

CORRELATION BETWEEN INTERFACIAL WIDTH AND FRACTURE TOUGHNESS IN GLASSY POLYMERS

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Introduction

It has been known for quite a while that polymer interdiffusion or at least interpenetration was a necessary condition to obtain a good adhesion at interfaces between glassy polymers. However initial studies focused on the relationship between annealing time and fracture toughness relying therefore on models to predict the degree of interpenetration of the chains for a given annealing time. In the present study[1,2], we have measured the interfacial width of interfaces between glassy polymers by neutron reflectivity (NR) and measured the fracture toughness of interfaces prepared in the same annealing conditions and with the same materials by the asymmetric double cantilever beam (ADCB) method in order to directly correlate the interfacial width a_i with the fracture toughness G_c .

Experimental methods

The polymers were all synthesized by anionic polymerization and had a narrow molecular weight distribution. Four types of interfaces were tested: polystyrene/polystyrene (PS/PS) interfaces, polystyrene/polyparamethylstyrene (PS/PpMS) and polystyrene/brominated polystyrene interfaces (PS/PBr_xS) interfaces. Finally a separate study was conducted on polymethylmethacrylate/polymethylmethacrylate (PMMA/PMMA) ($M_w = 134k$) interfaces. All molecular weights used were at least 160 kg/mole and some of the polymers (for the NR experiments) were deuterated. More detailed characterizations of the PS based samples are given in reference [2].

The fracture samples were prepared by separately molding 2 or 3 mm thick sheets of the polymers and then joining them together at different annealing times and temperatures. After cooling to room temperature the samples were tested by dynamic ADCB at a crack propagation velocity of

5 μ m/s or 10 μ m/s. Neutron reflectivity samples were prepared by spin-casting thin polymer films (80-100 nm) onto silicon or float glass substrates. For the preparation of the double layers, one of the films was floated on the substrate and picked up by a second film. deuterated PS and deuterated PMMA were used for the NR studies. Neutron reflectivity experiments were performed on the neutron reflectometer TOREMA II at GKSS in Geesthacht, Germany.

Theory

For A/B immiscible polymers of finite molecular weights, the interfacial width is predicted to vary as [3]:

$$a_i = \frac{2b}{\sqrt{6}\chi_{AB}} \frac{1}{\sqrt{1 - 2ln2 \left(\frac{1}{\chi_{AB}N_A} + \frac{1}{\chi_{AB}N_B} \right)}}$$

so that the width of the interface can be controlled by three independent parameters:

- 1) The interaction parameter χ_{AB}
- 2) The annealing temperature (since χ_{AB} varies as T^{-1})
- 3) The degrees of polymerizations N_A and N_B of the two polymers.

For interfaces between miscible or identical polymers on the other hand, the interfacial width is controlled by the kinetics of interdiffusion.

In order to scan a wide range of interfacial widths we have used polymer pairs with different χ parameters, different annealing temperatures and molecular weights (for the PS/PpMS interfaces).

The microscopic mechanisms of fracture of polymer interfaces are now starting to be well-known and in particular, the fact that an interface needs to be able to transfer a stress at least as high as the crazing stress of one of the two polymers to give a high value of G_c [4].

It is also important to point out that the fracture toughness of bulk polymers is strongly dependent on their molecular weight and only becomes independent of it for molecular weights of 5-10 times the average molecular weight between entanglements M_e .

In this study we always worked with polymers with M at least 8 times higher than M_e .

Results

On figure 1 we are plotting the fracture toughness and interfacial width of interfaces between PS ($M \sim 700$ kg/mole) as a function of annealing time. The interface width a_i has been determined from NR and data are scaled by an approximation factor to each other.

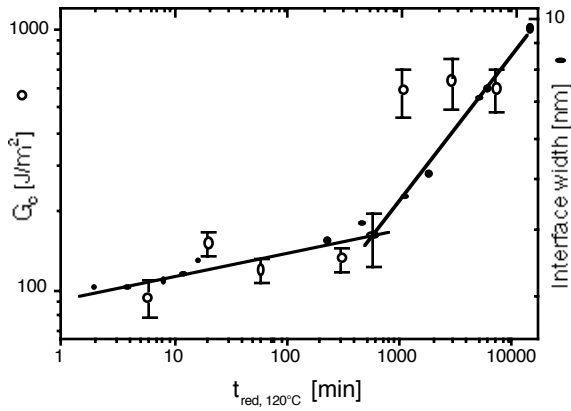


Figure 1: Fracture toughness \circ and interfacial width \bullet as a function of time for PS/PS interfaces.

Clearly there is a correlation between the two phenomena although, while the increase in interfacial width is rather progressive, the increase in G_c appears to be quite abrupt. A second example of interdiffusion is given on figure 2 by the fracture toughness and interfacial width of PMMA/PMMA interfaces as a function of annealing time. In this case also the fracture toughness increases in a rather sharp way while the interfacial width increases moderately with annealing time.

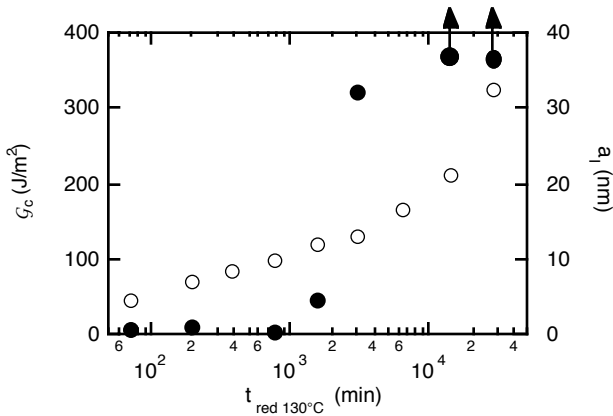


Figure 2: Fracture toughness \bullet and interfacial width \circ as a function of time for PMMA/PMMA interfaces[5].

Interfaces between immiscible polymers

In the case where the two polymers on either side of the interface are immiscible, the width of the interface is no longer controlled by kinetics but by thermodynamics. In figure 3, are shown the fracture toughnesses G_c of interfaces between immiscible polymer pairs PS/PpMS as a function of their interfacial width. Clearly there is a direct correlation between the interfacial width and G_c . One must point out however that:

- All polymers are styrenic and have very similar crazing stresses
- All polymers except one (which has a lower G_c) have molecular weights high enough to be in the regime where bulk toughness is molecular weight independent.

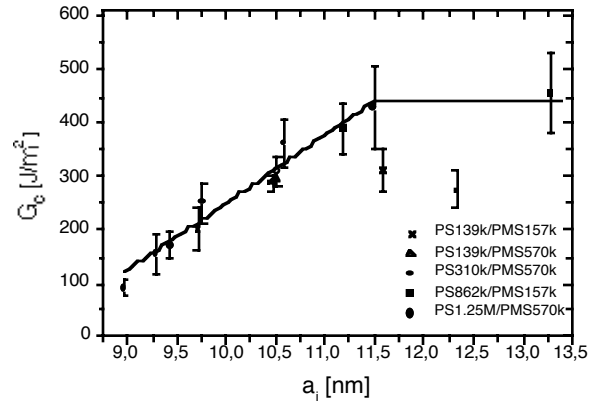


Figure 3: Fracture toughness vs. a_i of interfaces between PS and PpMS of varying molecular weights.

If the data on the styrenic copolymers, including the data on the interfaces between PS and PBr_xS are replotted together with the PS/PS data, three regimes can be clearly identified as shown on figure 4:

- regime I: $a_i < 6$ nm
 G_c is low and the interface presumably fails by chain disentanglement or by simple chain scission without much plastic deformation at the crack tip.
- regime II: $6\text{ nm} < a_i < 12$ nm
The plastic deformation mechanisms are activated and G_c increases sharply with interfacial width.
- regime III: $a_i > 12$ nm
 G_c is independent of a_i and the fracture toughness of the bulk material is recovered.

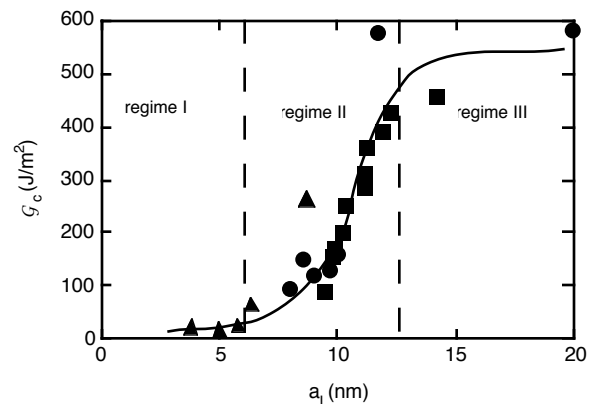


Figure 4: Fracture toughness G_c of interfaces between homopolymers. \bullet PS/PS, \blacktriangle PS/PBr_xS, \blacksquare PS/PpMS.

The transitions from regime I to regime II and from regime II to regime III provide us information on the mechanical effectiveness of the interfacial structure.

The first transition is representative of the activation of the plastic deformation mechanisms at the interface. This clearly indicates that the interface can sustain a stress at least as large as the crazing stress of PS.

From an estimated value of the monomer friction coefficient one can estimate what the interfacial stress would be if all chains were extracted from their mutual counterpart on the other side of the interface. This stress is lower than the crazing stress implying that a substantial number of loops as shown on figure 5, are present at the interface and contribute to the transfer of stress across the interface.

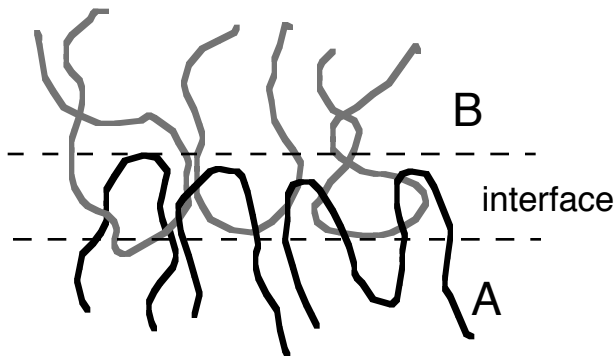


Figure 5: Schematics of the possible organization of chains at the interface between two homopolymers. The experimental data strongly suggests the presence of loops.

The second transition tells us at which point the interface is no longer detectable by mechanical means. This critical width should correspond to the minimum degree of interpenetration for which the stress that can be sustained by the interface is identical with the stress that could be sustained by any arbitrary plane in the bulk of the polymer. This interpenetration distance should be related to the molecular structure of the chains. Two working hypotheses could be:

- the II/III transition width is controlled by the radius of gyration of the polymer chain R_g .
- it is controlled by the average distance between entanglement points d_e .

Experimentally for very long PS chains ($M_n \sim 600$ kg/mole) as were used in this study, the transition from regime II to regime III occurs for $a_i = 12$ nm which is closer to d_e (9.3 nm for PS) than to the radius of gyration of the chains (21 nm for 570k PS).

Also within the range of molecular weights investigated (160 k-1250k) G_c is independent of molecular weight but depends only on the interfacial width a_i . These results strongly suggest that the chains need only to interpenetrate by an entanglement length to be as effective as in the bulk.

However if one applies the same reasoning to an interface between two high molecular weight PMMA ($M_w \sim 134$ kg/mole), two notable differences appear (see figure 2):

- the transition from regime I to regime II occurs between 10 and 12 nm, almost twice the value obtained for PS.
- the transition from regime II to regime III cannot yet be precisely identified but will be between 13 nm and 21 nm.

If the transition from II to III was controlled by the distance between entanglements, as suggested by the PS data, one would expect a lower value for PMMA than for PS. On the contrary the value of a_i at which the transition is observed is higher, more in line with the radius of gyration of the PMMA chains (10 nm for 134k PMMA). Furthermore, since PMMA has a much higher crazing stress than PS, one would expect the transition from regime I to regime II to occur for a somewhat larger value of a_i for PMMA, than for PS, but not to the extent which is observed.

Further experiments on different molecular weights of PMMA should provide some clues on the reasons for this discrepancy.

Conclusion

For interfaces, between homopolymers where a clear distinction between areal density of connecting strands and length of interpenetration cannot be made, the interfacial fracture toughness depends on the interfacial width only, provided that the molecular weight of the polymers is sufficiently high to be in the regime where the bulk fracture toughness is molecular weight independent.

The increase in G_c with interfacial width is highly non-linear and occurs over a fairly narrow range of interfacial widths. This has been confirmed both for PS and PMMA. However the connection between the characteristic widths where the toughness increases and the molecular structure of the interface is still unclear.

References

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