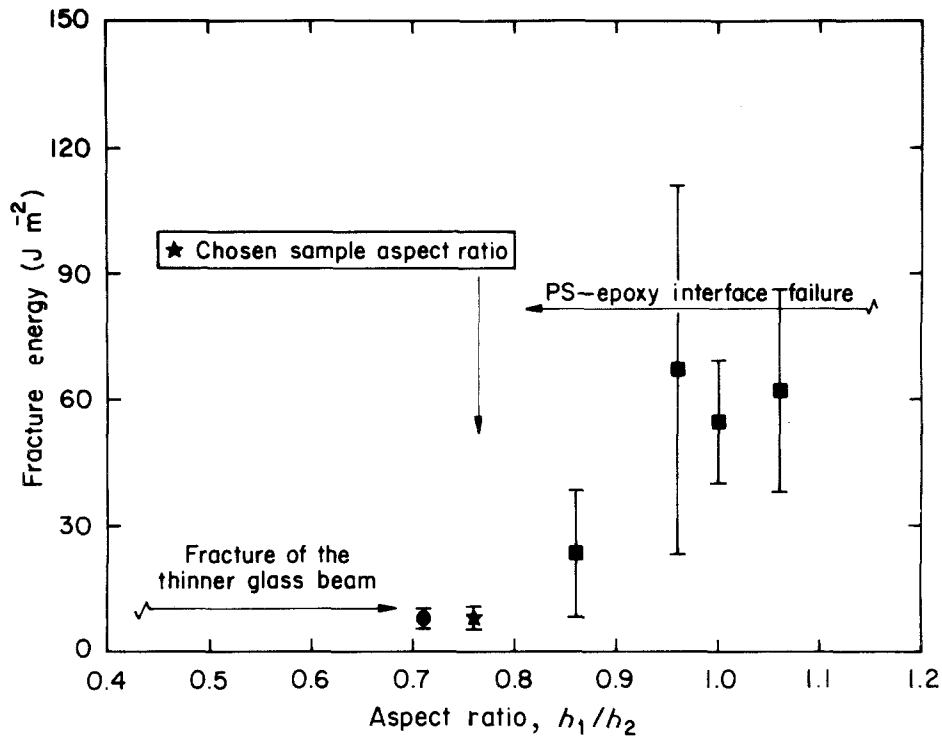


Figure 5 Interfacial fracture energy of a PS-glass interface modified with a dPS-PVP block copolymer (800–870) as a function of the beam thickness ratio. The starred value was used for the PS-glass experiments.

lies between these extremes. Examination of the failed specimens with forward recoil spectrometry ensured that fracture did indeed occur at the PS-glass interface. The maximum fracture energies that can be measured with these samples is on the order of $40 J m^{-2}$. The values reported in this work are limited to about $25 J m^{-2}$ as the tougher samples fractured prior to significant crack propagation and the exposed fracture surface area was too small to make the FRES measurements.

2.5. Polymer layer thickness

By confining the polymer to a thin layer sandwiched between two stiff linear elastic substrates, the influence of remote inelastic deformation (away from the fracture process zone) on the measured interfacial fracture energy is eliminated. It is also important to limit the thickness of the polymer layer to reduce the influence of residual stresses rising from the difference in thermal expansion coefficients between the glass and the polymer. The effect of thermal stresses on sandwiched films have been investigated by Suo and Hutchinson [11] and Evans *et al.* [13] who showed that residual stresses in thin adhesive films did not affect the measured fracture energies, provided that one side of the film remained attached to one of the substrates, thus maintaining the stress in the film after fracture. The effect of thermal stresses was demonstrated quite clearly in PS-silicon experiments. Curing the 0.5 mm thick epoxy layer on the silicon wafer at $100^{\circ}C$ as opposed to at room temperature resulted in a two-fold decrease in fracture toughness of the interface. No such difference was observed with the glass-PS samples where the thin $35 \mu m$ thick epoxy films are bonded to a thick rigid glass substrate.

TABLE II Thickness ratio and mixity

Aspect ratio (h_1/h_2)	a_{min} (mm)	a_{max} (mm)	Ψ_{min} (deg)	Ψ_{max} (deg)
0.71	10.3	11.6	- 9.0	- 8.0
0.76	10.6	11.6	- 7.6	- 6.4
0.86	7.0	11.1	- 4.1	- 3.5
0.96	6.3	9.2	- 1.8	- 1.5

There have been a number of studies addressing the influence of film thickness on the strength of adhesive joints [19]. The joint thickness becomes important when it is reduced to the order of magnitude of the crack-tip plastic zone. In the case of polymers that deform by crazing, this zone is quite small in comparison to practical film thicknesses. The thickness, t_c , of a craze may be estimated according to Brown *et al.* [3] from

$$t_c = \frac{G_c}{\sigma_c} \left(1 - \frac{1}{\lambda}\right)^{-1} \quad (10)$$

where σ_c is the crazing stress, λ is the craze fibril extension ratio and G_c is the fracture energy. The highest PS-glass interfacial toughnesses measured in these experiments were less than $40 J m^{-2}$. Taking appropriate values for the constants ($\lambda = 4$, and $\sigma_c = 55 MPa$) the craze opening displacement is $0.97 \mu m$. PS crazes are approximately 75% voids by volume so that the PS thickness required to form a $0.97 \mu m$ craze is about $0.24 \mu m$ which may be equated to a non-linear deformation zone at the crack tip. The PS film thicknesses used in the PS-glass experiments were of the order of $4 \mu m$ thick. This is thick enough to allow the full development of a craze

while still providing a fair margin of safety for the current experiments. Tests conducted over a range of PS layer thicknesses from 0.4–20 μm resulted in a constant fracture energy within the scatter of the data.

2.6. Ion-beam analysis

The measurement of the areal density of block copolymer chains at the PS–glass interface was made using forward recoil spectrometry (FRES) [12]. The technique measures the quantity of deuterium as a function of depth from the surface with a resolution of ~ 80 nm and a maximum probing depth of 700 nm. The PS blocks of the copolymers used in the PS–glass adhesion experiments were deuterated and thus the quantity of deuterium on each side of the fracture surface could be measured and summed to give the total quantity of deuterium at the interface. Knowing the degrees of polymerization of the dPS block and the quantity of deuterium as measured by FRES, the areal density, Σ , of block copolymer can be readily determined. The details of the RBS and FRES experiments are reported elsewhere [20].

2.7. Results for the glass–PS interface

Asymmetric double cantilever beam specimens were fabricated with varying quantities of block copolymers spun on the glass and annealed for 3 h at 160 $^{\circ}\text{C}$. Following fracture, each of the fractured specimens was examined with FRES to determine the areal density of deuterium atoms on each side of the fracture surface. The areal density of copolymer chains at the interface for a given specimen was determined by dividing the sum of the deuterium atoms from both sides by the number of deuterium atoms per chain.

Fig. 6 is a plot of the interfacial fracture energy measured from the double cantilever beam test versus the areal chain density of block copolymer at the interface. Each fracture measurement is an average of three samples and a minimum of 15 measurements were made for each sample. The fracture toughness of the PS–glass interface without any copolymer is shown in the lower left corner of the plot. The interface is very weak with a strength of about 1 J m^{-2} . The FRES results for these samples showed insignificant quantities of hydrogen on the glass surface indicating that fracture did occur at the PS–glass interface and that no PS homopolymer was left on the glass surface.

The addition of very small quantities of the block copolymer result in significant increases in the interfacial fracture toughness. The fracture energy rises quite rapidly for very small quantities of block copolymer exceeding a 20-fold increase in the fracture energy of the unmodified PS–glass interface. Further increases in the fracture energy could not be measured as the thinner glass beam breaks. It should be noted that these experiments are characterized by considerable scatter due to the weak nature of the interfaces being tested. However, there appears to be a transition at approximately $0.01 \text{ chains nm}^{-2}$ where G_c climbs from 3 J m^{-2} up to $10\text{--}12 \text{ J m}^{-2}$. The scatter also increases at the large fracture toughnesses.

3. PS–silicon adhesion

3.1. PS–silicon wafer sample preparation

The measurement of the PS–silicon interfacial adhesion is more difficult than the PS–glass adhesion as the silicon substrate is very brittle, fracturing after small displacements in bending. The silicon substrate

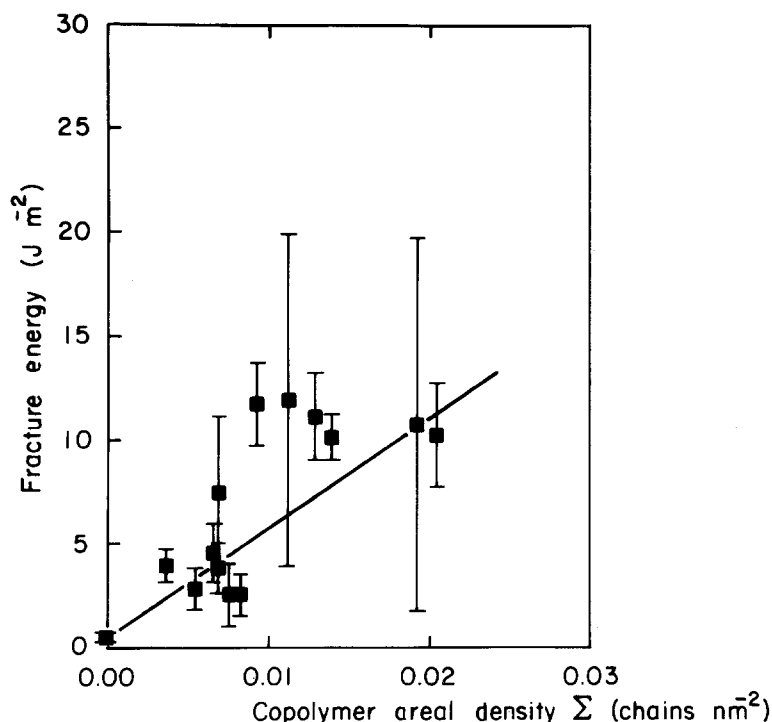


Figure 6 Interfacial fracture energy of a PS–glass interface modified with a dPS–PVP block copolymer (800–870) as a function of the areal density of block copolymer chains at the interface.

must be fixed to a rigid inflexible foundation throughout the experiment to prevent fracture of the silicon wafer. All of the deflection must then occur in the polymer side of the double cantilever beam. In terms of interfacial crack propagation, having the polymer beam more compliant than the silicon beam means that the shear component of K is expected to drive the crack into the polymer side of the interface. In spite of this fact we have been able, in certain circumstances, to obtain measurements of the interfacial fracture toughness.

The silicon wafers used in this experiment had a (100) orientation with a native oxide surface layer. They were 5.08 cm diameter and 0.4 mm thick. The PS-PMMA diblock copolymers of various molecular weights were dissolved in toluene and spun on to the silicon wafers. A 370 nm PS film ($M_w = 203\,000$) was spun-cast from toluene on to a glass slide and, after drying, was floated off on to the water surface from where it was picked up on top of the PS-PMMA block copolymer layer on the silicon. The wafer was then dried at 60 °C to remove the remaining solvent and subsequently annealed for 30 min at 115 °C. The backing selected for the PS-silicon studies was a composite beam consisting of a 0.5 mm thick layer of the Reichhold epoxy with two glass cover slips cemented to the outer surface as shown in Fig. 7. To obtain acceptable PS-epoxy adhesion, the PS surface was subjected to an ozone surface treatment from an ultraviolet ozone cleaning system (UVOCS ozone cleaning system). The surface treatment chemically alters the surface of the PS in a manner similar to the plasma treatment described in Section 2.

Following the ozone treatment, the epoxy was applied to the PS-coated wafers and allowed to cure at room temperature for 7 days. The wafers were then cut into strips 5 mm wide using a diamond wafering saw. Owing to the brittle nature of the silicon, it was necessary to cement the silicon side of the samples on to a 3 mm thick aluminium foundation using a cyanoacrylate adhesive. The rigid aluminium foundation prevented fracture of the brittle silicon wafer and facilitated subsequent handling. The cast epoxy backing was then ground with silicon carbide paper to a thickness of 0.5 mm. With only the epoxy backing material, the stiffness of the epoxy beam was so low

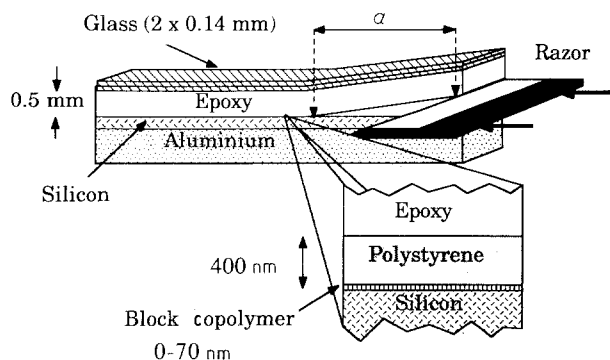


Figure 7 A schematic drawing of the PS-silicon asymmetric double cantilever beam test sample showing details of the sandwich structure.

that the crack preferred to propagate in the epoxy rather than at the PS-silicon interface. To stiffen the epoxy beam and thereby reduce the magnitude of the K_{II} component driving the crack into the PS and epoxy beam, two 0.14 mm thick glass cover slips were cemented to the ground epoxy surface.

3.2. Testing procedure for the PS-silicon samples

The thick aluminium foundation cemented on to the silicon wafer increases the stiffness of the silicon beam to the point where there is no significant deflection of this lower beam. The fracture energy may then be approximately determined using Equation 2 simplified to a flexible beam mounted on a rigid substrate where

$$G_c = \frac{3E_1 h_1^3 \Delta^2}{8a^4 [1 + 0.64(h_1/a)]^4} \quad (11)$$

The flexural modulus, E_1 , of the glass-epoxy composite beam was measured experimentally to be 5800 MPa. This value was used for all of the PS-silicon experiments. The thickness of the glass-epoxy beam, h_1 , was measured for each sample.

The PS-silicon sandwich specimens were tested by inserting the sharp end of a razor blade by hand into the interface. The crack front is clearly visible as light reflected from the fracture surfaces passes easily through the transparent epoxy. Complete detachment of the polymer films from the silicon wafer is easily detected as the highly polished wafer surface has an interference colour when the polymer layer is not removed by the passage of the crack. Conversely, the presence of interference colours well behind the crack tip is a clear indication of cohesive failure or failure at the PS-epoxy interface. In either case, the crack front is easily visible and the distance from the razor blade to the tip of the crack (a in Equation 11) may be measured using a reflected light microscope.

In many cases, the initial crack inserted in these specimens propagates within the PS film or oscillates between the PS-silicon interface and the bulk PS depending on the rate of insertion of the razor blade. Fast rates tended to send the crack into the PS. If the razor is stopped and left wedged in the specimen, the stored energy in the bent beam continues to propagate the crack albeit at a much slower rate. During this slower crack propagation, the crack moves back to the interface resulting in interfacial failure. Once the crack returns to the interface, the razor blade may be slowly driven further and the crack will run only at the PS-silicon interface.

3.3. Results of the PS-silicon wafer experiments

The adhesion of the PS to the silicon wafer in absence of block copolymer was measured as a function of the thickness of the PS layer which was varied from 100-400 nm (as measured by ellipsometry). The fracture energy of the PS-silicon interface annealed at

125 °C for 30 min was approximately 1 J m^{-2} independent of thickness in the range of thicknesses measured as shown in Table III.

The addition of a PS-PMMA ($N_{\text{PS}}/N_{\text{PMMA}} = 1460/1300$) diblock copolymer to the interface improved the interfacial adhesion. The improvement, however, was found to depend on the annealing temperature. The effect of the thickness of the block copolymer layer on G_c for interfaces annealed at 115 °C for 30 min is shown in Fig. 8. The thicknesses were varied by changing the concentrations of the spun-on solutions. The interfaces with a 10 nm thick block copolymer layer had an interfacial strength of 13 J m^{-2} while interfaces with the thicker films had fracture energies of the same order as the unmodified PS-silicon interface. If the annealing time and temperature were increased to 8 h at 170 °C, the interfacial adhesion then increased with increasing copolymer layer thickness at the interface as expected, attaining a value of 44 J m^{-2} for a 40 nm thick film as shown in Fig. 9.

4. Discussion

Previous investigations of interfaces between homopolymers have shown that an insignificantly negative mixity allows the interfacial crack to leave the interface and propagate into the less craze-resistant polymers [3-7, 14]. Even in the presence of very weak interfaces, these experiments may measure high fracture toughnesses. The G_c values of such experiments are often more representative of one of the bulk substrate materials than of the interface. The studies of mixity performed on the PS-glass specimen clearly demonstrate the importance of driving the crack to

the interface. In the case of the PS-glass adhesion, specimens with insufficient mixity (greater than -5) failed at the wrong interface and fracture energies of 100 J m^{-2} were measured. Specimens of the same composition with appropriate mixity forced the crack to remain at the interface and much lower fracture energies, of the order of 7 J m^{-2} , were measured.

The results of the PS-silicon interfacial experiments are interesting as the mixity of these samples should clearly bias the crack in the direction of the PS as the PS-epoxy-glass beam is at least an order of magnitude more compliant than the silicon-aluminium substrate. In fact, initial experiments with this system were dominated by cohesive failure. By stiffening the epoxy side of the specimen with glass cover slips, it was possible to reduce the mixity sufficiently to conduct the experiment successfully. Indeed, as might be expected, the cracks still propagate into the polymer and the initial toughnesses measured were quite high. It was found that by waiting overnight, the crack would slowly return to the interface and the next day it could be propagated at the proper interface, and lower, more reasonable values of the interfacial fracture toughness were obtained.

While silicon and soda-lime glass are clearly different materials, their surface chemistry is dominated by silanol groups. It is thus not at all unreasonable to compare the results of the PS-native oxide/silicon and the PS-glass adhesion results. The two experiments confirm, as expected, that the PS-silicate adhesion is indeed very poor and is of the order of 1 J m^{-2} .

4.1. Effect of block copolymer

The addition of either of the two block copolymers investigated caused substantial improvement in the fracture properties of the interface. We believe this improvement comes from the fact that the block copolymer chains form bonds between the silanol groups on the surface of the glass (or analogously on the native oxide of the silicon) and the PS homopolymer.

Creton *et al.* [6, 7] have shown that for effective reinforcement of a PS-PVP interface by a PS-PVP

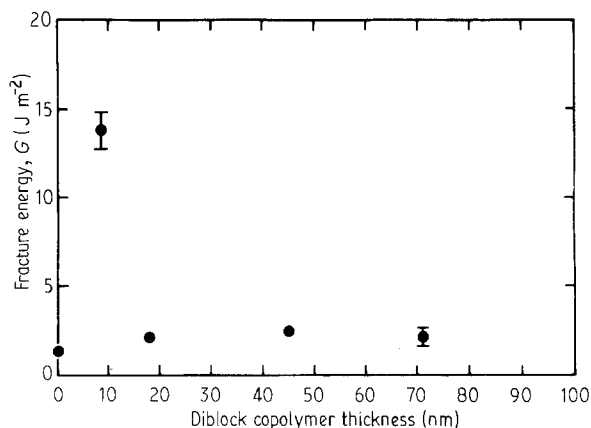


Figure 8 The effect of low-temperature annealing on the interfacial fracture energy of a PS-silicon interface modified with a PS-PMMA block copolymer (1460-1300) as a function of the thickness of the block copolymer layer as measured by ellipsometry.

TABLE III Effect of thickness of PS layer

Thickness (nm)	Fracture energy (J m^{-2})
100	0.8 ± 0.2
200	1.3 ± 0.2
400	1.3 ± 0.1

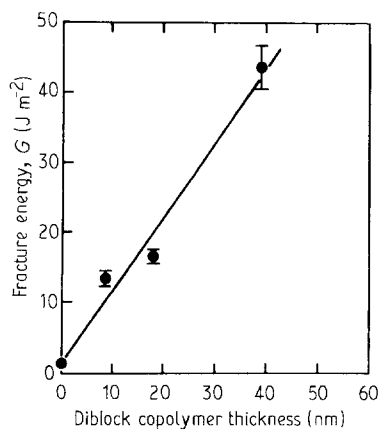


Figure 9 The interfacial fracture energy of a PS-silicon interface modified with a PS-PMMA block copolymer (1460-1300) as a function of the thickness of the block copolymer layer for specimens annealed at 170 °C for 8 h.

diblock copolymer, it is necessary that the copolymer blocks must be sufficiently long and have sufficient mobility to entangle in their respective homopolymers. In the current experiments, the entanglement of the PS blocks within the matrix PS is clearly of importance. In addition, it is important that the remaining block (PVP or PMMA) should be able to interact with the non-polymer substrate. Implicit in the above development is the assumption that the copolymers have sufficient mobility as well as a driving force to organize themselves at the interface with the respective blocks interacting with their respective substrates. The failure of the thicker PS-PMMA layers to strengthen the native oxide/PS interfaces after an anneal at 115 °C would seem to underline the importance of this requirement.

It has been shown that the polar groups on the PVP blocks (and the PMMA blocks analogously) have an affinity for the glass, or native oxide, surfaces. In addition, the incompatibility of the PMMA and the PVP with PS results in an entropic force which drives segregation of the PVP and PMMA blocks to the interface. Similarly there are entropic forces which tend to induce mixing of the PS blocks into the PS matrix. Indeed, such segregation has been shown to occur at PS-silicon interfaces [1, 2].

In both the PS-glass and PS-silicon experiments the fracture toughness of the PS-silicate interfaces was substantially improved by the addition of the block copolymer. The difference in the fracture toughnesses of the PS-silicon interfaces for the two annealing times demonstrates the importance of the organization of the block copolymer at the interface. While some organization of the PS-PMMA occurred during spinning of the thinner layer, it is clear that the 30 min anneal at 115 °C, only 10 °C above T_g of the PS, was insufficient. Annealing at 178 °C for 8 h ensured a more equilibrated configuration of the interface and much higher fracture energies were measured.

It is of interest to compare the fracture results of the PS-glass and the PS-silicon interfaces. In Fig. 10, the thicknesses measured by ellipsometry for the PS-PMMA copolymer layers on silicon have been converted to areal chain densities (assuming a copolymer density equal to that of PS). The resulting plot compares well with the accompanying plot of the PS-PVP modified PS-glass interface plotted on the same scale. The higher fracture energies measured for the PS-native oxide silicon interfaces correspond to higher areal densities of block copolymer at the interface. The increase in fracture energy with increasing areal density corresponds to an increase in the number of chains that are capable of transferring load across the interface.

The results may be compared with Creton's measurements of a PS-PVP homopolymer-homopolymer interface which was modified with the identical 800-870 PS-PVP block copolymer [6, 7]. The PS-glass interface results are only analogous to the PS-PVP interface if the PVP chains remain firmly attached to the glass substrate (as they were firmly entangled in the PVP matrix in the investigations of Creton). The data for the PS-glass interface and the

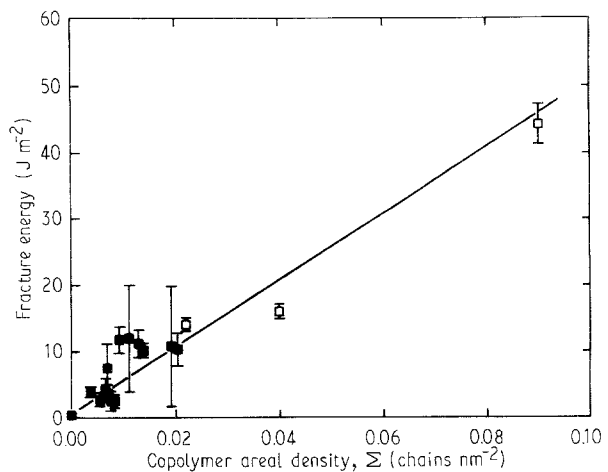


Figure 10 Comparison of the interfacial fracture energy of the (□) PS-silicon ($N_{PS} - N_{PMMA}$, 1460-650) and (■) PS-glass ($N_{PS} - N_{PVP}$, 800-870) interfaces. The PS-PMMA layer thicknesses were converted to chain densities assuming a standard PMMA density value for the block copolymer layer.

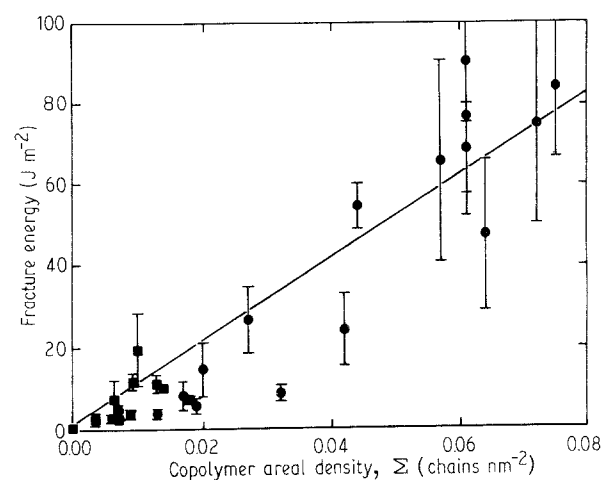


Figure 11 Comparison plot of (■) the PS-glass interfacial fracture toughness with that of (●) the PS homopolymer-PVP homopolymer interface (Creton) as a function of copolymer areal chain density. The PS-PVP copolymer was the same for each experiment. $N_{PS} - N_{PVP}$, 800-870.

PS-PVP interface are plotted together in Fig. 11. While Creton was able to measure much higher interfacial strengths and thus go out to larger areal densities, the PS-glass interface demonstrates the same general trend with comparable G_c values being measured at comparable values of Σ .

5. Conclusions

1. The double cantilever beam testing geometry has been adapted to test the fracture toughness of PS-glass interfaces. The upper limit of the fracture energies that may be measured with this technique may be limited by the strength of the substrates (glass or silicon). The selection of substitute materials is limited, because the materials must be stiff and have a high yield stress to modulus ratio to prevent substrate deformation and be transparent to allow

observation of the crack front. There are, however, no restrictions on the type of polymer that may be used. Contrary to other tests such as the peel test whose results are strongly influenced by the stiffness and overall ductility of the polymer, the mechanics of the sandwich double cantilever beam test depend on the properties of the glass and the local deformations at the crack tip and are independent of the bulk properties of the polymer. Using this test, it should be possible to compare the interfacial toughnesses of a much broader range of polymers using the same testing conditions.

2. By controlling the mixity of the asymmetric sample, the crack trajectory is biased toward the interface and fracture at the PS-glass interface is ensured. The mixity may be controlled by careful selection of the appropriate beam thickness ratio.

3. The addition of a PS-PVP block copolymer to the PS-glass interface increases the fracture toughness of the interface. Using FRES, the magnitude of improvement can be correlated with the areal density of block copolymer chains at the interface. For the 800–870 dPS-PVP block copolymer, the interfacial fracture toughness increases strongly with increasing dPS-PVP areal density for the range of density used in our experiment.

4. In the case of the brittle silicon substrate which could not be tested in the same manner as the glass, an asymmetric sample could still be fabricated and successfully tested in spite of a mixity which tended to drive the crack from the interface. While the crack trajectory at normal rates of testing propagated into the PS, at very slow rates it was possible to drive the crack to the interface. Future experiments to determine the effects of rate on the crack trajectory will be pursued to allow a more complete understanding of this phenomenon to be achieved.

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