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Effect of block copolymer dopants and alkylsilane monolayers on the fracture toughness of polystyrene–glass interfaces

M. CALISTRI-YEH*, E. J. PARK, E. J. KRAMER, J. W. SMITH‡
Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, NY 14853, USA
R. SHARMA
Research Laboratories B-82, Eastman Kodak Company, Rochester, NY 14650–2104, USA

The asymmetric double cantilever beam fracture test has been used to study the fracture toughness of polystyrene (PS)–glass interfaces reinforced with poly(deuterostyrene-b-2 vinyl pyridine) (dPS–PVP) as a function of degree of polymerization of the blocks. The effect of modifying the glass substrate with various selfassembled monolayers is also described. For the block copolymer with degrees of polymerization, $N_{\mathrm{dPS}} = 656$ and $N_{\mathrm{PVP}} = 46$ (referred to as $N_{\mathrm{dPS}} - N_{\mathrm{PVP}}$ or 656–46), located at the interface between glass and PS, the interface fails by chain scission at areal chain densities, Σ, of the block copolymer below a critical value, Σ^*. Above this value, e.g. $\Sigma > \Sigma^*$, the interface fails by crazing followed by chain scission. For the 656–46 diblock copolymer, the transition is located at $\Sigma^* = 0.03$ chains nm^{-2}, which results in a calculated force to break a C–C bond along the polymer backbone of approximately 2×10^{-9}N. For the 800–870 diblock copolymer at the interface between glass and PS, failure occurs due to chain scission. Fracture of both the 656–46 and the 800–870 block copolymers at the interface between (OTS) octadecyltrichlorosilane monolayer coated glass and PS is due to chain pulloff of the block copolymer from the OTS coated glass. Very little additional stress was transferred across the interface, resulting in fracture toughnesses comparable to that of a PS–glass interface with no block copolymer added.

1. Introduction

For a large variety of applications, including those of automotive safety glass [1], electronic packaging with polymer dielectric materials sandwiched between metals and semiconductors [2], and adhesive tapes and glues, the interfacial properties of polymer–inorganic interfaces are very important. There has been a large amount of interest in characterizing interfacial properties and interface durability, as well as in new techniques for forming polymer–inorganic interfaces [3]. A fundamental understanding of the mechanisms controlling the failure of polymer-inorganic interfaces is important for eventual tailoring of interfacial properties.

Diblock copolymers, consisting of blocks of two different polymers covalently bonded together, have been found to increase the mechanical strength of the interface between two immiscible polymers [4–8]. Diblock copolymers have also been used to reinforce a polymer–non-polymer interface [9, 10]. An increase in the fracture toughness of polymer–glass interfaces and polymer–silicon oxide interfaces has been observed with the addition of block copolymers to those interfaces.

To customize interfaces in an effective manner, an understanding of the variables affecting the fracture of the interface is needed. In this study, the effect on fracture toughness of a polystyrene–glass interface of a number of factors, including copolymer block lengths, and monolayer modifications to the glass surface, is examined. The glass is modified with an organic molecule which can spontaneously form an organized monolayer structure on glass and silicon oxide, known as a selfassembled monolayer [11]. This class of materials shows potential for a variety of engineering applications, and their interfacial properties are of great interest.

2. Experimental procedure

2.1. Materials

The polymer side of the interfaces studied was composed of a 670 000 molecular weight polystyrene (PS) with polydispersity index < 1.15. The block copolymers being investigated at the interface were deuterated polystyrene-poly(2-vinyl pyridine) (dPS–PVP). These copolymers were synthesized by

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*Current address: Xerox Corp., 800 Phillips Road, Building 201–08L, Webster, NY 14580, USA.
‡Current address: 3M Corp., Building 201-1E–17, St Paul, MN 55144–1000, USA.

TABLE I Characterization of poly(deuterostyrene-b-2-vinyl pyridine) copolymers

N_{dPS}–N_{PVP} [a]	$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ [b]
800–870	1.10
656–46	1.02

[a] Degrees of polymerization of the dPS and PVP blocks of the copolymer, respectively.

[b] $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$, ratio of average molecular weight to average molecular number.

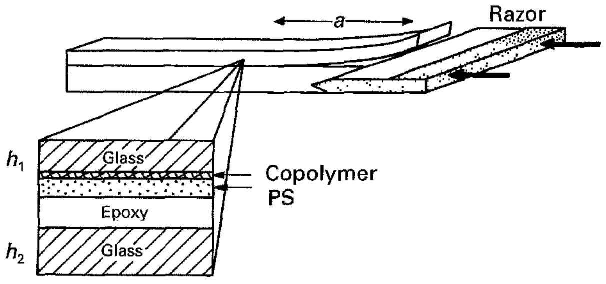

Figure 1 A schematic representation of the asymmetric double cantilever beam specimen showing details of the multilayer structure.

anionic polymerization [12]. Their degrees of polymerization and polydispersity indices were determined with gel permeation chromatography (GPC), forward recoil spectrometry (FRES), and C^{13} nuclear magnetic resonance (NMR) and are shown in Table I. The PS block of the copolymers was deuterated for later analysis purposes with FRES.

The non-polymer material making up the other side of the interface was composed of different types of glass: (a) standard microscope slides with thicknesses, $h_1 = 0.97 \pm 0.013$ mm and, $h_2 = 1.27 \pm 0.013$ mm; and (b) glass plates with thicknesses, $h_1 = 4.69 \pm 0.03$ mm and $h_2 = 5.66 \pm 0.03$ mm, where h_1 is the thickness of the beam along which crack propagation will occur, and h_2 is the thickness of the beam making up the other portion of the asymmetric double cantilever beam sample. Use of the thicker glass plates permits interfaces with higher fracture toughnesses to be tested [13].

2.2. Sample preparation

Asymmetric double cantilever beam specimens were prepared using a technique of measuring fracture toughness of polymer–non-polymer interfaces developed by Smith *et al.* [10]. A schematic of a typical sample is shown in Fig. 1. These specimens consist of two glass beams with different thicknesses, sandwiching a thin polymer layer between them. The ratio of the thickness of the glass beam at the interface reinforced with copolymer, h_1, to the thickness of the second (backing) beam, h_2, has been chosen to give the ratio $h_1/h_2 = 0.76$. Smith *et al.* showed that this aspect ratio affected the value of the phase angle in such a way as to drive the crack trajectory along the interface between the polystyrene and the thinner glass beam. The phase angle is a measure of the relative amount of shear and tensile loading at the crack tip and can be used as a rough predictor of crack propagation direction (which is also dependent on the details of failure and deformation of the interface as well as on the bulk materials on both sides of the interface) [14].

The glass plates were used as-received so that no additional polishing of the surfaces was done. All of the glass plates were washed with a solution made of one part Multi-Terge detergent to eight parts water, rinsed in deionized water, and dried in N_2 gas. Two types of glass surfaces were then prepared to be tested: one set which was composed of the ordinary glass surface, and a second set which was completely coated with an octadecyltrichlorosilane (OTS) selfassembled monolayer.

On the ordinary glass surfaces, the very extreme end of the glass beam was coated with an OTS layer to facilitate crack initiation. The OTS monolayers were formed using the standard solution deposition technique [15, 16]. The end of the thinner glass plates was dipped in a 1mM solution of OTS in an 80:20 mixture of hexadecane and high pressure liquid chromatography (HPLC) grade carbon tetrachloride for 20 min. The silane groups of the OTS chemically react with the silanol groups on the glass surface and the 18 carbon-atom-long chains assemble themselves into a highly ordered layer. The glass plates were rinsed in chloroform and water and dried.

The second set of samples, which were completely coated with OTS monolayer, were subjected to a more rigorous cleaning, including a 3 min etching in a Branson P2000 barrel etcher with 300 W power and 70 Pa of argon gas. Thereafter, the solution deposition took place in a 3 mM solution of OTS with an 80:20 mixture of hexadecane and carbon tetrachloride for 35–40 min at room temperature. The beakers used in the deposition were new, cleaned and subjected to argon plasma as well. The glass plates were dry when pulled from the solutions, rinsed in one chloroform bath, placed in a second chloroform bath in a sonicator for 2 min, rinsed in distilled water and excess water droplets were blown away with N_2 gas. Analysis of the OTS coated glass with water contact angle hysteresis, $\theta_a - \theta_r = 7°$, and atomic force microscopy (AFM) indicated that the OTS monolayer was quite complete and of good quality (but not as flat as OTS monolayers obtained on polished silicon wafers).

The glass plates were rinsed with toluene immediately before any polymer films were spun cast. Solutions with different concentrations of the block copolymers in toluene were spun cast at 2500 r.p.m. for 20 s (5–20 nm thick). Thicker (4–15 μm) polystyrene films were spun onto glass plates, floated off on water and transferred under dry conditions to the copolymer coated glass plates (with the thicker polystyrene films on the thicker glass plates). These glass plates were annealed for 3 h at 160 °C in a 133Pa vacuum oven.

Once annealed, the thicker backing glass pieces were attached to the samples using an epoxy. To enhance the adhesion of the PS film to the epoxy, additional polar surface groups were produced by oxygen plasma etching in the Branson barrel etcher. The exposure time for three to four samples was 10 min at 300 W with an oxygen flow rate of 300 standard cm^{3}min^{-1}. The epoxy resin and hardener were partially cured before being applied at the interface of the backing glass plate and the polystyrene, resulting in films about 50 μm thick. These samples were then annealed for 2 h at 100 °C to complete the epoxy cross linking.

The edges of the glass plates were trimmed to prevent epoxy from bridging the interface. The glass plates were cut into specimens 7.5 mm wide. The thinner glass plates produced three specimens per plate; the thicker glass plates produced six specimens per plate. Rough edges were wet-polished with 240–600 grit SiC paper to remove defects introduced by the sawing procedure. The specimens were blown dry and stored in vacuum desiccators for at least 12 h to remove any remaining moisture.

2.3. Fracture testing procedure

A razor blade with thickness 0.1 mm was driven at constant velocity between the two beams, forcing a crack to propagate. The velocity was maintained at 3×10^{-6}m s^{-1}. The crack was observed through a video camera which magnified the image, allowing crack length measurements to be taken. Steady state crack measurements were taken periodically as the crack propagated along the sample.

An expression for fracture toughness for the cantilever beam specimens has been obtained by Creton and coworkers [4, 17] who extended a model developed by Kanninen [18]. This model represents the specimen as a cantilever beam which is partly free and partly on an elastic foundation. The fracture toughness, G_c, can be determined using

$$G_c = \frac{3\Delta^2 E_1 E_2 h_1^3 h_2^3}{8a^4} \times \frac{C_2^2 E_1 h_1^3 + C_1^2 E_2 h_2^3}{(C_2^3 E_1 h_1^3 + C_1^3 E_2 h_2^3)^2} \quad (1)$$

where Δ is the thickness of the razor blade, $E_{i=1,2}$ are the Young's moduli of each glass beam, respectively, $h_{i=1,2}$ are the thicknesses of the glass beams, a is the crack length, $C_1 = (1 + 0.64h_1)/a$, and $C_2 = (1 + 0.64h_2)/a$. The expression is valid when a/h is large and when the length of the unfractured interface ahead of the crack tip is much greater than h [19]. The value of Young's modulus for this glass is 69 000MPa.

2.4. Analysis of fracture surfaces

To probe the location of the block copolymer chains, the experimental techniques of FRES were used [20], which is sensitive to the energy of recoiled hydrogen and deuterium ions, and Rutherford backscattering spectrometry (RBS) [21], which is sensitive to the energy of helium ions backscattered from heavy nuclei. First, the two fracture surfaces are stained with methyl iodide, which quaternizes the PVP block of the copolymer, and the relative quantity and location of the PVP blocks can be determined using RBS. Second, since the block copolymer has been deuterated, it is possible to determine the location and areal density of the dPS blocks of the copolymer using FRES. To obtain the total areal density of the block copolymer at the interface, the areal densities obtained on each side of the fracture surface are summed.

3. Results and discussion

3.1. 656–46 dPS–PVP block copolymer

The fracture toughness, G_c, as a function of the areal chain density, Σ, for the 656–46 dPS–PVP block copolymer at the interface of PS and glass are shown in Fig. 2a. These data were obtained under a constant

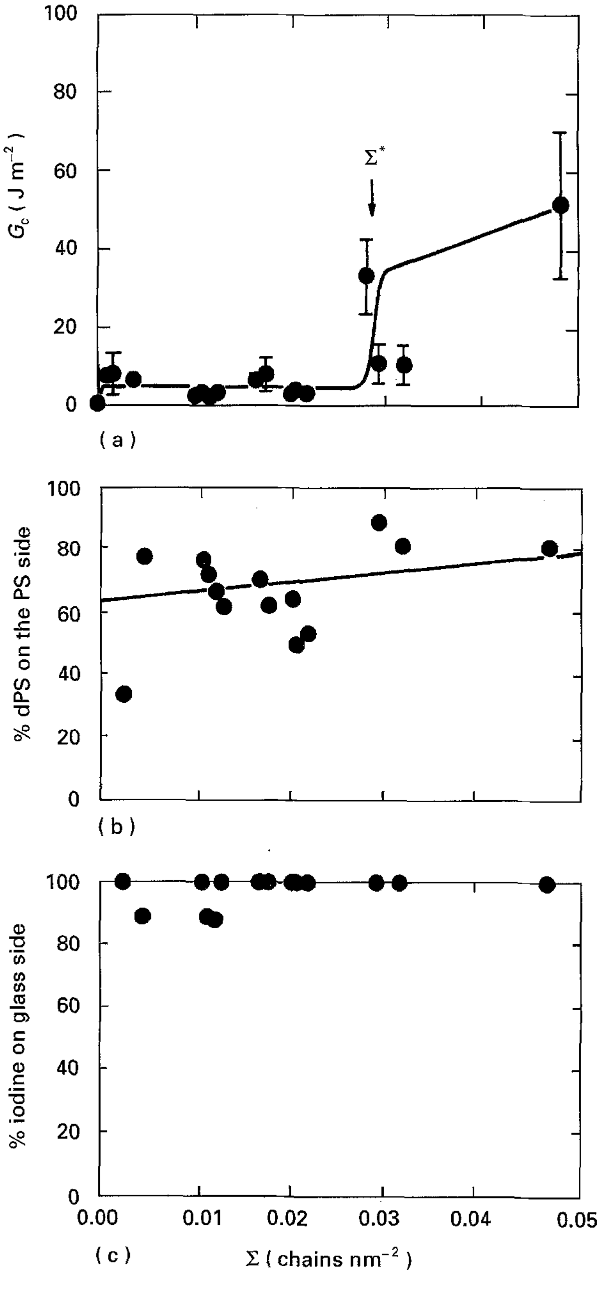

Figure 2 Results for 656–46 dPS–PVP block copolymer at crack velocity 3×10^{-6} cm s^{-1} at interface between PS and glass: (a) fracture toughness versus areal chain density of copolymer chains at the interface, (b) ratio of dPS found on the PS side to total dPS at the interface, and (c) ratio of iodine (which tags the PVP block) found on the glass side to total iodine at the fracture interface. The lines are guides to the eye.

crack propagation velocity of $3 \times 10^{-6}\,\mathrm{m\,s^{-1}}$. The results for fraction of dPS found on the PS side of the interface are shown in Fig. 2b. The results for fraction of iodine tagging the PVP block found on the glass side are shown in Fig. 2c. The lines are drawn as guides to the eye.

The fracture toughness, G_c as a function of the areal chain density, Σ, for the 656–46 dPS–PVP block copolymer at the interface of PS and OTS coated glass are shown in Fig. 3a. These data were also obtained under a constant crack propagation velocity of $3 \times 10^{-6}\mathrm{ms^{-1}}$. The results for fraction of dPS found on the PS side of the interface are shown in Fig. 3b. The results for fraction of iodine tagging the PVP block found on the OTS coated glass side are shown in Fig. 3c. The lines are drawn as guides to the eye.

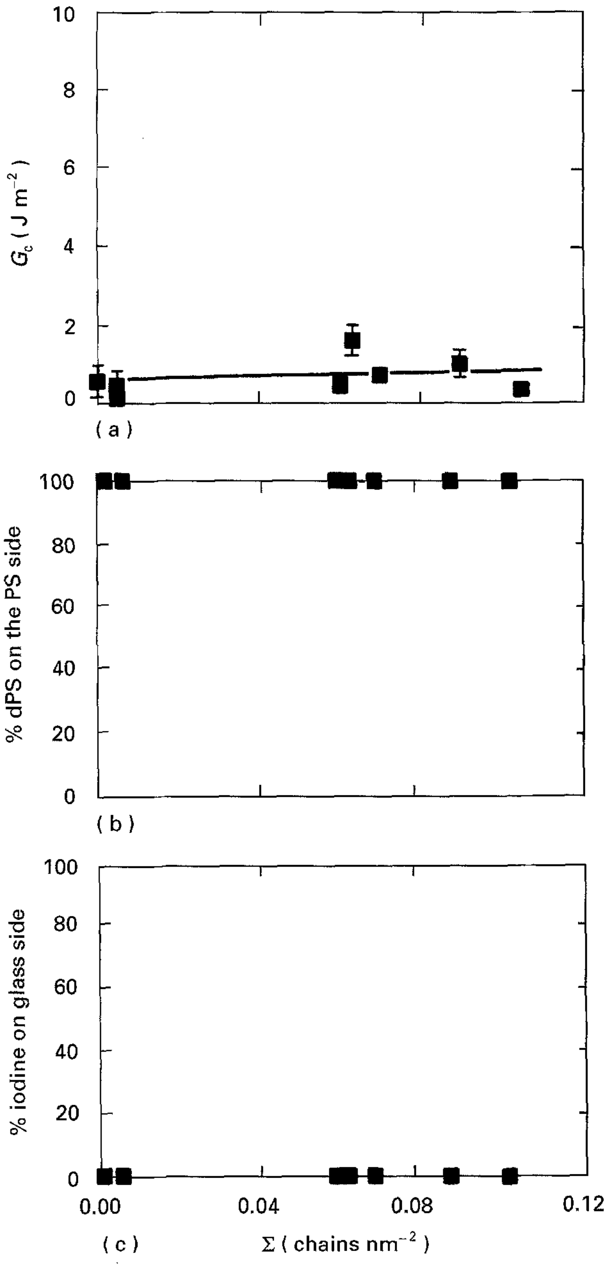

Figure 3 Results for 656–46 dPS–PVP block copolymer at crack velocity $3 \times 10^{-6}\,\mathrm{cm\,s^{-1}}$ at interface between PS and OTS glass: (a) fracture toughness versus areal chain density of copolymer chains at the interface, (b) ratio of dPS found on the PS side to total dPS at the interface, and (c) ratio of iodine (which tags the PVP block) found on the glass side to total iodine at the fracture interface. The lines are guides to the eye.

For the interface reinforced with 656–46 dPS–PVP, the fracture toughness at the PS–glass interface increases from the value of a bare interface, then rises rapidly when the areal density of chains rises above 0.03 chains $\mathrm{nm^{-2}}$. Throughout the range of areal densities tested, about 80% of the dPS was found on the PS side of the interface, leaving 20% of the dPS on the glass side of the interface. Virtually all of the iodine, tagging the PVP block, was found on the glass surface; only trace amounts of iodine were observable on the PS surface. For most of these samples, and in particular all those with fracture toughnesses over 25 $\mathrm{J\,m^{-2}}$, the RBS spectra showed a very small ($\ll 10$ nm) surface peak of $SiO_{2.55}Na_{0.24}Ca_{0.12}$ on the PS side, which agrees well with the composition of soda-lime glass (nominally $SiO_{2.36}Na_{0.42}Ca_{0.14}$) [22]. Small particles about 30 µm in size with low density and apparent random distribution were observed with the optical microscope on the PS side of the fracture interface.

These observations lead to the conclusion that the failure mechanism at low Σ of the 656–46 dPS–PVP involved chain scission in the dPS block of the block copolymer. The rapid rise in fracture toughness above 0.03 chains $\mathrm{nm^{-2}}$ can be attributed to the formation of a craze in the PS polymer layer immediately adjacent to the glass surface, followed by subsequent breakdown of the craze by chain scission, resulting in continued crack propagation along the interface. It is likely that small pieces of the glass bonded to the PVP block cohesively failed, quite possibly due to tiny preexisting defects in the surface. Soda-lime glass [22] has a low fracture toughness of $7\,\mathrm{J\,m^{-2}}$. At these locations, it would be more difficult for the methyl iodide to stain the PVP, which was covered with glass, explaining the reason why virtually no iodine was observed on the PS side despite observing some glass.

From the value of areal chain density at the transition, Σ^*, it is possible to calculate the force, f_b, to break a C–C bond along the backbone of the polymer. The amount of stress on the interface which is needed to fracture all the block copolymer chains is given by

$$\sigma_b = \sum \times f_b \tag{2}$$

At the transition, the stress to fracture the interface, σ_b, must exceed the crazing stress, σ_c, of PS (approximately 55 MPa) above the transition $\Sigma^* = 0.03$ chains $\mathrm{nm^{-2}}$. Therefore, the force, f_b, can be determined by

$$\sum^* = \sigma_c \times f_b \tag{3}$$

One finds that the force, f_b, to break a chain is approximately 2×10^{-9}N for the 656–46 dPS–PVP block copolymer.

These results can be compared with the results found for the 625–49 dPS–PVP block copolymer at the immiscible PS and PVP homopolymer interface [23]. These PS–PVP interfaces showed a minimal increase in fracture toughness from the bare interface ($1\,\mathrm{J\,m^{-2}}$), to values of about $3\,\mathrm{J\,m^{-2}}$ for $\Sigma = 0.10$ chains $\mathrm{nm^{-2}}$. The failure mechanism for these interfaces was from chain pull out of the PVP phase, because the PVP block length was not sufficient to form entanglements with the PVP homopolymer.

The fracture toughness of the OTS coated glass to PS interface remained at low values for areal chain densities of the block copolymer, equivalent within error bars to the unreinforced interface. All of the iodine was found on the PS side of the fracture samples. These results indicate that the bond between the OTS coated glass and the PVP is very weak.

3.2. 800–870 dPS–PVP block copolymer

The fracture toughness, G_c, versus areal chain density, Σ, results for the 800–870 dPS–PVP at the PS–glass interface are shown in Fig. 4a. The fracture toughness, G_c, versus areal chain density, Σ, results for the 800–870 dPS–PVP at the PS–chlorodimethyloctadecylsilane (CDMOS) modified glass interface are shown in Fig. 4b. These data are from Smith *et al.* [9]. The lines are drawn as guides to the eye.

The fracture toughness, G_c, versus areal chain density, Σ, results for the 800–870 dPS–PVP at the PS–OTS glass interface are shown in Fig. 5a. The results for the ratio of deuterium found on the dPS side to the total amount of deuterium at the interface are shown in Fig. 5b. The ratio of iodine, which tags the PVP block, found on the glass side of the interface to the total amount of iodine is shown in Fig. 5c. The lines are drawn as guides to the eye.

For the glass–PS interface reinforced with 800–870 dPS–PVP, the fracture toughness increases from the value of a bare interface to values $\approx 10\,\mathrm{J\,m^{-2}}$. Throughout the range of areal densities tested, about 70% of the dPS was found on the PS side of the interface, leaving 30% of the dPS on the glass side of the interface. These observations lead to the conclusion that the failure mechanism of the 800–870 dPS–PVP involved chain scission in the block copolymer.

The fracture toughness at the CDMOS coated glass–PS interface remained at low values, slightly

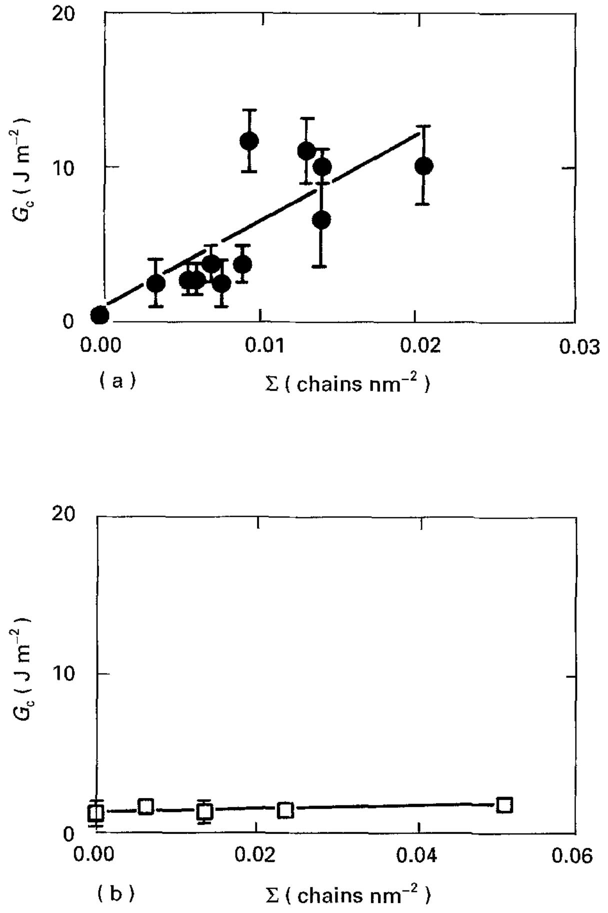

Figure 4 Results for 800–870 dPS–PVP block copolymer. Fracture toughness versus areal chain density of copolymer chains at the interface: (a) (●) data are at the interface between PS and glass, and (b) (☐) data are at the interface between PS and CDMOS–glass. Data are taken from [9]. Lines are guides to the eye.

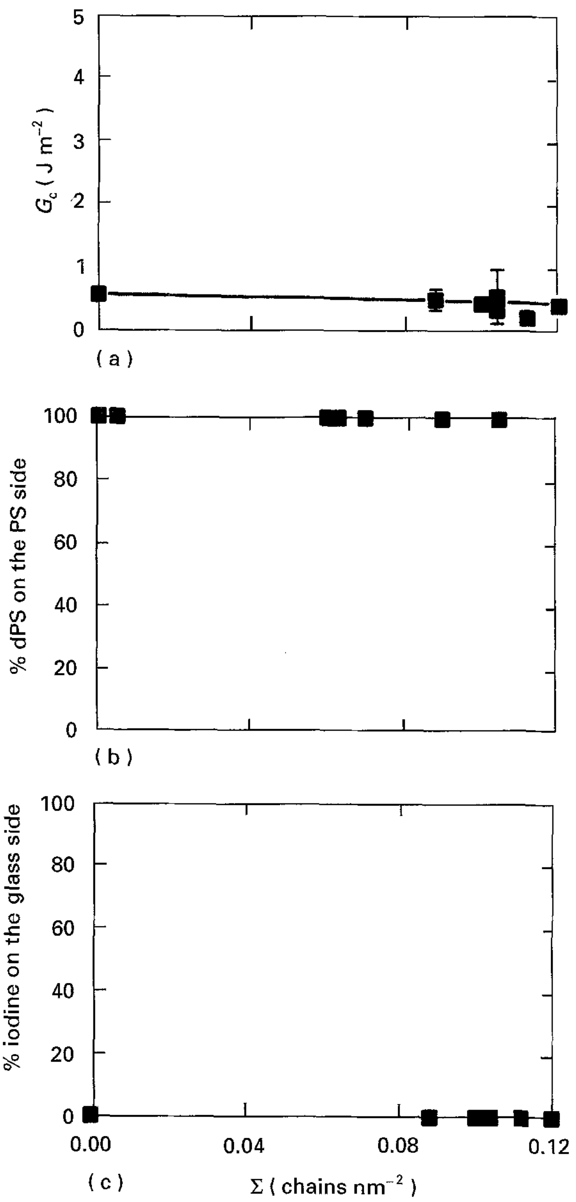

Figure 5 Results for 800–870 dPS–PVP block copolymer at the interface between PS and OTS glass: (a) fracture toughness versus areal chain density of copolymer chains at the interface; (b) ratio of deuterium, tagging the dPS, found on the PS side of the fracture interface to the total amount of deuterium at the interface; and (c) ratio of iodine found on the glass side of the interface to the total amount of iodine.

greater than values obtained for the unreinforced interface and the OTS coated glass–PS interface. All of the iodine was found on the PS side of the fracture samples. The mechanism of fracture is chain pulloff from the CDMOS coated glass. The fracture toughness values indicate that the bond between the CDMOS coated glass and the PVP is slightly stronger than between the OTS coated glass and the PVP. Further analysis of the CDMOS coated glass using contact angle hysteresis, θ_a–$\theta_r = 30°$, and AFM indicated that the CDMOS layer has many imperfections and cannot satisfy all the qualities required to be considered a full monolayer. The imperfections in the layer allow the PVP and the underlying glass to have more interaction than exists at the OTS–PS interface with dPS–PVP at the interface. But since there is a layer of CDMOS, albeit an imperfect layer, the strength of the interface is lower than with a bare glass–PS interface reinforced with dPS–PVP.

The fracture toughness of the OTS coated glass–PS interface remained at low values, equivalent within error bars to the unreinforced interface. All of the iodine was found on the PS side of the fracture samples. These results indicate that the bond between the OTS coated glass and the PVP is very weak. Contact angle hysteresis measurements resulted in θ_a–$\theta_r = 7°$, indicating that the OTS monolayer was of good quality. The OTS monolayer reduced the interactions between the PVP block and the underlying glass to the extent of weakening the interface to levels comparable with the PS–glass interface with no block copolymer.

3.3. Comparison of different N_{dPS}–N_{PVP}

The failure mechanism of the 656–46 dPS–PVP at the glass–PS interface can be compared with results [9] by Smith *et al.* of the 680–95 dPS–PVP block copolymers at the glass–PS interface. His results for this block copolymer indicated that failure occurred by chain scission at low areal chain densities, and by craze formation followed by chain pulloff from the glass surface at high areal chain densities. The authors' results, with a comparable dPS block length (656 compared with 680), but shorter PVP block length (46 compared with 95) showed that failure occurred due to chain scission at low areal chain densities and due to craze formation followed by chain scission at high areal chain densities.

These results can be reconciled using results from segregation experiments of dPS–PVP block copolymers to silicon oxide [24]. The segregation experiments showed that the effective attractive interaction between the PVP block and the silicon oxide increased with decreasing PVP block length in the range of $N_{PVP} = 68 \sim 22$. The segregation results and the fracture toughness results both indicate that the amount of attraction between the 680–95 dPS–PVP block copolymer and the glass is less than between the 656–46 dPS–PVP block copolymer and the glass.

Experiments by Washiyama *et al.* [7, 25] at the immiscible polymer interface between PS and PVP homopolymers reinforced with dPS-b–PVP also found $\Sigma^* = 0.03$ chains nm^{-2}, for chain scission–crazing (followed by scission) transition. Experiments by Norton *et al.* [26] at the interface between epoxy and PS reinforced with a carboxylic acid terminated dPS also found $\Sigma^* = 0.03$ chains nm^{-2}, for a chain scission–crazing transition. The consistency of the location of Σ^* amongst these three polymer interface systems is quite striking and serves to reinforce the interpretation that $\Sigma^* \approx 0.03$ chains nm^{-2} is due to C–C bond breaking as this is a common denominator through the three systems. These values for the C–C bond breaking strength are quite close to those found for 656–46 dPS–PVP at the PS–glass interface, which had $\Sigma^* = 0.03$ chains nm^{-2}.

The types of bonds possible between the PVP and the glass are discussed in [27]. In that discussion, dipole-induced dipole interactions were determined to be most likely for the attractive interactions in the segregation experiments of dPS–PVP block copolymers $\sim$ silicon oxide interfaces. In these experiments, where the glass is first coated with dPS–PVP block copolymer, a PS film is then transferred onto the dPS–PVP, and then the sample is annealed for a relatively shorter period of time. The dPS–PVP block copolymer is not in the equilibrium configuration, but is concentrated at the interface. With the additional loading of the copolymer at the glass surface, there will be a greater possibility for the transfer of a proton from the SiOH groups on the silicon oxide to the pyridine group of the PVP block of the copolymer [28], thus resulting in the formation of a strong ionic bond. Ionic bond formation would be necessary in order for the transfer of sufficient stress across the interface that covalent bonds would become the "weakest link" and that interface failure at higher areal chain densities would occur due to fracture of the C–C bond of the backbone of the block copolymer chains.

3.4. Comparison of different substrates

The results of the 800–870 dPS–PVP block copolymer at the PS–glass interface, PS–CDMOS interface and PS–OTS glass interface show that varying amounts of adhesion due to the attractive interaction between the PVP block and the glass can be obtained. The highest fracture toughnesses were measured at the PS–glass interface; lower fracture toughnesses were measured at the PS–CDMOS interface, where the CDMOS interface was analysed and discovered to have numerous imperfections; and the lowest fracture toughness was measured for the block copolymer at the PS–OTS interface where the OTS was found to be a monolayer.

4. Conclusions

These results in conjunction with the previous work by Smith *et al.* [9, 10] on the reinforcement of polymer–glass interfaces using poly(deuterostyrene-b-2 vinyl pyridine) copolymer chains suggest the following summary of fracture mechanisms based on degree of polymerization of each block. Note that while the entanglement molecular weight [29] for PS ($M_e \approx 20\,000$, $N_e = 173$) [30], the experimental results for the 280–50 dPS–PVP block copolymer indicate that it is necessary for a chain to be longer in order to entangle sufficiently to support craze formation.

1. When $N_{dPS} < 300$, the mode of fracture will be dPS pull out of the PS layer and very little stress can be transferred across the interface, resulting in minimal enhancement of fracture toughness.
2. When $N_{dPS} > \sim 300$ and $N_{PVP} <$ threshold value, $170 <$ threshold value < 870, the mode of fracture will be chain scission below $\Sigma^* \approx 0.03$ chains nm^{-2} and crazing followed by chain scission above $\Sigma^* \approx 0.03$ chains nm^{-2}.

The interfaces between OTS monolayer coated glass plates and PS were weak because no bonding was possible between the PVP block and the glass. The fracture toughness of the imperfect layer of CDMOS on glass permitted slightly increased fracture toughness. Since it is possible to form selfassembled monolayers with varying degrees of perfection and coverage [31], it may be possible to use this technique to provide a range of strengths for PVP bonding with the underlying glass.

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