

FRACTURE TOUGHNESS OF POLYMER INTERFACES: FROM THE MOLECULAR TO THE CONTINUUM SCALE

C. Creton¹, E.J. Kramer², H.R. Brown³ and C.Y. Hui⁴

¹ Laboratoire PCSM, E.S.P.C.I. 10, Rue Vauquelin, 75231 Paris Cédex 05, FRANCE

² Department of Materials Engineering, University of California, Santa Barbara, CA 93106, USA

³ BHP Steel Institute, University of Wollongong, Wollongong, NSW 2522, AUSTRALIA

⁴ Department of Theoretical and Applied Mechanics, Cornell University, Ithaca, NY 14853, USA

ABSTRACT

In order to be mechanically strong, an interface must be able to transfer stress across it. For very narrow interfaces between polymers, this capability is weak and a significant reinforcement can be achieved by the use of suitably chosen connector molecules (block copolymers) or by a broadening of the interface (random copolymers). In both of these cases the stress is transferred by entanglements between polymer chains. We review the main molecular characteristics which are necessary for this reinforcement effect to take place. Furthermore, recent theoretical advances on the relationship between interfacial stress and fracture toughness are discussed and the essential role of plastic deformation in the immediate vicinity of the interface is specifically addressed.

KEYWORDS

Fracture, polymer interfaces, adhesion, crazing, block copolymer, random copolymer

INTRODUCTION

Controlling the level of adhesion between two polymers is essential for many applications such as multiphase polymeric alloys, multilayer structures or adhesives. In all of these cases adhesion is caused by molecular interactions at the interface, but the level of adhesion is typically measured with a destructive test. Ideally one would like to be able to relate the macroscopic measurement of fracture toughness, which typically gives a critical energy release rate G_c , with the underlying surface chemistry (chemical bonds, specific interactions or simply entanglements). Recent experimental advances on the micromechanics of cracking at interfaces combined with easier access to polymers with well-defined chemical structures and surface analysis techniques have made it possible, at least for glassy polymers, to bridge the gap between the molecular and the continuum scale[1].

Interfaces between polymers which are immiscible are typically very narrow, with an interpenetration distance which is significantly smaller than the average distance between entanglement points in the bulk polymers. This lack of entanglements is responsible for the very low level of adhesion (typically a few J/m^2) which is measured. One strategy to increase the level of adhesion of such interfaces is to replace the natural entanglement network

at the interface with connecting molecules such as block copolymers which will be able to entangle with the bulk polymers on either side of the interface acting as molecular stitches. An example of such molecules are given on figure 1. Alternatively random copolymers, also shown on figure 1, can reinforce the interface by effectively reducing the immiscibility and increasing the interfacial width.

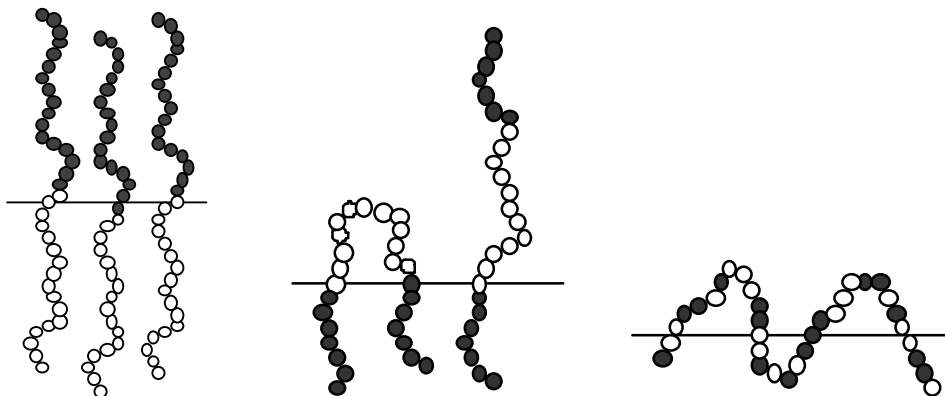


Figure 1: Schematic of connecting molecules at interfaces between A and B immiscible polymers. (Dark beads represent monomers of A and light beads represent B monomers). From left, diblock copolymers, triblock copolymers and random copolymers. The latter type of molecule acts by broadening the interface.

EXPERIMENTAL METHODS

In order to obtain the necessary information to bridge the gap between the molecular scale and the continuum scale, several techniques must be used. At the molecular level, one must be able to work with well-defined molecules, in particular for the block copolymers which are used as connecting chains. The molecular structure of the interface must be characterized before and after fracture if possible. For this purpose partial deuteration of the molecules present at the interface is invaluable and allows the use of ion beam techniques (to measure the amount of deuterium present on each surface after fracture) or neutron reflectivity (to measure interfacial width before fracture). If nitrogen is present, X-ray photoelectron spectroscopy (XPS) can also be quantitative to measure the amount of block copolymer at the interface.

At the macroscopic level, suitable fracture mechanics tests are needed to characterize the fracture toughness of the interface G_c . The double cantilever beam test combines ease of sample preparation and measurement with a great flexibility in controlling the degree of mode mixity at the interface during crack propagation[2]. This last point is important because the G_c of interfaces generally depends on the phase angle of loading in a non-trivial way. We found this to be particularly true of interfaces between glassy polymers where very small amounts of shear stresses could significantly modify the measured G_c by causing small crazes to grow in the bulk polymers[2,3].

Finally at the intermediate microscopic level, it is important to use observation tools such as electron or optical microscopy to investigate how local plasticity near the interface is affected by a modification of the molecular structure at the interface or by a change in the plastic deformation properties of the bulk polymers.

CONNECTING CHAINS BETWEEN GLASSY POLYMERS

The simplest and most informative case is that of an interface between immiscible A/B glassy polymers reinforced with a variable amount of A-B diblock copolymer. In that case one can safely assume that all the stress transfer capability is due to the presence of the block copolymers. For long copolymer chains, which do not disentangle, the stress transfer capability of the interface σ_{int} is given by:

$$\sigma_{int} = f_b \Sigma \quad (1)$$

where f_b is the force to break a covalent bond (approximately $2nN$) and Σ is the areal density of connector chains present at the interface. As long as σ_{int} remains below the crazing stress of both A and B polymers, G_c is low and the interface fails by simple chain fracture. If $\sigma_{int} > \sigma_{craze}$, i.e. if $\Sigma > \Sigma^* = \sigma_{int}/f_b$, a craze precedes the propagating crack and G_c becomes much higher. If shorter copolymer chains are used, and the interface fails by chain pullout rather than by chain scission this transition can be shifted to higher values of areal density Σ^* or suppressed altogether[4]. The degree of polymerization of the block where this starts to occur is of the order of the average degree of polymerization between entanglements N_e . Therefore a reasonably good picture of the fracture mechanisms is given by a plot of Σ/Σ^* as a function of N/N_e as shown on figure 2[1]. The limiting value for Σ , which we will define as Σ_{sat} is a decreasing function of N for steric reasons so that maximum values of G_c are typically obtained for values of N/N_e between 4 and 8.

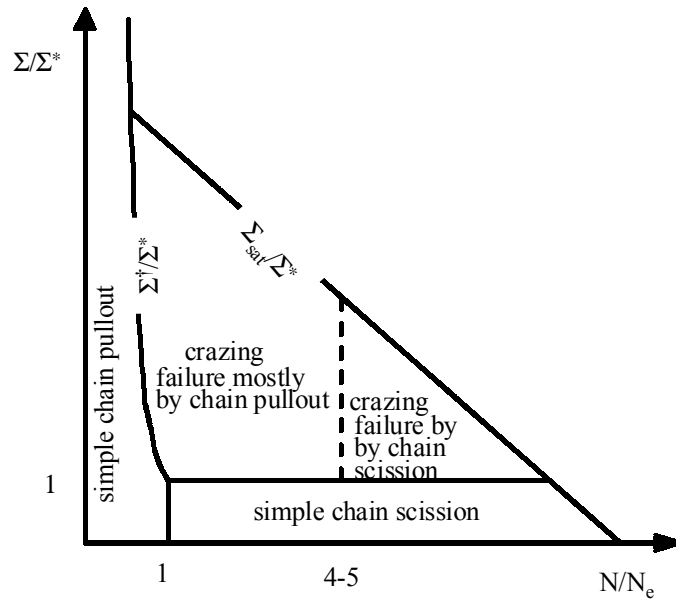


Figure 2: Fracture mechanisms map for interfaces between glassy polymers reinforced with connecting chains. Failure mechanisms are represented as a function of normalized degree of polymerization N/N_e and normalized areal density of connectors Σ/Σ^* .

CRAZE GROWTH AND STABILITY

In the regime where fracture of the interface is preceded by a craze, the fracture toughness can be related to the interfacial stress with the help of a model recently proposed by Brown for crack growth in a craze[5]. The key features of the model are the description of the craze zone as an elastic anisotropic strip with a local stress concentration at the crack tip. The larger the stress that the interface can sustain and the larger will be the amount of elastic energy needed in the strip for the crack to propagate. Since this amount of elastic energy is directly proportional to the width of the craze, we now have a direct connection between the maximum width of the craze h_f and the interfacial stress. Remembering that the macroscopic G_c is given for such a strip model by[6]:

$$G_c \sim \sigma_{craze} h_f$$

A direct connection can be made between G_c and the interfacial stress. The final result of the model which can be experimentally tested is[5,7,8]:

$$G_c = \frac{\delta^\mp \sigma_{craze}}{\ln \left\{ \left[1 - (1.2 \sigma_{craze} / \sigma_{int})^2 \right]^{-1} \right\}} \quad (3)$$

which reduces to:

$$G_c = \frac{\delta^\mp \sigma_{int}^2}{1.44 \sigma_{craze}} \quad (4)$$

for strong interfaces where $G_c > 50 \text{ J/m}^2$. δ^\mp has the physical meaning of an opening displacement and is characteristic of the elastic and geometric parameters of the craze itself. It does not vary much from one polymer to another.

It should be noted that σ_{craze} and h_f are directly analogous to the parameters $\hat{\sigma}$ and $\hat{\delta}$ used in cohesive zone models[9].

The dependence of G_c on σ_{int}^2 has been mainly tested for two experimental systems: diblock copolymers of polystyrene-poly2-vinylpyridine (PS-PVP) at the interface between PS and PVP[4] and for diblock copolymers of PS-polymethylmethacrylate (PS-PMMA) at the interface between poly(oxyphenylene) (PPO) and PMMA[10]. The agreement between the model is qualitatively and quantitatively very good.

REINFORCEMENT BY BROADENING OF THE INTERFACE

While in the case of connector molecules at the interface of very immiscible polymers, the value of σ_{int} is unambiguously given by equation 1, if the two polymers are less immiscible and the interfacial width becomes of the order of the average distance between entanglement points, a significant stress can be transferred by the entanglements formed at the interface. In this case experiments have shown that G_c is a unique function of the width of the interface a_i , provided that the molecular weight of the polymers is well above the average molecular weight between entanglements[11]. As shown on figure 3, however the increase in G_c with a_i shows clear transitions between different regimes: for thin interfaces one can argue that $\sigma_{int} < \sigma_{craze}$ and no plastic zone is formed at the interface; above a certain value of a_i , G_c increases dramatically implying that the crack is preceded by a craze. Finally at high values of a_i , G_c saturates and bulk toughness is retrieved. Although the exact value of a_i at the transition point varies somewhat from a system to another, it is always of the order of 10 nm. Therefore if a random copolymer is able to sufficiently reduce the immiscibility and broaden the interface to 10 nm, one expects to see a very large effect on the adhesive properties. This result has been confirmed experimentally for PS-r-PMMA random copolymers[12] and PS-r-PVP random copolymers at interfaces between their respective homopolymers[13,14].

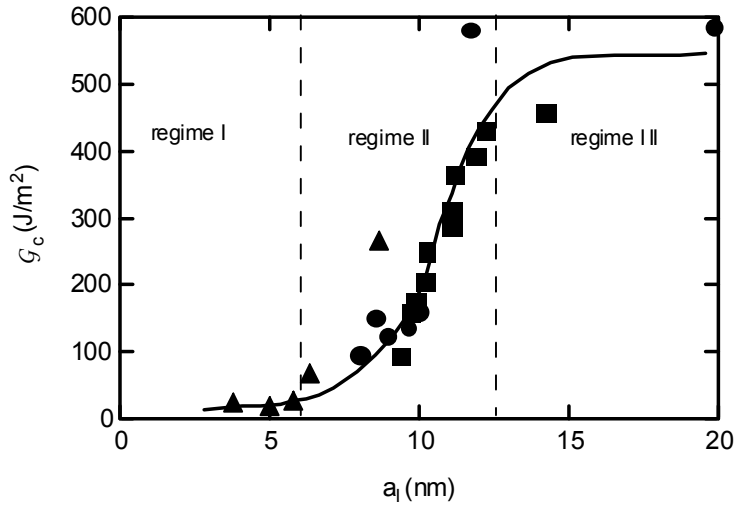


Figure 3: Fracture toughness G_c of interfaces between glassy homopolymers as a function of their width a_i . Data from [15].

GENERALIZATION OF THE MODEL

The craze growth model developed in the preceding sections is very attractive since it directly relates a macroscopic value G_c with molecular parameters and material parameters such as σ_{craze} which can be independently measured. While the original model was developed for glassy polymers which readily craze, subsequent studies have shown that the main features of the model (summarized in equations 3 and 4) may be much more robust. Fracture experiments of interfaces between semi-crystalline polymers, reinforced with polymer chains chemically grafted at the interface followed well equation 4 [16]. Furthermore, in the crazing regime, the measured value of G_c was found to directly increase with $1/\sigma_{craze}$ as predicted by equation 4. Figure 5 shows experiments performed on two systems where the molecular structure at the interface is identical (giving therefore the same value of σ_{int}) but the crazing stress (in this case rather the yield stress in hydrostatic tension) varies by a factor of 5. Accordingly the G_c values for the system with the lower yield stress are five times higher than for the harder system [17].

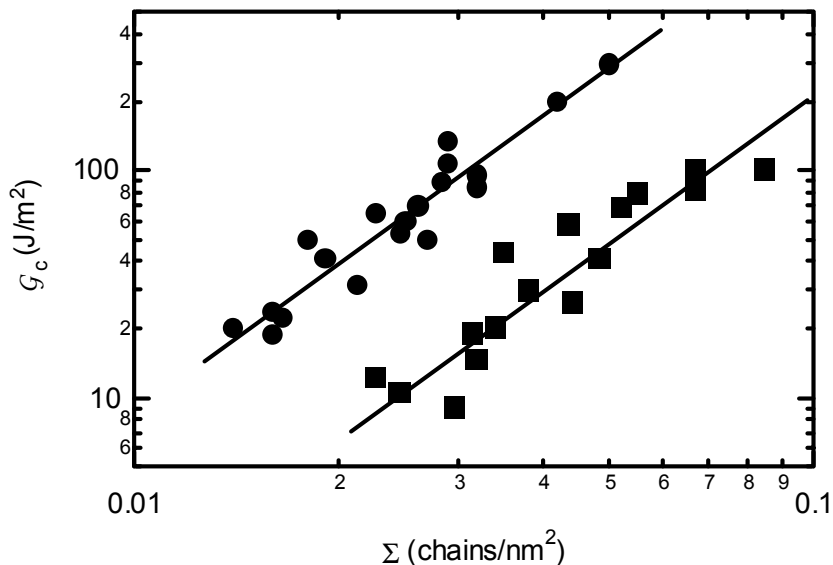


Figure 5: G_c vs. Σ for an interface between polypropylene (PP) (■) or a blend of PP with ethylene-propylene rubber (PP/EPDM)(●) and polyamide-6 (PA6), reinforced by end-grafted PP chains. The yield stresses of the PP and PP/EPDM blends are 21 and 4 MPa respectively. Data from [17].

Optical and electron microscopy observations of the plastically deformed zone ahead of the crack tip show that in both systems the dissipation is localized in a strip analogous to a Dugdale plastic zone near the interface. This is not however a very general case. If the softer polymer for example, is able to nucleate diffuse plasticity in the hard matrix, far away from the crack tip, greatly increasing the dissipated energy associated with the propagation of the crack, the correlation between interfacial structure and G_c can be much more complicated and is no longer described by Brown's model[18].

CONCLUSIONS

We have shown that the fracture toughness of interfaces between polymers is dependent on the molecular structure at the interface as well as on the bulk properties of the polymers on either side of the interface. This relationship is now relatively well established for interfaces between glassy polymers and the main results have been summarized here. Two important points must be emphasized:

- In order to obtain a high value of fracture toughness, the interface must be able to transfer a stress which is at least as high as the crazing stress of one of the bulk polymers on either side of the interface.
- If this condition is met, G_c will depend on the interfacial stress σ_{int} and on the bulk crazing stress σ_{craze} . If all the plastic deformation is confined in a localized craze near the interface, G_c is well predicted by equations 3 and 4.

REFERENCES

1. Creton, C.,Kramer, E. J.,Brown, H. R.and Hui, C. Y. to appear in *Adv. Polym. Sci.*
2. Brown, H. R. (1990) *J.Mat.Sci.* 25, 2791.
3. Xiao, F.,Hui, C.-Y.,Washiyama, J.and Kramer, E. J. (1994) *Macromolecules* 27, 4382.
4. Creton, C.,Kramer, E. J.,Hui, C. Y.and Brown, H. R. (1992) *Macromolecules* 25, 3075.
5. Brown, H. R. (1991) *Macromolecules* 24, 2752.
6. Dugdale, D. S. (1960) *J. Mech. Phys. Solids* 8, 100.
7. Hui, C. Y.,Ruina, A.,Creton, C.and Kramer, E. J. (1992) *Macromolecules* 25, 3948.
8. Sha, Y.,Hui, C. Y.,Ruina, A.and Kramer, E. J. (1995) *Macromolecules* 28, 2450.
9. Zehnder, A. T.and Hui, C. Y. (2000) *Scripta mater.* 42, 1001.
10. Char, K.,Brown, H. R.and Deline, V. R. (1993) *Macromolecules* 26, 4164.
11. Schnell, R.,Stamm, M.and Creton, C. (1998) *Macromolecules* 31, 2284.
12. Brown, H. R. to appear in *Macromolecules*.
13. Dai, C. A.,Osuji, C. O.,Jandt, K. D.,Dair, B. J.,Ober, C. K.and Kramer, E. J. (1997) *Macromolecules* 30, 6727.
14. Xu, Z.,Kramer, E. J.,Edgecombe, B. D.and Fréchet, J. M. J. (1997) *Macromolecules* 30, 79.
15. Schnell, R.,Stamm, M.and Creton, C. (1999) *Macromolecules* 32, 3420.
16. Boucher, E.,Folkers, J. P.,Hervet, H.,Léger, L.and Creton, C. (1996) *Macromolecules* 29, 774.
17. Kalb, F.,Léger, L.,Creton, C.,Plummer, C. J. G.,Marcus, P.and Magalhaes, A. to appear in *Macromolecules*
18. Plummer, C. J. G.,Kausch, H. H.,Creton, C.,Kalb, F.and Léger, L. (1998) *Macromolecules* 31, 6164.