Fracture of polymer interfaces: what are the relevant length scales ?

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SUMMARY: While it is tempting to relate directly the molecular structure of an interface (between glassy or between semi-cristalline polymers) with its fracture toughness, these two parameters are simply the two end-points of a complex network which needs to be understood in order to control the mechanical strength of the interface. The important mechanisms occur at three different length scales: the molecular scale (stress-transfer across the interface), the microscopic scale (plastic deformation at the crack tip) and the macroscopic scale (loading geometry and elastic constants of the polymers). The couplings existing between these length scales in glassy polymer interfaces are reviewed in this paper in light of the latest experimental studies.

Introduction

The mechanical strength of interfaces plays a key role in the mechanical performance of multiphase polymer blends. Yet a precise quantification of the mechanical strength of the interfaces in a phase-separated blend is difficult because the local stress field that one specific interface is submitted to, varies depending on the orientation of that interface relative to the main tensile direction of a macroscopic stress field.

What is possible however, is to do a qualitative experiment such as that performed by Creton and al. (1)on block copolymer reinforced interfaces : In that case a uniform stress is applied to a thin film containing second-phase particles, and upon onset of plastic deformation in the matrix majority phase, either the interface with the minority phase fails in a brittle manner

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and a hole is observed at the interface, or the interface is strong and the particle deforms affinely with the matrix.

A more quantitative evaluation of the fracture toughness of the interface can be obtained with a fracture mechanics test on a macroscopically planar interface[2, 3]. In this case, a planar crack is driven at an interface, with a molecular structure identical to what is expected at the interface between the matrix and a particle in a blend. The energy per unit area necessary to propagate the crack is called G_c and can be precisely evaluated if the geometry of the sample is known.

Experimentally G_c depends on three main factors occurring at three different length scales:

1) The molecular structure at the interface which is responsible for the transfer of stress from one side to the other. This occurs at the molecular scale (50 nm)

2) The plastic deformation properties of the polymers on both sides of the interface, in particular those of the softer (meaning here with the lower yield stress) polymer. This factor needs to be well controlled at the microscopic scale (1-10 μm)

3) The details of the stress field applied at the interface and in particular, the ratio between the shear and the tensile component of the stress field in the plane of the interface[4, 5]. This ratio is characterized by the phase angle ψ[Hutchinson, 1991 #298] and is dependent on parameters at the macroscopic scale (sample size).

The first factor has been extensively investigated for the case of block copolymers at interfaces and for random copolymers [6, 7]. The second factor on the other hand has been much less studied mostly because it is difficult to change the yield stress of the bulk polymers without changing the molecular structure at the interface. However, a few studies have recently appeared comparing adhesion between glassy polymers, with adhesion with their identical rubber-reinforced counterparts. In this case the stress transfer mechanism at the interface is identical but the plastic deformation of the polymer near the interface occurs for a lower value of stress[8-10] for the rubber-reinforced polymers. The third factor was neglected in earlier studies[Willett, 1993 #281][Cho, 1990 #185] but after recognizing that the degree of mode mixity at the interface could lead to vastly different values of G_c 2), a more systematic study was undertaken, showing that a mode mixity which tended to drive the crack into the softer material could lead to the presence of microscopic crazes ahead of the crack tip. oriented at 45° into this material5) giving abnormally high values of G_c which were not very sensitive to the interfacial structure. More recent experiments, where the diblock copolymers were replaced with random copolymers, suggested also that the nature of the compatibilizing agent at the interface could be important for the degree of observed crack deviation11)[Bernard, 1999 #1337].

However these studies were limited to cases where the size of the sample on either side of the interface was essentially infinitely large relative to the volume where plastic deformation mechanisms took place. It was not therefore clear, over which length scale were these spurious plastic deformation mechanisms important.

If the plastic zone formed at the interface is a simple craze, one expects the thickness of the zone δ to scale approximately as:

$$\delta \approx \frac{G_c}{\sigma_c} \qquad (1)$$

where σ_c is the yield stress of the polymer in hydrostatic tension. In principle therefore. for a glassy polymer with a yield stress comprised between 25 and 100 MPa, and an interface with a fracture toughness of 2-300 J/m^2 the plastic zone should not exceed 10-15 μm in thickness. If however 45° crazes are observed ahead of the crack tip, the relevant thickness of material over which this mechanism takes place maybe larger.

One would therefore expect that when the layer of polymer near the interface becomes thinner than a certain critical value, G_c could vary with layer thickness.

The investigation of this critical length scale and also of the coupling effects existing between molecular structure, plastic deformation properties and loading mode have been the main goal of recent experiments performed in our laboratory [12].

Experimental

The experimental system was mainly composed of two immiscible polymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA). A PS/Poly (2,6, dimethyl,1,4 phenylene oxide) blend (PS/PPO) was used in some experiments instead of PS and two compatibilizers, a random copolymer of PS-r-PMMA with 75% styrene content and a symmetric diblock copolymer of PS-b-PMMA were used at the interface between PS and PMMA. Both copolymers were chosen in order to give a high level of mechanical reinforcement to the PS/PMMA interface[11, 13-16]. The schematics of the sandwich sample used for fracture experiments is shown on figure 1.

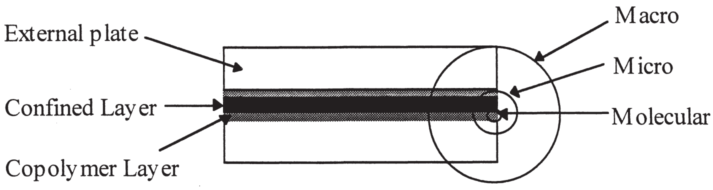

Figure 1: Schematics of the sandwich sample. The thickness of the outside layer is typically 1-3 mm, the central layer is between 0.5 μm and 100 μm thick an the copolymer layer is about 2-400 Å thick.

We prepared sandwich specimens with two outside layers of the same polymer (PS or PMMA) and a central layer of the other polymer. The thickness of the central layer was varied between 0.5 and 100 μm while the outside layers were typically 2 mm thick. A molecular layer of copolymer was deposited by spin coating at the interface between the PS and the PMMA. Its thickness (200-400 Å) was chosen in order to give maximum mechanical reinforcement for that particular polymer[11, 14]. These sandwich samples were then fractured with the well-known DCB test by driving a razor blade at one of the interfaces as shown schematically on figure 2. G was calculated with the beam on an elastic foundation model used in earlier studies[Creton, 1992 #707][17].

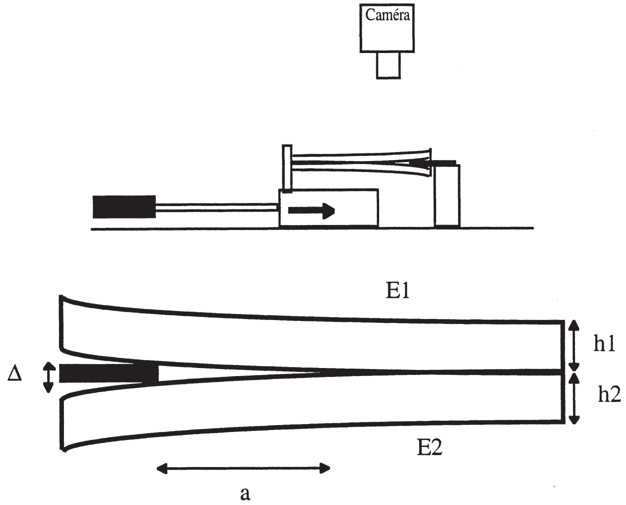

Fig.2: Schematics of the experimental setup for the asymmetric DCB tests.

The advantage of our configuration resided in the possibility of applying a mode I loading to the interface and at the same time, by varying the thickness of the central layer, of investigating the length scale over which the effect of the interfacial structure was important.

Note that given the difference in elastic moduli, a simple bilayer of PS and PMMA loaded in mode I, would have a local mode mixity of 8° [4]. However in our configuration, the thin layer of polymer sandwiched in the center did not change the mode mixity in any significant manner, so that, the interface was loaded essentially in mode I independently of the thickness of the central layer.

Results

The salient results of this investigation are that the fracture toughness of an interface of a trilayer sandwich PMMA/PS/PMMA varies with layer thickness much beyond the value one would expect from the argument given in equation 1. G_c goes through a maximum around 75 μm and decreases subsequently suggesting the occurrence of a transition in fracture mechanism with layer thickness (c.f. figure 3).

If the geometry is reversed, i.e. the thick layers are now PS and the confined layer is PMMA, the thickness dependence is markedly different and decreases first with layer thickness before being relatively constant with h.

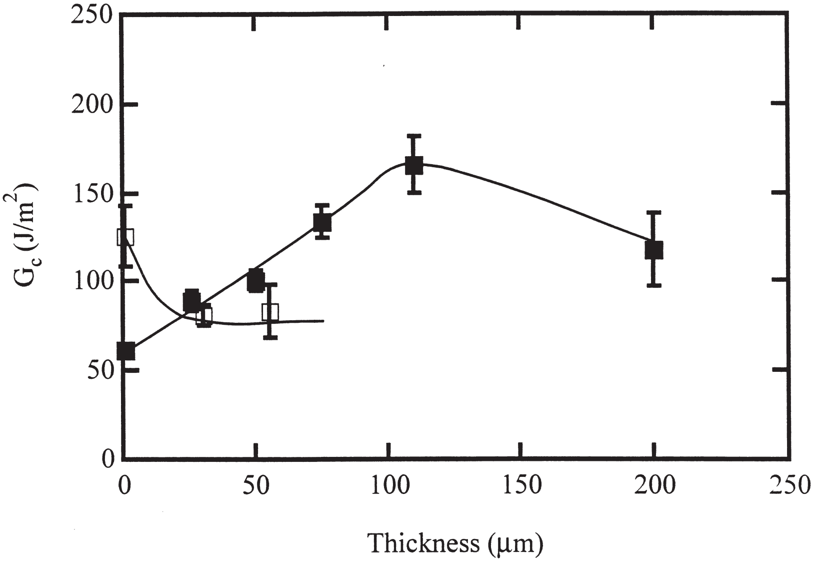

Fig.3: Fracture toughness of interfaces PS/PMMA/PS (❑) and PMMA/PS/PMMA (■) reinforced with PS-r-PMMA block copolymers as a function of the thickness of the central layer.

Microscopic observations of the fracture zone show that in both cases, oblique crazes are observed at 45° relative to the crack propagation direction. These crazes are always observed inside the PS layer, whether it is the central layer or the outside layer. Additionally, for PS layers thicker than about 50 μm, cracks normal to the propagation direction are also observed. These cracks do not seem to modify G_c so that presumably most of the observed dissipation is due to the presence of the oblique crazes.

In order to investigate the effect of the molecular layer at the interface, of the plastic deformation properties of the confined layer and of the degree of mixity of the loading, we have performed the same test with three variations:

1) The central layer has been replaced with a miscible blend of PS/PPO (80% wt PS). This blend has identical elastic properties as pure PS but a different crazing stress (higher).

2) The stress transfer layer has been replaced with a PS-b-PMMA layer (a block copolymer).

3) The outside beams have been made asymmetric; i.e. 3 mm and 1mm respectively

In the first case, the oblique crazes are completely suppressed and the fracture toughness becomes independent of layer thickness as predicted by equation 1. These results are shown on figure 4.

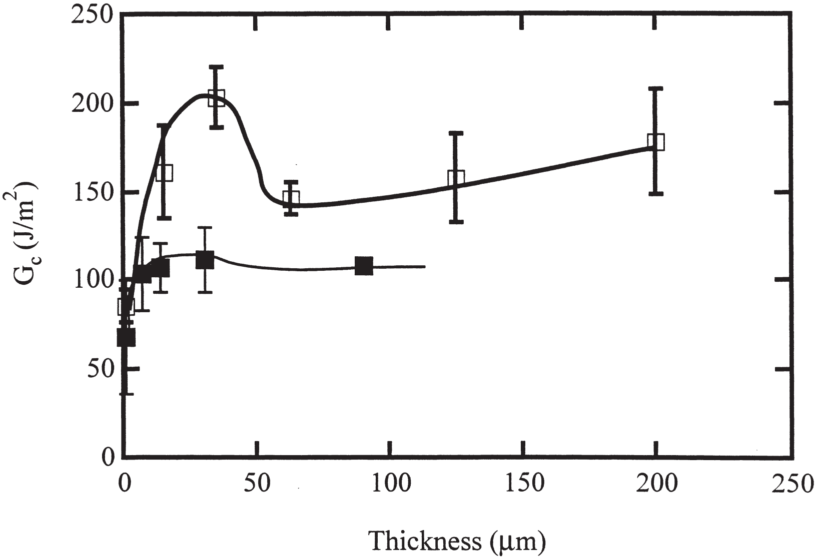

Fig. 4: Fracture toughness of interfaces PMMA/PS/PMMA (❑) and PMMA/(PS/PPO)/PMMA (■) reinforced with PS-b-PMMA block copolymers as a function of the thickness of the central layer.

In the second case, surprisingly the variation of G_c with layer thickness follows the same pattern as for the random copolymer (compare unfilled symbols on figures 2 and 3) but the maximum occurs at a lower thickness, implying that the stress transfer mechanism is different or that the nucleation of plastic deformation at the interface is affected by the precise nature of the reinforcing agent.

The same suppression of the oblique crazes occurs if the sample is made asymmetric. In this case the loading mode is no longer mode I and the mode mixity tends to drive the crack in the less compliant PMMA beam and suppresses the oblique crazes in the PS forcing the main craze to stay at the interface. As opposed to what has been observed by others on this system, we do not observe 135° crazes for negative phase angles[Bernard, 1999 #1337][Sikka, 1997 #1163].

Discussion

Since, in the experiments where the layer thickness was modified, the mode mixity did not change with increasing thickness and was basically mode I, one can propose the following tentative explanation:

The oblique crazes observed in the PS are nucleated at the interface ahead of the crack tip and the nucleation process is controlled by the precise structure of the interface and by the loading mode. While a significant amount of mode II, tending to deviate the crack towards the PMMA suppresses altogether the nucleation process of these crazes, in pure mode I, these crazes can be nucleated and grow at 45° from the crack direction. This occurs presumably because at the microscopic level, roughness causes the phase angle to fluctuate around its mean value and a very slight positive phase angle (driving the crack into the PS) is sufficient to nucleate crazes. Once the crazes are nucleated near the interface, their growth in the PS layer is probably relatively insensitive to the details of the molecular structure of the interface. They will stop either when they encounter the other interface, or when the local energy release rate becomes too low to propagate the craze in the pure PS material. If the nucleation is suppressed by the replacement of PS with PS/PPO, polymer having a higher crazing stress, no oblique crazes are observed.

An interesting observation is the comparison between the diblock and the random copolymer. The dependence of G_c with the central layer thickness changes markedly when going from one to the other, implying that while the stress transfer process may be identical in both cases. the nucleation process of oblique crazes is not. Furthermore, the occurrence of perpendicular cracks due to tensile stresses in the PS in the direction of crack propagation (one has to remember that these are plane strain experiments) is shifted markedly towards smaller thicknesses. Since it is unlikely that the stress field near the interface would be very different between the two copolymer cases, one has to speculate that the nucleation process of the perpendicular cracks is favored by the presence of block copolymers and occurs at lower levels of stress.

On the other hand the process of nucleation of oblique crazes seems to be favored by the presence of random copolymers relative to block copolymers.

Concluding remarks

The fracture toughness of the interface between two glassy polymers is determined by a combination of parameters which are acting over different length scales. At the molecular scale (50 nm), the polymer chains transfer the stress across the interface but can also provide nucleation sites for crack deviations. At the microscopic scale 1-10μm , the plastic deformation properties of the polymers on either side of the interface control the location and size of the plastically deformed zone. At the sample size scale, the far-field loading mode controls the nucleation of crack deviations and their length. The combination of parameters at all three length scales will control the total amount of energy irreversibly dissipated upon propagation of an interfacial crack. This result calls for two remarks:

1) If a characterization of the effect of the molecular structure on the strength of the interface is desired, one must be careful to specify the geometry of the test in a precise way and to

avoid situations where dissipation mechanisms which are not related to the interface are dominant.

2) It is not clear that a result of G_c obtained in that way on a planar interface between two polymers would be relevant when predicting the toughness of a phase-separated blend made from these same two polymers. Since in this case interfaces between phases are submitted to a variety of stress fields. Within that context, the capacity of a particular interfacial agent (such as a block or random copolymer) to nucleate plastic deformation mechanisms in the bulk, may be useful to maximize the total amount of energy dissipation upon crack propagation in the blend.

Acknowledgments

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