

Relation between the Width of an Interface between Two Polymers and Its Toughness

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ABSTRACT: Thin layers of a series of random PS/PMMS copolymers have been used to couple two sheets of PMMA, thereby permitting a study of the effect of interface width on interface toughness. The interface width and toughness varied with the copolymer composition. The use of a thin coupling layer between two PMMA sheets ensured that the crack tip craze occurred mainly in PMMA, so the material within which the crack tip deformation occurred did not change as the interface width was changed. The interface toughness was found to remain low for narrow interfaces until the interface width became larger than the mean entanglement spacing in the bulk. The toughness then climbs rapidly to saturation at an interface width of perhaps three times the entanglement spacing. A model is proposed here for the relation between interface width and interface toughness based on a well-tested model for interface toughness and known interface profile. However the assumptions made within the model, that entanglement density is constant through the interface and that the probability of a chain passing through the interface can be described just by a volume fraction ratio, are probably incorrect. The measured toughness is significantly less than that predicted at widths equal to and below the entanglement spacing. This disparity is probably caused by the entanglement spacing increasing over the bulk value in the area of the interface. For broad interfaces, where the entanglement density is expected to be close to bulk values, the predicted toughness agrees reasonably with experiment.

Introduction

There are a number of situations, including polymer blends and adhesive joints, where the adhesion between a pair of immiscible polymers is of considerable practical importance. Understanding of polymer–polymer adhesion and polymer toughness has improved considerably in the past few years. It is now clear that, for glassy polymers, adhesion, defined as the toughness of an interface, is controlled by both the chain coupling across the interface and energy dissipation processes in the materials. For tough systems, the chain coupling is described by the number of lengths of polymer chain between entanglements, Σ , that cross the unit area of the interface. Energy dissipation normally occurs by the growth of one or more crack tip crazes. At an interface between two materials, these crazes normally form in the material with lower crazing stress. Cohesive toughness is controlled in a similar way by the number of entangled chain lengths that cross any plane within the material. An important issue, then, in understanding and controlling adhesion is to understand, and perhaps alter, the areal density of such entangled chains. Placing a diblock copolymer layer at an interface is a classic technique for controlling Σ in a well-defined way.

The equilibrium interface between a pair of immiscible amorphous polymers has a profile, that is the variation of the volume fraction of the segments of one of the polymers in a direction normal to the interface plane, that is thought to be universal and given by a hyperbolic tangent function. The width of the interface is described by a parameter a_1 that is controlled by the Flory–Huggins interaction parameter χ of the pair of polymers and the chain stiffnesses. Hence, it is expected that coupling across the interface, and thus the adhesion between the polymers, is controlled by a_1 and the entanglement densities of the polymers.

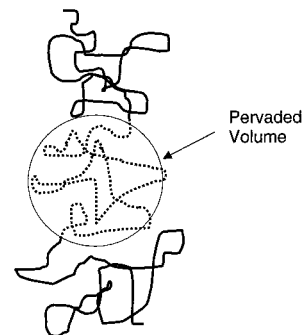


Figure 1. Illustration of the relation between chain packing and entanglement. A section of chain of molecular weight M_e (shown dotted) pervades a volume about 10 times its hard core volume.

De Gennes¹ proposed a model that relates the interface coupling Σ to a_1 by assuming that Σ is given by the number of loops of length at least N_e (the number of repeat units between entanglements) that cross the interface. This assumption gave an interface coupling density that varied as $\exp(-L_e/a_1)^2$ where L_e is the mean distance between entanglements along a chain, otherwise known as the tube diameter. The actual nature of polymer entanglements is poorly understood. However there is good experimental evidence that the length of chain between entanglements in the bulk is the length which pervades a volume that is about 10 times the volume that it actually occupies,² as illustrated in Figure 1. Within this model, one can consider entanglements as approximately evenly distributed along a chain, so that it is not obvious that a loop has to be of length L_e across an interface to be entangled. An alternative approach, considered here, is to assume entanglements evenly spaced along a chain and to estimate the number of strands between entanglements

that have a terminating entanglement on each side of the interface.

The relation between interface toughness and Σ is reasonably well understood for high molecular weight glassy polymers as long as their primary failure mechanism is the propagation and breakdown of a single crack-tip craze. The craze fibril closest to the crack tip is believed to break when the force within it becomes large enough to cause molecular scission of the entangled strands.³ The mechanics of this model were first solved using a continuum approximation that is suitable for crazes that are much wider than typical fibril spacings or diameters. For wide crazes the toughness, G_c varied as Σ^2 . This result has been confirmed in a number of diblock toughened systems.³⁻⁶ When Σ is small and the interface is weak, so the craze is narrow, an improved continuum approximation has been proposed and validated by comparison with a discrete mechanical model.⁷

The relation between a_i and G_c has been examined experimentally in a number of systems using a range of techniques. Schnell et al.^{8,9} studied interfaces between polystyrene and either poly(paramethylstyrene) or a statistical copolymer poly(styrene-*co-p*-bromostyrene). The interface width was varied in the former system by changing the annealing temperature and polymer molecular weight and in the latter system by varying the bromine concentration. They measured the interface width using neutron reflection and the interface toughness using an asymmetric double cantilever beam technique. The use of the two different systems permitted them to study a broad range of interface widths and hence interface toughnesses. Cho et al.¹⁰ used a similar test to measure the interface toughness between a series of styrene acrylonitrile (SAN) copolymers and poly(methyl methacrylate) (PMMA). They estimated the interface width from calculated values of the χ parameter. Most other published work has involved not equilibrium interfaces between immiscible polymers but partially welded interfaces between slabs of the same polymer. The process of welding, i.e., short time interdiffusion, is believed to occur by reptation in which first a chain end crosses the interface and then the rest of the chain follows. Hence a partly joined interface, formed by reptation, with a given width may contain a quite different chain topography from that of an equilibrium interface of the same width. Thus, one would not expect the same relations between toughness and a_i for equilibrium interfaces and partially welded systems.

The aim of this paper is to propose a model that predicts the variation of Σ with a_i for polymer interfaces and compare its predictions with the results of some new fracture experiments where a random polystyrene-poly(methyl methacrylate) (PS-PMMA) copolymer layer has been placed between two PMMA sheets. An advantage of this approach is that, although the molecular level failure must occur on the random copolymer to PMMA interface, the primary crack tip craze, which dissipates most of the energy, grows within the PMMA. Hence the relevant material properties do not change as the interface width changes. Interface widths between the random copolymers and the relevant homopolymers have already been measured using neutron reflection.¹¹

The Model

The model proposed here is based entirely on the simple assumption that the interface gains its toughness entirely from the energy dissipated in the formation of a primary crack tip craze. In addition, it is assumed that the stress across the interface required to form and grow the craze is borne entirely by chain sections that, between adjacent entanglements, cross the center of the interface. The entangled strands are assumed to break when the interface fails. This model ignores chain pullout and friction, both as an energy dissipation mechanism in its own right and as a stress transfer mechanism to help form a craze. These chain pullout processes are significant for weak interfaces so the model will underestimate the toughness at low interface widths.

The profile of an interface between high molecular weight polymers A and B can be represented by a function of the form

$$\phi_A(z) = \frac{1}{2}(1 + \tanh(2z/a_i)) \quad (1)$$

$$\phi_B = 1 - \phi_A$$

where $\phi_A(z)$ is the volume fraction of polymer A at a position z relative to the center of the interface and the interface width a_i is given by

$$a_i = \frac{2b}{\sqrt{6\chi_{AB}}} \quad (2)$$

with b being a segment dimension. This relation was first derived by Helfand and co-workers and has been extended to polymers A and B with finite molecular weight and different size and stiffness.¹²⁻¹⁵ It is also consistent with a number of experimental observations.¹⁶

Assume that a chain of polymer B has an entanglement at position $z = -h$ on the majority B ($-ve z$) side of the interface within a distance L_e of the interface. The probability that the next entanglement along the chain is on the majority A side of the interface can be approximated by

$$P(h) = \int_0^{L_e-h} \frac{\phi_B(z)}{2L_e\phi_B(h)} dz \quad (3)$$

where it is assumed that the distance between entanglements is constant through the interface and that the probability of a strand crossing the interface from position h to z is controlled by the ratio of the volume fractions of the B material at those two locations. We recognize that these two assumptions are not likely to be correct but assume that they give a good first-order approach to the problem. If the volume density of entanglements is given by ρ_e , then the areal density of B chains that cross $z = 0$ with adjacent entanglements on either side will be given by

$$\Sigma_B = 4\rho_e \int_0^{L_e} \phi_B(h) P(h) dh = \frac{2\rho_e}{L_e} \int_0^{L_e} \int_0^{L_e-h} (1 - \phi_A(z)) dz dh \quad (4)$$

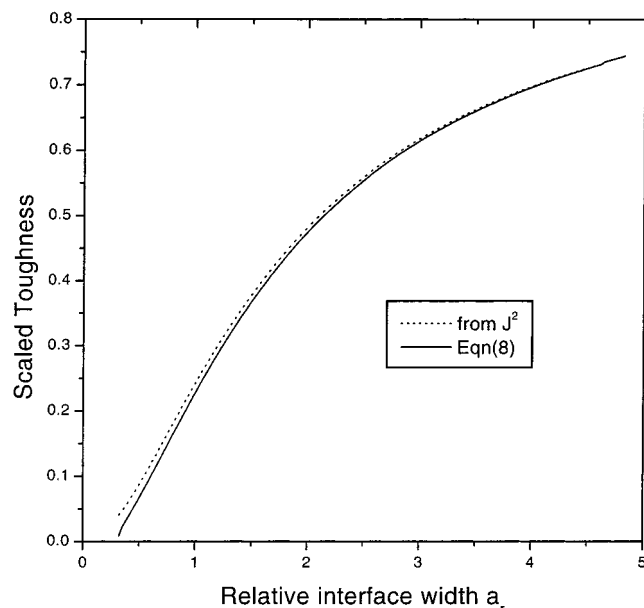


Figure 2. Calculated variation of toughness with relative interface width over a wide range of interface widths. The toughness is scaled by the expected bulk toughness.

where it is assumed that four strands emanate from each entanglement. From the relation for $\phi_A(z)$ given above it can be shown that

$$\Sigma_B = 4L_e\rho_e \left(\frac{1}{384} [48\ln(2)a_r - \pi^2 a_r^2] - \frac{a_r^2}{32} \int_1^{1+\exp(-4/a_r)} \frac{\ln(\nu)}{1-\nu} d\nu \right) \quad (5)$$

or

$$\Sigma_B = 4L_e\rho_e J(a_r) \quad (6)$$

where the relative interface width a_r is defined as a_l/L_e .

As mentioned above, within the simple model of crazing failure, the interface toughness varies as Σ^2 and so as J^2 . The more sophisticated failure model proposed by Sha et al. predicts that

$$G_c = \frac{A}{\ln\left(\left\{1 - \left[\frac{1.2\sigma_d}{\Sigma(a_r)f_b}\right]^2\right\}^{-1}\right)} \quad (7)$$

where A is a constant, σ_d is the craze stress, and f_b is the force to break a chain.

For failure in PMMA, using literature values for f_b , σ_d , ρ_e , and L_e , this relation can be written as

$$G_c = \frac{A}{\ln\left(\left\{1 - \left[\frac{0.025}{J(a_r)}\right]^2\right\}^{-1}\right)} \quad (8)$$

Figures 2 and 3 show the predicted variation of toughness with a_r , using both the simple model where toughness varies as J^2 , and the more sophisticated relation, eq 8. The interface toughness is predicted to remain very small as the craze fibrils are not stable when a_r is less than about 0.3. For a_r greater than 0.3 the toughness will increase approximately linearly with a_r , up to an a_r value of about 1.5, and then slowly

Table 1. Characteristics of the Random Copolymers

composition, %PS	M_w	M_w/M_n
20	165 000	1.24
30	300 000	1.24
40	265 000	1.25
55	125 000	1.62
68	160 000	1.51
78	173 000	1.26
89	180 000	1.40

saturate. The differences between the two models are only apparent for very weak interfaces, where the craze is narrow, as expected. At a relative interface width of 1, the toughness is predicted to have reached about one-fourth of the saturation value, and by $a_r = 2$, it will be at 50% of saturation.

Experimental Technique

Materials. The PS (Styron 685) was obtained from Dow Chemical Co.; it has a molecular weight $M_w = 330\,000$. The PMMA (Elvacite 2021) was obtained from Dupont with $M_w = 127\,000$. The compositions and molecular weights of the random copolymers of PS and PMMA are given in Table 1. All of the random copolymers were synthesized by Dr. Craig Hawker of IBM using a TEMPO free radical polymerization techniques which yielded narrow molecular weight distribution copolymers.^{17,18}

Sample Preparation. Sheets of PMMA and PS (51 mm \times 57.5 mm \times 2.4 mm) were compression molded in brass molds between two chrome steel ferrotype plates with mirror finishes at 165 °C, under a low pressure for 5–10 min and then under high pressure for 25–35 min. The samples were then rapidly cooled by placing on a metal surface at room temperature.

Thin copolymer films were spin coated onto the PMMA sheets from toluene solutions. The nominal thickness was measured by ellipsometry on films spun from the same solution and spin speed onto silicon wafers. Residual solvent was baked off in a vacuum oven for 1 h at 50–60 °C. The PMMA sheets with copolymer films were then joined to the other PMMA (or PS) sheets by compression molding at low pressure. The resulting “polymer sandwiches” were cut with a diamond-tipped saw into strips 6–8 mm wide and 50 mm long.

Fracture Tests. A single-edge razor blade of thickness Δ was manually forced into the interface of the sandwich and pushed forward at a low speed until the crack was across the width of the specimen. One end of the sample was placed on a padded surface on top of a hard table, and the blade was pushed in from above. The crack was left to propagate for 24 h after insertion of the razor blade before measurement. The crack length, a (distance from the razor edge to the crack tip), was measured with optical microscopy. The critical energy release rate, G_c , or fracture toughness, of the interfacial crack, was obtained from the sample geometry and crack length using a model derived by Kanninen in which the beam is supported by an elastic foundation ahead of the crack tip.^{5,19}

$$G_c = \frac{3\Delta^2 E_1 E_2 h_1^3 h_2^3}{8a^4} \left(\frac{C_1^2 E_2 h_2^3 + C_2^2 E_1 h_1^3}{(C_1^3 E_2 h_2^3 + C_2^3 E_1 h_1^3)^2} \right) \quad (9)$$

$$C_1 = 1 + 0.64 \frac{h_1}{a}$$

$$C_2 = 1 + 0.64 \frac{h_2}{a}$$

The subscripts “1” and “2” stand for PMMA and PS, respectively, “ E ” stands for Young’s modulus, and “ h ” stands for the thickness of the beams. The error in G_c was taken as the standard deviation of the mean for each group of samples in the window mold.

Results and Discussion

Figures 4 and 5 show the measured variation of interface toughness with interface width. To obtain the

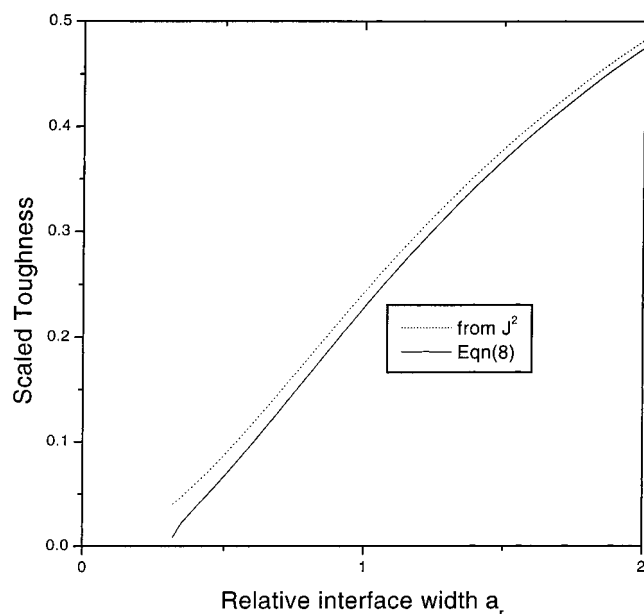


Figure 3. Same as Figure 2, showing the linear variation at low interface widths and the difference between the two models of craze toughness.

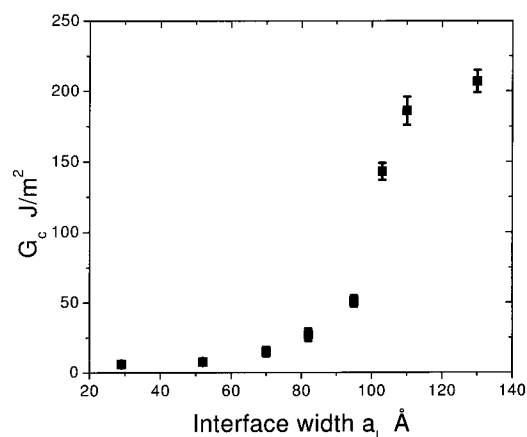


Figure 4. Measured variation of toughness with interface width.

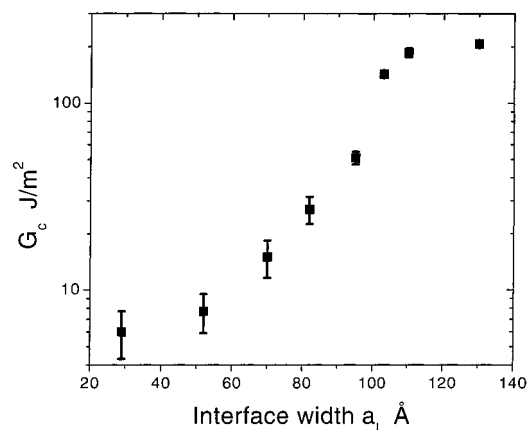


Figure 5. Same as Figure 4 with a log scale.

values of interface width used here, the measured values¹¹ were corrected for thermal fluctuations in the manner consistent with the relations suggested by Shull and co-workers and by Semenov.^{16,20} They both showed that the measured interface width can be described as a sum in quadrature (square root of sum of squares) of

Table 2. Interface Widths between the Copolymers and Homopolymers

copolymer, %PS	homopolymer	measured a_l nm	bare a_l nm
20	PMMA	15.7	13.0
30	PMMA	13.7	11.1
40	PMMA	12.9	10.3
55	PMMA	12.0	9.5
68	PMMA	10.7	8.2
78	PMMA	9.5	7.0
89	PMMA	7.6	5.2
100	PMMA	5.0	2.9
30	PS	8.4	6.0
55	PS	9.8	7.3

a bare interface width which varies as $\chi^{-1/2}$ and a fluctuation component that varies as $\chi^{-1/4}$. The precise size of the fluctuation term depends on the relevant long wavelength cutoff. Rather than directly using an estimate of this cutoff here, we chose the coefficients of the two terms by assuming that, for PS/PMMA, the bare interface width was 2.9 nm and the fluctuation component was 4.1 nm. This latter value is between the values chosen by Semenov and Shull et al. The measured and corrected (bare) interface widths are given in Table 2.

It is evident from Figure 4 that the measured variation of toughness with interface width is fairly different from that predicted by the model. It is worth noting that the values of L_e for PMMA and PS are 6.7 and 7.7 nm respectively² and that, for failure in PMMA, the saturated value of G_c (i.e. the value of G_c for cohesive failure) is about 500 J m⁻². For narrow interfaces the measured toughness is significantly less than that predicted, being only about 4% of the saturated value rather than 25% at a relative interface width a_l of 1. By $a_l = 2$, the toughness is about 50% of saturation, in agreement with the model. Evidently the model overpredicts the toughness for interfaces of width less than about twice the mean distance between entanglements. It is worth noting that the deviation between the model predictions and the experimental results cannot come from the fluctuation corrections to the measured a_l . Without such corrections, the deviations would be larger.

The basic pattern of the variation of G_c with a_l shown in Figures 4 and 5 is very similar to that observed by Schnell et al.⁸ in systems where the failure was mainly within PS. They considered the results to show three regions: region I at $a_l < 6$ nm where G_c was low, region II at $6 \text{ nm} < a_l < 12$ nm where G_c changed rapidly and region III at $a_l > 12$ nm where G_c appeared to have saturated at a high value. They suggested that the energy was dissipated mainly in chain pullout without crazing in region I, with a transition first to crazing, then from chain pullout to scission in region II. The model proposed here assumes that the scission of entangled chains is the only microscopic failure mechanism that initiates significant energy dissipation and so ignores the very real contribution of chain pullout in regions I and II. Hence, if the model was correct for chain scission, one might expect the measured toughness to be higher than that predicted for narrow interface widths. In reality, of course, the measured toughness is lower than that predicted. Of course chain pullout, if it occurs instead of chain scission, can reduce the toughness but it is unclear how this could happen except near the end of an entangled chain. If pullout tends to occur in a strand adjacent to a scission, then it would have its main toughness reducing effect in the more entangled systems.

It is worth speculating why the model overestimates the interface toughness. One possible reason is that the mean distance between entanglements, L_e , is assumed to be unaltered by the presence of an interface. Although the precise nature of entanglement is not understood, there is excellent evidence that it is controlled by the chain packing.^{2,21–23} The more densely a chain packs in a melt, the greater the distance between entanglements. It has been suggested that, close to a surface, the packing density of individual chains increases because the chains must reflect back from the surface, so the entanglement density should decrease.²⁴ This same argument would apply near an interface, though inevitably the strength of the effect should depend on the width of the interface. For broad interfaces, the effect of the interface on entanglement density would probably be very small. For sharp interfaces, the entanglement density may decrease by close to the factor of 4 predicted close to surfaces. Without more information on chain packing close to an interface, it is not possible to obtain numerical predictions of the strength of this effect (if it exists); however, it is clear that as the interface becomes significantly broader than the unconstrained entanglement spacing (about 6–7 nm), the entanglement in the interfacial region will become similar to that in the bulk.

Conclusions

The use of thin layers of a series of random PS/PMMS copolymers between two sheets of PMMA has permitted the examination of the effect of interface width on interface toughness. The interface width and toughness varied with the copolymer composition. The use of a thin coupling layer between two PMMA sheets ensured that the crack tip craze occurred within PMMA. The results therefore are not complicated by the deformation processes changing with interface width. The interface toughness was found to remain low until the interface width became larger than the mean entanglement spacing in the bulk and then to climb rapidly to saturation at a width of perhaps three times the entanglement spacing.

The model proposed here for the relation between interface width and interface toughness is based on a well-tested model for interface toughness and known interface profile. However, the assumptions that entanglement density is constant through the interface and that the probability of a chain passing through the

interface can be described just by a volume fraction ratio are probably incorrect. The measured toughness is significantly less than that predicted at widths equal to and below the entanglement spacing. This disparity is probably caused by the entanglement spacing increasing over the bulk value in the area of the interface. For broad interfaces, where the entanglement density is expected to be close to bulk values, the predicted toughness agrees reasonably with experiment.

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