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Communications to the Editor

Effect of a Diblock Copolymer on the Adhesion between Incompatible Polymers

A/B block copolymers are known to act as interfacial agents between incompatible homopolymers A and B.[1-5] They concentrate at the interface with each block dissolved in the relevant homopolymer.[6-8] It has been assumed that a thin film of block copolymer would considerably enhance the adhesion between incompatible polymers[1,2] though there have been no direct experimental measurements of this effect. The aim of the work presented here is to examine the toughness of the interface as a function of the amount and molecular weight of the copolymer employed. It is assumed that the copolymer had a high enough molecular weight that its diffusion coefficients and solubilities in the homopolymers were low enough to ensure that it remained at the interface during the relatively short-time joining process.

Experimental Techniques. The polymers used in this study were polystyrene (PS) and poly(methyl methacrylate) (PMMA), as they are glassy amorphous materials with similar glass transition temperatures (100 and 105 °C, respectively). They are incompatible with a Flory interaction parameter χ that has been estimated in the range of 0.03–0.04.[9,10] The block copolymers used were approximately symmetric and with a narrow molecular weight distribution. Their molecular weights, polydispersities, and compositions given in Table I. The block copolymer film was spin coated from toluene solution directly onto the PMMA with the film thickness controlled by solution concentration (between 0.25% and 2%) and spin speed (between 1000 and 4000 rpm). Films were also spin coated onto gold substrates at the same time for ellipsometric thickness measurement.

The samples were made by joining sheets of PS and PMMA at slight pressure in a press at 150 °C for 2 h. Hence it is likely that the samples were not at thermodynamic equilibrium. The block copolymer must have a finite, though very small, solubility within the homopolymers and so might be expected to diffuse away from the interface. This effect would be expected to be most noticeable in the lowest molecular weight copolymer. However, joints made with the latter polymer showed little toughness variation with joining times up to 18 h, so the loss of copolymer from the interface must be insignificant within the time scale of the experiment.

The value obtained for the toughness, *G*, of a PS/PMMA joint depends greatly on the details of the fracture toughness test employed[11,12] because there is a tendency for crazes to grow into the PS during crack propagation.[13] These crazes dissipate much energy and cause a high measured toughness. This excess crazing can be avoided by the use of an asymmetric fracture toughness test that tends to drive the crack toward the PMMA. As the PMMA requires a considerably greater stress to craze than does PS, this test causes the crack to travel along the interface without excess crazing. Details of the fracture test will be published elsewhere.[14]

G was obtained at room temperature (23 °C) at two testing rates. It was measured by using a mechanical testing machine (Instron) where the sample was loaded at constant rate so that the loading time before crack propagation was between about 3 and 10 min, depending on the crack length and sample toughness. The other test involved inserting a razor into the crack and leaving the crack to propagate slowly for 24 h before measuring the distance between the razor tip and crack tip and hence finding *G*.[14]

Table I
Characteristics of the Block Copolymers

M_w^{total}, kg/mol	M_w/N_n	mol % styrene	t_m, nm	$L/2$, nm
84	1.2	50	14	19
280	1.07	57	32	35
355	1.22	44	40	40
900	1.12	37	51	63

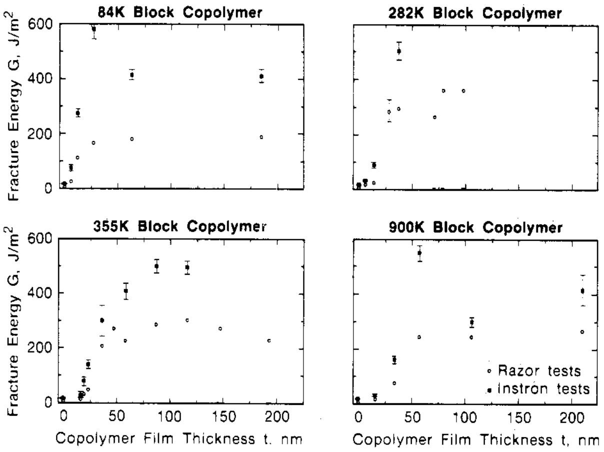

Figure 1. Variation of the interface toughness *G* with the thickness *t* of the block copolymer film. Clearly the faster Instron test gave higher values as is commonly observed. The error bars show the standard deviation of the measurements.

Results and Discussion. Figure 1 shows the toughness of the joint as a function of the thickness of the block copolymer layer for the four block copolymers used. The block copolymer increased the toughness of the joint by a factor of up to 50, with the joint going from very weak to sufficiently strong to be close to the cohesive strength of the homopolymers. (The fracture toughnesses of PS and PMMA are of course rate and molecular weight dependent but typical values are 400 and 500 J/m^2, respectively.[15]) The saturation toughness was achieved with very little block copolymer; for example, for the lowest molecular weight material a film of 20-nm thickness was sufficient. Clearly the adhesion between the incompatible polymers was greatly increased by the presence of a small amount of block copolymer. Values of the minimum thickness to reach saturation toughness (t_m) were obtained from the intercept on a plot of log *G* versus *t* (see Figure 2) of the initial straight line with a horizontal straight line representing the average of *G* values obtained at large *t*. The results obtained are compared in Table I with $L/2$ where *L* is the long period (the repeat distance) of the undiluted block copolymer. Values of *L* were obtained from Russell[10] who found from SAXS experiments that *L* varied as $M^{0.5}$ for this material, suggesting that the copolymers are in the weak segregation regime. The block copolymer has a lamellar microstructure so $L/2$ is a measure of the thickness of a film that corresponds to a single interface. The similarity of $L/2$ and t_m suggests that the block copolymer organizes at the interface and saturates it when there is sufficient block copolymer to exclude the homopolymer

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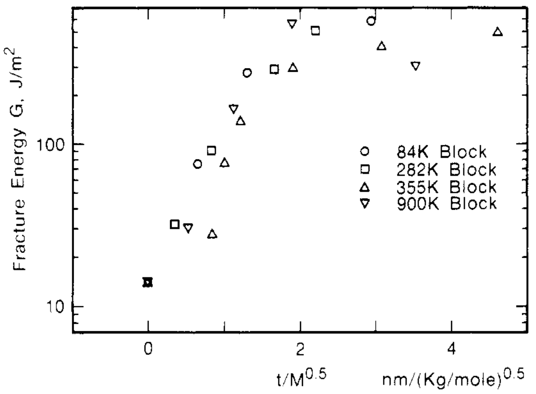

Figure 2. Data in Figure 1 taken with the Instron are plotted to test the relation $G \simeq \exp(t/M^{0.5})$.

from the interface. At this point the block copolymer has a structure similar to that obtained without homopolymer. This observation is consistent with a recent theoretical model for block copolymers at homopolymer interfaces presented by Leibler.[8] From the Instron data for two of the block copolymers (84K and 900K) there is some evidence that the joint toughness decreased a little for $t > t_m$. This observation is consistent with the excess block copolymer forming additional lamellar micelles close to the interface and so forming subsidiary weak interfaces. It is possible that the peak in G at $t = L/2$ (if it exists) is elusive, as it requires a very uniform layer thickness of block copolymer so that the interface is saturated over large areas with little fluctuation in copolymer thickness.

It is evident from Figure 2 that for film thicknesses less than saturation, the toughness G varied exponentially with t and, within the uncertainty of the measurements, could be represented by the form

$$G \sim e^{t/M^{122}} \sim e^{(t/t_m)} \qquad t < t_m \tag{1}$$

This result was unexpected, as a considerable body of crack healing and welding data on polymers has been interpreted by models that relate toughness to the number of strands, σ[16-18] that cross the interface. A number of models exist that differ in detail but none predict that the variation of toughness with σ is greater than a square law. The exponential dependence observed here has not been seen. Also the molecular weight dependence in the relation is surprising. As $\sigma \sim t/M$, it is evident that the number of strands required for a given toughness goes as $M^{-0.5}$. For all the copolymers M is greater than the entanglement molecular weight so one might have expected the toughness to be controlled by σ, independent of M.

The variation of toughness with film thickness might have its origin in the effect of the block copolymer on the thickness of the interface between the PS and PMMA. Fernandez et al.[19] have recently used neutron reflection to measure the thickness of the interface between PS and PMMA homopolymers and obtained a value of less than 20 Å. Anastasiadis and Russell[20] used the same technique to find a value of 54 Å for the interfacial thickness of a PS/PMMA block copolymer, showing that the interface in the block polymer is considerably broader than that between the homopolymers. Noolandi and Hong[6] predicted this effect for the quaternary system containing two homopolymers, a diblock copolymer and a mutual solvent, and suggested its origin in the entropy required to place the block copolymer junction points at the interface. I wish to suggest that such an effect may be occurring here. As block copolymer is added to the interface it broadens, and hence the degree of entanglement between the PS and PMMA chains increases. If, as has been suggested, the interfacial thickness of the pure block copolymer is independent of its molecular weight,[21] then the thickness of the interface between PS segments and PMMA segments might be expected to vary just as its fractional saturation by the block copolymer. Within this argument the exponential form would come from the variation of PS-PMMA entanglement with interfacial thickness and the rapid variation of toughness with entanglement.

The most important observation in this work is that the presence of the block copolymer can increase the toughness of the PS-PMMA interface by up to a factor of 50. The toughness saturates at a block copolymer film thickness equal to half the long period of the neat block copolymer. This suggests that the block copolymer can organize in a simple way at the interface and saturate it. It is perhaps unusual that such morphological information is obtainable from mechanical tests.

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Registry No. PS, 9003-53-6; PMMA, 9011-14-7; (PS)(PMMA) (block copolymer), 106911-77-7.

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^{15}N NMR Chemical Shift Tensors and Conformation of Some ^{15}N-Labeled Polypeptides in the Solid State

Recently, high-resolution ^{15}N NMR in the solid state has been increasingly applied to the investigation of polypeptides, proteins, and biopolymers.[1-12] In a previous

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