Influence of the Molecular Structure in the Interfacial Region on the Measured Adhesion between two Immiscible Polymers

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Introduction

The adhesion of polymer-polymer interfaces has been the focus of extensive work in the recent years, most of it in the area of interfaces between immiscible glassy polymers reinforced by block copolymers(Brown and Reichert 1992; Kramer, Norton et al. 1994).
This work has shown that a necessary condition to achieve a high toughness at the interface between solid polymers (as opposed to elastomers which do not have a yield stress) is to be able to develop a large localized plastic zone ahead of a propagating crack. The formation of this plastic zone requires the existence of molecular bridges across the interfaces which can sustain an applied stress higher than the yield stress (usually in plane strain) of at least one of the two bulk polymers on either side of the interface. Most of the recent work has focused on what are the molecular requirements to obtain efficient molecular bridges. In particular the mechanical effect of the presence of a molecular layer of diblock, triblock and random copolymers at the interface has been investigated in detail.
An important common feature of these micromechanical reinforcing mechanisms is that a change in the molecular layer at the interface (thickness $\approx R_g$) controls the size of a plastic zone which is several microns or tenths of microns in width.

A model for the mechanism through which this "amplification" could occur has been recently proposed by Brown(Brown 1991). He considered that the plastic zone was able to transfer stress laterally and that a stress concentration could therefore occur at the crack tip as opposed to the constant stress predicted by the Dugdale model. This picture allows to incorporate a molecular failure criterion (chain scission or chain pullout) for the plastic zone which in turn controls its maximum width.
Although appealing, the concept that a modification of a molecular layer at the interface is all one needs to optimize adhesion, is misconceived. In fact the observed fracture toughness of an interface will also depend on the bulk properties of an adjacent layer of material which is several microns thick.
This paper will focus on some recent results where the molecular connecting chains is kept constant but the bulk properties of the polymers on either side of the interface are modified.

Glassy polymers

Within the simple framework of Brown's model, the bulk polymers can affect the fracture toughness in two ways: Either by forming near the interface a layer of lower cohesive strength than that of the bridging chains, i.e. by lowering the critical stress necessary to fracture a volume element at the crack tip; or by a change in yield stress (σ_y) which will affect the possibility of formation of the plastic zone or its maximum width. G_c is predicted to scale as $f_b{}^2/(\sigma_y)$ where f_b is a molecular failure force (be it a scission force or a static pullout force) so that a low yield stress should give a higher fracture toughness.

In glassy polymers, there are several cases where bulk properties of polymers influence the adhesion properties. When comparing data obtained for the reinforcement of interfaces between poly(2,6 dimethyl phenylene oxide) and polymethyl methacrylate with PS-PMMA block copolymers and data obtained for the reinforcement of interfaces between polystyrene and poly(2-vinyl pyridine), one can see that G_c scales well with $\sum^2/\sigma_{craze}$ where σ_{craze} is the crazing stress of PMMA and PS respectively(Creton, Kramer et al. 1992). In certain cases one can also suppress the formation of a plastic zone altogether by increasing the crazing stress of the bulk polymers(Washiyama, Kramer et al. 1993).Another important case where bulk properties influence adhesion is the case of the formation of a weak boundary layer near the interface, in particular through the diffusion of low molecular weight polymer. A recent investigation by Dai et al.(Dai, Kramer et al. 1996) has shown that for PS if the M_n of the homopolymer near the interface is below about 200000, there is a significant decrease in the fracture toughness of the interface even for a high density of effective connecting chains.

Semi-crystalline polymers

However, generally, in the case of glassy polymers, the bulk properties do not change much above a certain molecular weight. This is very different from the case of adhesion between semi-crystalline polymers. It is well known that their plastic deformation in the bulk state can be modified by different thermal treatments (which will affect the crystalline microstructure). Therefore one can assume that, in adhesion experiments involving flat interfaces, similar annealing and cooling thermal treatments will affect the microstructure near the interface without affecting much the areal density of connecting chains at the interface.

Boucher et al.(Boucher, Folkers et al. 1996a; Boucher, Folkers et al. 1996b) have recently studied the reinforcement of a polyamide-6/polypropylene interface reinforced with PA6-PP block copolymers formed in situ through the interfacial reaction of maleic anhydride-endgrafted polypropylene (PP-g-MAH) with the amine endgroup of PA-6. The PP-g-MA is initially blended (~5 wt %) in the PP and the reaction at the interface with the PA-6 takes place during the annealing treatment above the melting point of PP but below or near that of PA-6. In this case the rate of formation of copolymer is controlled by the diffusion of the PP-g-MA at the interface with PA-6 and the areal density of block copolymer can be measured after fracture by XPS.

While at annealing temperatures between 180 °C and 220 °C, the measured fracture toughness of the interface is a unique function of the areal density of chains $\sum$ regardless of the time and temperature of anneal, this is no longer the case when the temperature is increased to 223 °C. As shown on figure 1, G_c increases by a factor of 4 for the same measured value of $\sum$. A similar increase has also been observed by Bidaux et al.(Bidaux, Smith et al. 1996) on a similar PA-6/PP system although the areal density in that case was not measured.

While the exact reason of this increase in adhesion is not yet fully understood, several reasons can be proposed:

First, the observation of the fracture surfaces as well as thin film deformation experiments show that the plastic deformation zone at the interface occurs only on the PP side of the interface, consistent with its lower yield stress. The increased adhesion at the higher annealing temperature can then be due either to an increased anchoring between the PP-g-MA and bulk PP or to the change in bulk properties of the PP near the interface. Complementary TEM investigations have shown that the interface remains flat regardless of the annealing temperature excluding therefore a mechanical anchoring mechanism. An interesting observation came from X-ray diffraction experiments at a grazing angle (sensitive therefore to in-plane correlations in the 20 μm or so near the surface). The samples showing an increased adhesion had some β-form of polypropylene near the interface while this was not found in the low adhesion samples. As the β-PP is known to have a higher fracture toughness than the α-PP, this could be a possible explanation. However the orientation of the lamellae of PP near the interface appears to equally play a role in the increased adhesion.

Conclusion

These results show conclusively that a correct interpretation of adhesion results in the case of high adhesion, where a plastic zone forms ahead of the propagating crack tip, must take into account the mechanical properties of a layer with a thickness comparable with the plastic zone width (several microns). This relevant layer is much wider than, either the interpenetration length of the polymer segments (which is normally called the interfacial width a_I) or the molecular layer of connector molecules which effectively transfers the stress across the interface.

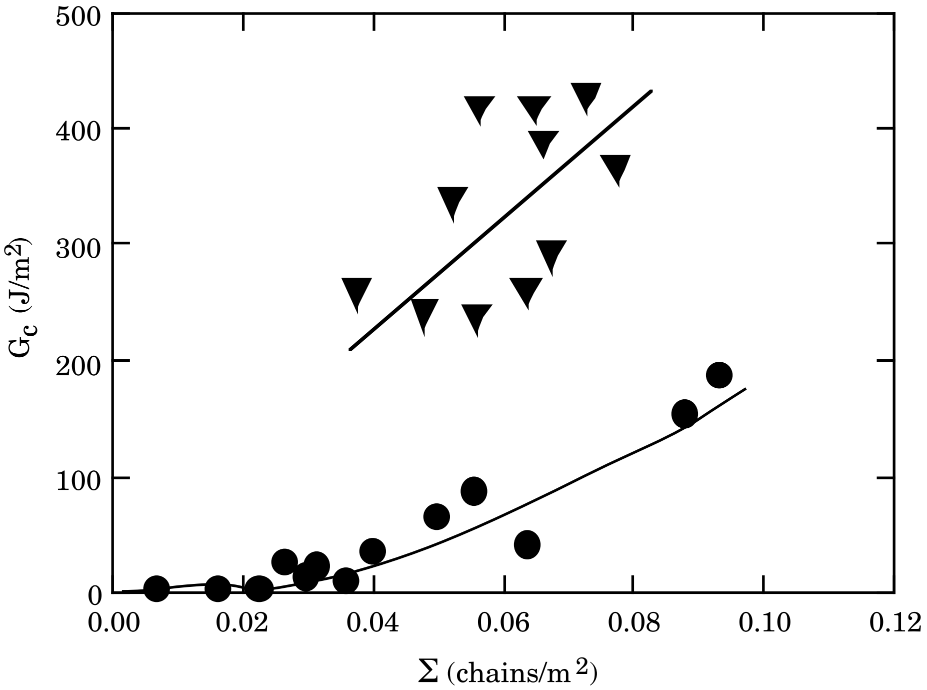

Figure 1: Fracture toughness G_c of the interface between PA-6 and PP as a function of the areal density of a PA6-PP block copolymer formed in-situ: ● samples annealed at $T < 223$°C where only α-form PP was present near the interface. ▼ samples annealed at T= 223°C where β-form PP was present in the 20μm near the interface. Data from (Boucher, Folkers et al. 1996)

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