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## **The Adhesion of Polymers: Relations Between Properties of Polymer Chains and Interface Toughness**

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## The Adhesion of Polymers: Relations Between Properties of Polymer Chains and Interface Toughness

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*A review is presented of the adhesion between polymers with particular emphasis on the processes that occur during failure at the level of polymer chains and how these processes relate to the macroscopic interface toughness. The same processes at the chain level, pull-out and scission, occur in both glassy polymers and elastomers, but the two classes of material are considered separately because their deformation processes around a crack tip are so different. Emphasis is placed on the work in which the author has participated and so the review makes no attempt to be an unbiased survey of the field.*

**Keywords:** Block copolymers; Chain scission; Craze; Elastomers; Fracture toughness; Glassy polymers; Polymer interfaces

### INTRODUCTION

The aim of this article is to present a biased review of the area of adhesion between polymers. The review is biased in that it emphasizes the work done by the author and his group, as is perhaps appropriate for a collection of papers in his honor. The main emphasis of the work is the relationships between the structure and properties of polymer chains at an interface and resistance that the interface shows to crack propagation, normally measured by  $G_c$ . Although consideration is given to both glassy and rubbery polymer systems—classic polymeric

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adhesives—both reactive systems, such as epoxies, urethanes, and non-reactive pressure sensitive elastomeric adhesives I are not considered.

Valuable information on the basic mechanisms of adhesion between different polymers has been obtained by the use of well-characterized model systems where the coupling between the different materials is done by well-defined coupling chains. In such systems the areal density of coupling chains ( $\Sigma$ ) can be controlled and, hence, relations can be found between the interface coupling at the scale of a polymer chain and the macroscopic toughness.  $\Sigma$  can easily be controlled by the use of block polymers or end-attached polymer chains at the interface, or alternatively by controlling the width of the interface between the two materials (by controlling their chemistry) in the absence of specific, chemically-different, coupling chains.

It is necessary to consider adhesion of glassy polymers and elastomers separately as their properties are so different. Both classes of material can undergo chain scission or pullout at a crack tip, but the very different local viscosities ensure that the forces for chain pullout are very different, as are the lengths of chain that can be pulled out. In addition, they require different adhesion tests because their macroscopic mechanical properties are so different.

## GLASSY POLYMERS

### Overview

The mode of failure of a polymer at the scale of a polymer chain depends strongly on its molecular weight. At a minimum, the chains that cross the crack path must either pull out from the rest of the material on one side or break. At low molecular weights glassy polymers fail by chain pullout with little deformation around the crack tip. As the molecular weight is increased the force required to pull-out chains that cross the crack path from the matrix increases, initially causing some form of local yield. As the chain length continues to increase the stress borne by the chains across the crack path becomes high enough to cause a local yield and voiding process called crazing. At this point the material obtains some useful toughness. Increasing chain length to significantly above the entanglement molecular weight changes the chain failure mode from pullout to scission and continues to increase the energy dissipated in the craze, and hence the toughness. Eventually the toughness saturates at high molecular weight as the chain lengths between entanglements that cross the interface all fail by scission.

The processes that occur during adhesive failure are similar to those described above for cohesive failure. There are two basic

situations: (1) when specific coupling chains are placed or formed at the interface and (2) when two pieces of the same or different polymers are welded together. The main differences between these two situations originate in the fact that for case (1) both the areal density  $\Sigma$  (at the interface) and the length of coupling chains can be altered independently of the molecular weight and nature of the materials being coupled. There is, however, a maximum areal density of the coupling chains  $\Sigma_{\text{sat}}$  that can be accommodated at the interface. The situation is more complex for case (2) as the chains diffuse across the interface during the welding process; so, the time dependence of the interface structure is important. However, here I will only consider the equilibrium situation and so am concerned with situations where the interdiffusion is limited either because the two materials are chemically different and immiscible or because the materials are crosslinked and so have limited mobility.

Consider first the case of specific coupling chains. If the coupling chains are very short, the failure is by simple chain pullout with little deformation around the crack tip and low toughness. As the coupling chain length increases, the pullout force increases and the failure mode can change to crazing and chain pullout with a significant increase in toughness. This change occurs when the stress at the interface, controlled by coupling chain length and  $\Sigma$ , becomes greater than the stress to cause crazing. This transition is only observed at high  $\Sigma$ . As the length of the coupling chains is increased more, the pullout force becomes greater than the force to cause chain scission, so the chains fail by scission. When  $\Sigma$  is low with long coupling chains, the stress at the interface can be too low to cause much deformation, even when the chains break, and so the toughness is low. As  $\Sigma$  is increased and yielding and crazing start to occur around the crack tip, the toughness increases and in favorable circumstances the interface toughness can become almost as large as the bulk toughness of the material being joined.

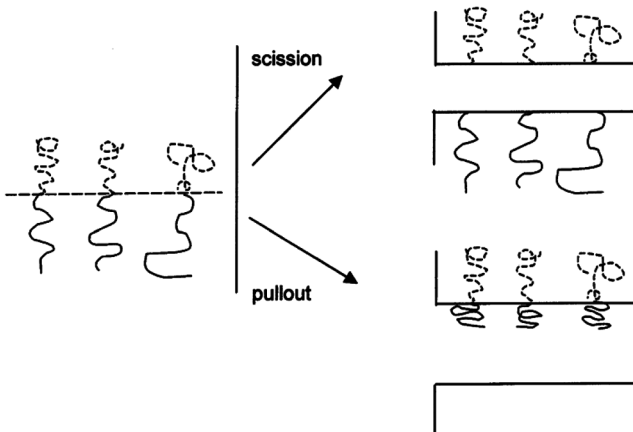
When dissimilar polymers are joined the toughness is controlled by the width of the interface between them. For narrow interfaces the fracture energy is dissipated in chain pullout while for broader interfaces the important parameter is the areal density of chain segments that have adjacent entanglements on either side of the interface and so experience scission.

The micromechanical processes will be presented next, followed by the models used to describe them. The predictions of the models will then be compared with results obtained using well-defined coupling chains. Application of the models to the joining of dissimilar polymers will then be described.

## Experimental Studies of Micro-Mechanical Processes

The main experimental techniques used to study the failure processes at the scale of a chain have involved the use of deuterated polymers, particularly copolymers, at the interface and the measurement of the amounts of the deuterated copolymers at each of the fracture surfaces. The quantity of the deuterated copolymer has typically been measured using Forward Recoil Elastic Ion Scattering (FRES) or Secondary Ion Mass Spectroscopy (SIMS). The technique was originally used in a study of the effects of placing polystyrene-polymethyl methacrylate (PS-PMMA) block copolymers of total molecular weight of  $\sim 200,000$  Daltons at an interface between poly phenylene ether (PPE) and PMMA [1]. The PS block is miscible in the PPE. The use of copolymers where just the PS block was deuterated and copolymers where just the PMMA block was deuterated showed that, when the interface was fractured, the copolymer molecules all broke close to their junction points. The basic idea of this technique is shown in Figure 1.

The techniques described above have been used to demonstrate that failure can occur by (1) simple chain pullout, (2) chain scission close to the interface, or (3) chain scission within one of the blocks (typically PS).



**FIGURE 1** Block copolymers tend to organize at an interface so that the two blocks, shown here as solid and dashed lines, are on either side of the interface. If one of the blocks is deuterated than chain pullout can be distinguished from chain scission by the location of the deuterium on the fracture surface. Reprinted from Adhesion science and Engineering Vol. 2, *Micro-mechanical processes in adhesion and fracture* by H. R. Brown, pp. 221–242. Copyright 2002 with permission from Elsevier.

The transition from chain pullout to scission is essentially controlled by block molecular weight whilst the location of the scission seems to depend on the entanglement density.

Processes that occur at a size scale larger than the individual chain have been studied using microscopy, mainly transmission electron microscopy (TEM), but optical microscopy has been useful to examine craze shapes. At an interface between two polymers a craze often forms within one of the materials, typically the one with lower crazing stress. TEM has been used to demonstrate that the craze normally fails at the material interface [2–4]. In addition, the fracture energy calculated from the craze shape tends to agree well with the macroscopic measure of toughness.

### Models of Chain Pullout in Glassy Polymers without Crazing

Xu *et al.* developed a model of chain pullout in glassy polymers [5]. The chain, embedded in the polymer, is pulled at one end with a force  $f$  which is larger than the critical value  $f = Nf_{mono}$  below which chain pull-out cannot occur, where  $f_{mono}$  is a static monomer friction coefficient and  $N$  is the number of monomers in the chain. If the length of the connector chain pulled out by the force  $f$  is given by  $\delta$ , when  $\delta = \Delta$ , where  $\Delta$  is the total connector chain length, the chain is completely pulled out and the force vanishes. Assuming that the chains are pulled out normal to the interface, then  $\sigma$ , the stress normal to the planar interface, is related to the force  $f$  and  $\Sigma$ , by  $\sigma = f\Sigma$ . The stress  $\sigma$  is related to the rate of chain pullout  $\dot{\delta}$  and the remaining chain length  $\Delta - \delta$  by:

$$\sigma = b(\Delta - \delta)(\dot{\delta} + \dot{\delta}^*) \quad \dot{\delta} > 0 \quad (1)$$

where  $b$  and  $\dot{\delta}^*$  are material constants. In this model, when the normal stress on the interface is less than  $\sigma^* = b\Delta\dot{\delta}^* \equiv f_{mono}N\Sigma$ , chain pullout cannot occur. For such a model  $f_{mono}$  can be considered to be a monomer static friction coefficient.

Using this model, Xu *et al.* have demonstrated that for sufficiently slow crack growth rate, *i.e.*,  $V \rightarrow 0$ , the fracture toughness  $G(V)$  is given by:

$$G(V) = G_o = \frac{\sigma^* \Delta}{2} = \frac{f_{mono} \Sigma N^2 \alpha}{2} \quad (2)$$

where  $E^* = E/4(1 - \nu^2)$ ,  $E$  being the Young's modulus and  $\nu$  the Poisson's ratio and  $\alpha$  is a monomer length so that  $\Delta = Na$ .

The main results of this micromechanical model in the quasistatic regime have been compared with experimental results obtained

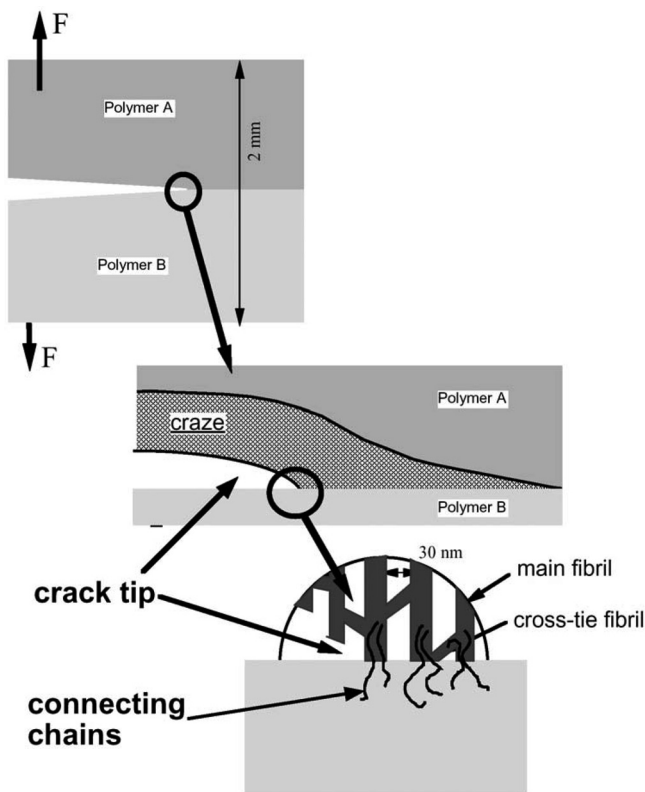
by placing PS-polyvinyl pyridine (PVP) diblock copolymers with a short PVP block between PS and PVP homopolymers. The fracture toughness was found to increase linearly with  $\Sigma$  from that of the bare PS/PVP interface while the slope of the line increased with the degree of polymerization of the block being pulled out. If the data for the different copolymers were plotted as  $\Delta\mathcal{G}_c$  vs.  $(N_{PVP})^2\Sigma$  (where  $\Delta\mathcal{G}_c = \mathcal{G}_c(\Sigma) - \mathcal{G}_c(0)$ ), they would fall on a single line consistent with a single value of the monomer friction coefficient. This value can be estimated by assuming that the only dissipative process is the frictional extraction of the PVP block. The value obtained for  $f_{mono}$ ,  $2.5 \times 10^{-11}$  N/monomer is, however, an overestimate as it does not take into account any viscoelastic dissipation near the interface. The most important point to emphasize is that the maximum  $\Delta\mathcal{G}_c$  that can be obtained from this pullout mechanism is very low, less than  $5 \text{ J/m}^2$ . The reason for this low maximum toughness is that the maximum displacement of the pullout zone at the crack tip is only of order 40 nm, the length of an disentangled connector chain.

## Models of Crazing Failure for Glassy Polymers

### The Models

When the stress that can be borne at the interface between two glassy polymers increases to the point that a craze can form, then the toughness increases considerably as energy is now dissipated in forming and extending the craze structure. The most used model that describes the micro mechanics of crazing failure was proposed by Brown [6] in a fairly simple and approximate form. This model has since been improved and extended by a number of authors. As the original form of the model is simple and physically intuitive it will be described first and then the improvements will be discussed.

A craze is a planar (crack-like) deformation zone that can form normal to the maximum principal stress in a glassy polymer. The two sides of the craze are joined by an array of fine interconnected fibrils that together hold the craze stress  $\sigma_c$ . The toughness of a polymer material that fails by a crazing mechanism is essentially the energy required to grow the crack tip craze(s) to their maximum width. The maximum craze width occurs at the crack tip. The model of failure by crazing is concerned with situations where there is one crack tip craze in which most of the fracture energy is dissipated, see Figure 2. As the craze fibrils are interconnected with cross-tie fibrils, a stress concentration can occur within the craze. Therefore, even if the stress at the craze-matrix interfaces is approximately constant,



**FIGURE 2** An illustration of the basic idea of the model of failure by crazing showing the different relevant length scales. Reprinted from *Advances in Polymer Science* Vol. 156, 2002, pp. 53–136, *Adhesion and fracture of interfaces between immiscible polymers*, C. Creton et al. Fig. 20a, with kind permission of Springer Science and Business Media.

the stress at the crack tip (within the craze) can be high enough to cause chain scission or pullout, and hence fibril failure occurs.

The aim of the model is to find the relation between the energy dissipated in growing the crack tip craze, as that is the macroscopic toughness, and the local force at the fibril closest to the crack tip which controls the molecular level failure process. In the original model the craze was modelled as a highly anisotropic continuum between rigid clamps with a longitudinal modulus  $C_{22}$  and shear modulus  $C_{66}$ . The stress intensity at the crack tip ( $K_{tip}$ ) was estimated from relations derived for elastomer failure. The craze is assumed to be a parallel sided elastic strip of material between rigid clamps. The tensile stress



$\sigma_{22}$  directly ahead of the crack tip that is located at the origin ( $x = 0, y = 0$ ) has a inverse square root singularity as  $x \rightarrow 0$ , i.e.,

$$\sigma_{22} \cong K_{tip}(2\pi x)^{-1/2} \quad (3)$$

$K_{tip}$  is found to be

$$K_{tip} = A\sigma_c(C_{66}/C_{22})^{1/4}\sqrt{h} \quad (4)$$

where  $\sigma_c$  is the crazing stress,  $h$  is the half width of the craze at the crack tip and  $A$  is a constant of order one. The important issue here is that the crack tip stress increases with the width of the craze.

The stress on the craze fibril directly ahead of the crack tip was assumed to be

$$\sigma_{fibril} = K_{tip}(\pi d)^{-1/2} \quad (5)$$

where  $d$  is a fibril diameter.

To obtain  $G_c$ ,  $\sigma_{fibril}$  is set equal to the failure stress  $\sigma_{fibril} = \Sigma f_c$  where  $f_c$  is the force to break or pull out a chain,  $f_b$  or  $f_p$ .

The toughness  $G_c$  is the energy per unit area to grow the craze to its maximum width so, assuming that the stress  $\sigma_c$  along the craze is constant,

$$G_c = \sigma_c(1 - v_f)h \quad (6)$$

where  $v_f$  is volume fraction of the fibrils in the craze.

By combining Equations (4)–(6) one obtains the basic relation between interface toughness and the force required to break or pull out a chain

$$G_c = \frac{\pi d(1 - v_f)}{A^2} \sqrt{\frac{C_{22}}{C_{66}}} \frac{\Sigma^2 f_c^2}{\sigma_c} \quad (7)$$

The constant  $A$  was assumed equal to 1 in the original work.

The model has been improved by Hui *et al.* [7–9] in three distinct ways. Firstly, they obtained a more accurate relation for the stress within the craze, while still assuming the displacement boundary conditions. They found that, for broad crazes, the best value for  $A^2$  is 2.88. Secondly, the simple model is bound to fail for weak crazes (low  $\Sigma$ ) where the craze opening is narrow, the same order as the distance between the craze fibrils, and so the continuum solution cannot be valid. Discrete models have been constructed for this case [8–10]. Thirdly, they relaxed the displacement boundary conditions for the strip and studied models, consisting of arrays of springs, where craze shape and craze/matrix stress are determined self-consistently. The

craze shapes were found to be similar to the predictions of the Dugdale model assumed in the early work. They found that the following relation is an excellent approximation over the whole range from narrow to very wide crazes. The  $\ln$  factor agrees with the square law of Equation [7] for wide crazes and the factor of 1.2 was found empirically to make the strip model results agree with those from the anisotropic self-consistent spring model [9].

$$G_c = \frac{\pi d \sigma_c (1 - v_f) \sqrt{C_{22}/C_{66}}}{2 \ln \left( \left\{ 1 - \left[ \frac{1.2 \sigma_c}{\Sigma f_c} \right]^2 \right\}^{-1} \right)} \quad (8)$$

In order to use this model it is necessary to estimate the ratio of the longitudinal to shear elastic constants,  $C_{22}/C_{66}$ . In the original model this quantity was estimated crudely from typical distribution of the fibril directions of a craze from the tensile stress direction obtained experimentally by transmission electron microscopy and low angle electron diffraction. A more sophisticated mechanical modelling approach was used by Hui *et al.* [7], who considered the mechanics of a couple of possible microstructural models for the craze matter and obtained estimates of 0.02–0.03 for the modulus ratio. More recently, Robbins *et al.* [11] have used coarse grained molecular simulation to grow a craze, obtaining a structure similar to those typically seen by transmission electron microscopy. They then deformed the simulated structure to find the relevant moduli directly.

In the discussion so far it has been assumed that  $\Sigma$ , the areal density of chains connecting across the interface, is the same as the density of such chains before the craze forms. However, it has been argued that a considerable number of chains are broken during the crazing process and so the number of effective chains,  $\Sigma_{eff}$ , is less than the number of chains before crazing. If the surviving fraction of load bearing chain strands is given by  $q$ , then  $\Sigma_{eff} = q\Sigma$  if specific coupling chains are placed at the interface [12]. Alternatively, if bulk polymer failure is the main concern, then [13]

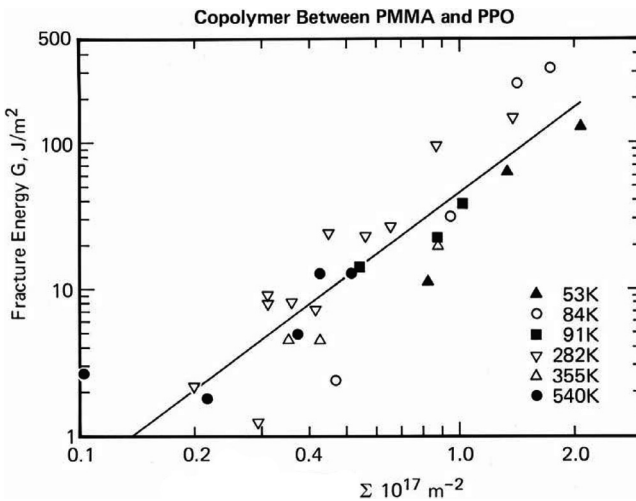
$$\Sigma_{eff} = q\Sigma [1 - (M_e/qM_n)] \quad (9)$$

where  $M_e$  is the molecular weight between entanglements and  $M_n$  is the number average molecular weight of the polymer.

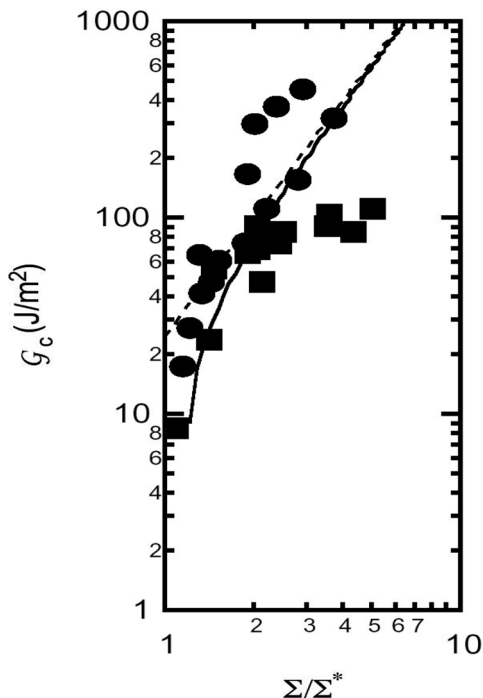
### Comparison with Experiments using Defined Coupling Chains

The model of crazing failure has been compared with experimental results obtained in a number of systems. The most direct tests have

been obtained by measurement of the fracture toughness of interfaces between immiscible polymers that have been toughened by placing a known amount of diblock copolymer at the interface. The immiscible polymers were chosen so that the interface had low toughness without diblock and the diblock chosen so that each molecule could be expected to act as a single stitch between the bulk polymers, so one block was miscible in each of the homopolymers. The main systems studied have been (1) PS-PMMA diblock copolymers joining PS and PMMA homopolymers or PPE and PMMA homopolymers and (2) PS-PVP copolymers joining PS and PVP homopolymers. Typical results, shown in Figures 3 and 4, agree well with the predictions of Equation (8) (and often the simpler Equation [7]) over a wide range of  $\Sigma$  and toughness. It is clear that the model works well when the molecular level failure process is chain scission, but not enough experimental data exist to be confident of its applicability when the failure is by chain pullout. The chain scission force  $f_b$  has been estimated to be in the range of 1.2–4 nN, where the main uncertainty comes from the uncertainty in the craze modulus ratio. In principle, the chain scission force would be expected to be time dependent. However, the time dependencies of the other parameters in Equation (8) are unknown, so it would not be possible to



**FIGURE 3** Variation of interface toughness with area density of copolymer for a range of different molecular weight PS-PMMA copolymers between PMMA and PPO (or PPE). Reprinted from Adhesion science and Engineering Vol. 2, *Micro-mechanical processes in adhesion and fracture* by H. R. Brown, pp. 221–242. Copyright 2002 with permission from Elsevier.



**FIGURE 4** Variation of  $G_c$  with  $\Sigma$  for both PS-PMMA diblocks between PPE and PMMA (●) and PS-PVP diblocks between PS and PVP (■) [9]. The solid line is a fit to Equation (8) and the dashed line to Equation (7). Reprinted from *Advances in Polymer Science* Vol. 156, 2002, pp. 53–136, *Adhesion and fracture of interfaces between immiscible polymers*, C. Creton et al. Fig. 22, with kind permission of Springer Science and Business Media.

estimate the time dependence of  $f_b$ . The model has also been found to work well in describing the mechanics of the interface between the semicrystalline polymers polyamide 6 and polypropylene coupled by the *in-situ* formation of a diblock copolymer at the interface. The toughness in this system was found to vary as  $\Sigma^2$  where  $\Sigma$  was measured after the sample was fractured. The model probably applied to this system because the failure occurred by the formation and breakdown of a primary craze in the polypropylene [14,15].

### Joining Immiscible Glassy Polymers

It has always seemed reasonable that the toughness of an interface between immiscible polymers would be controlled by either (1) the

amount of cross-interface entanglement, which itself is controlled by the interface width scaled by the distance between entanglements, or (2) the pullout of loops that cross the interface if they are not long enough to entangle. The validity of speculation (1) has been demonstrated by Cole *et al.* [16]. The main difficulty in application of the simple chain pullout model and the crazing failure model to the interfaces between immiscible polymers without coupling chains has been in estimating the effective value of  $\Sigma$  from the interface width and the known chain topologies. Silvestri and Brown [17] used a self consistent mean field technique to calculate the relation between interface width and  $\Sigma$ , based on the idea that the important molecular failure process is scission of entangled strands (the strands are really loops). The polymers are assumed to be of high molecular weight (ignoring the effect of chain ends) and  $\Sigma$  is taken as a measure of the number of polymer strands that have consecutive entanglements on each side of the interface. (The probability of a chain of material A crossing the interface from a position  $z$  to a position  $z'$  is found to be approximately proportional to the square route of the volume fractions of the material A at  $z$  and  $z'$ .) The volume fractions are assumed to follow the normal hyperbolic tangent law. The calculated values of  $\Sigma$  were used in Equation (8) to find the expected toughness.

A second model was proposed by Benkoski *et al.* [18,19] based on the idea that chain friction and pullout, rather than chain scission, are the important molecular scale failure processes. It is assumed that the chain failure force is given by  $f_c = Nf_{mono}$ , where  $N$  is the number of monomers in a loop that crosses the interface, and that

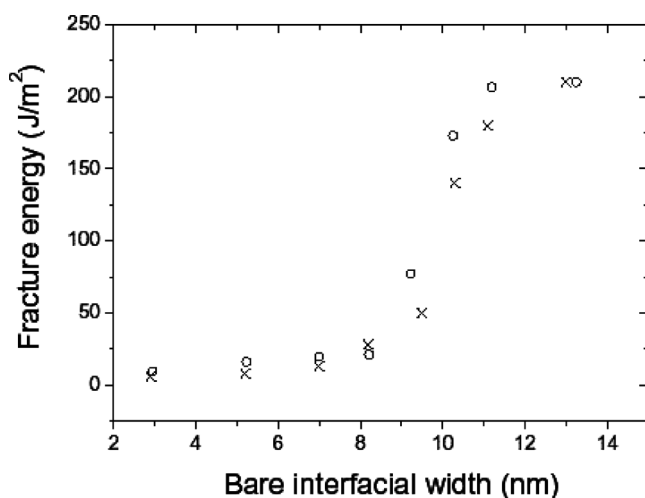
$$N\Sigma = \rho_{mer}w/2$$

where  $\rho_{mer}$  is the number density of monomers in the material and  $w$  is the interface width. The important parameter that is required for use in Equations (7) or (8) is the product  $\Sigma f_c$ , which in this model equals  $\rho_{mer}wf_{mono}/2$ .

The toughness of interfaces between immiscible amorphous polymers without any coupling agent has been the subject of a number of experimental studies [19–22]. The width of a polymer/polymer interface is known to be controlled by the Flory-Huggins interaction parameter  $\chi$  between the two polymers. The value of  $\chi$  between a random copolymer and a homopolymer can be adjusted by changing the copolymer composition, so the main experimental protocol has been to measure the interface toughness between a copolymer and a homopolymer as a function of copolymer composition. In addition, the interface width has been measured by neutron reflection. Four different

experimental systems have been used, all containing styrene. Snell *et al.* studied PS joined to random copolymers of styrene with bromostyrene and styrene with paramethyl styrene [21,22]. Benkoski joined polystyrene to a random copolymer of styrene with vinyl pyridine (PS/PS-r-PVP) [19] whilst Brown joined PMMA to a random copolymer of styrene with methacrylate (PMMA/PS-r-PMMA) [20]. The results of the latter study are shown in Figure 5.

The different experimental systems all yield a similar pattern of variation of toughness with interface width. The toughness initially increases slowly with width at low interface width, and then increases rapidly with width and saturates at high width at a value close to the bulk toughness. The PMMA/PS-r-PMMA results are entirely consistent with Silvestri and Brown's model (also shown in Figure 5). The data obtained on the PS/PS-r-PVP was shown by Benkoski *et al.* to be consistent with their pullout model and they suggested that chain friction increases with the  $\chi$  value between the units of the copolymer. Hence, they suggested that chain friction might be dominant in PS/PS-r-PVP while entanglement and scission are dominant in PMMA/PS-r-PMMA. This explanation can qualitatively explain the differences between the different polymer systems studied and is consistent with the shape of the toughness *vs.* interface width curve seen with PS/PS-r-PVP.



**FIGURE 5** Comparison of the predictions of Silvestri and Brown's model of interface coupling (o) [20] with Brown's experimental data (x). Reprinted with permission from Silvestri, L., Brown, H. R., and Carra, S., *J. Chem. Phys.* **119**, 8140–8149. Copyright 2003, American Institute of Physics.

In addition to the experiments on joining immiscible polymers using diblock copolymers, a significant amount of work has been done on the use of multiblock and random copolymer layers following the observation that random copolymers can be effective coupling agents [23]. Some of the most recent work in this area has recently been summarized [24].

## Joining Cross-linked Polymers

When two cross-linked slabs of the same polymer are joined at a temperature above their  $T_g$  their interdiffusion is limited to just chain ends and loops between crosslink points. The toughness of such interfaces in polystyrene has been studied by Perez-Salas *et al.* [25]. In their system the interface was too weak to form a craze and the variation of toughness with crosslink density was entirely consistent with the pull-out model of Xu *et al.* [5].

## ELASTOMERIC POLYMERS

Micromechanical processes that control the adhesion and fracture of elastomeric polymers occur at two different size scales. On the size scale of the chain the failure is by breakage of van der Waals attractions, chain pullout or by chain scission. The viscoelastic deformation in which most of the energy is dissipated occurs at a larger size scale but is controlled by the processes that occur on the scale of a chain. The situation is, in principle, very similar to that of glassy polymers except that crack growth rate and temperature dependence of the micromechanical processes are very important.

### Chain Pullout

The main difference between chain pullout processes in glassy polymers and in elastomers is that the friction per monomer in elastomers is expected to be very much lower than that in glasses and to be essentially viscous. The friction at zero rate is, thus, expected to be zero. However, as pointed out by Raphael and de Gennes [26], it does not follow that the toughness contribution from pullout should tend to zero as the crack velocity tends to zero. They considered a situation where connector molecules, chemically identical to a cross-linked network, were grafted to a rigid substrate. The network was left in contact with the substrate so that the connector molecules diffused into it. They pointed out that single or multiple chain fibrils would be expected to form in a craze-like zone at the crack tip when a crack propagates

along the interface. The dimensions (diameter) of these fibrils would be controlled by equilibrium between the fibril surface energy, tending to make them narrow, and the stretching energy of the chain. Thus, the connector chains formed highly stretched fibrils and when eventually these connectors pulled out the surface the stretching energy was dissipated. At zero crack growth rate Raphael and de Gennes predicted a toughness  $G_o$  given by

$$G_o - W_A \approx \gamma N \Sigma a^2 \approx k T N \Sigma \quad (10)$$

where  $W_A$  is the work of adhesion of the interface,  $\gamma$  is the surface energy of the polymer whose monomer dimension is  $a$  and  $N$  is the degree of polymerisation of a connector chain. This threshold toughness is relevant when the crack speed is below a critical value  $V^*$  where

$$V^* \approx \frac{E}{3 \Sigma \zeta_o N}$$

and  $\zeta_o$  is a monomer friction coefficient. Above the crack velocity  $V^*$  the toughness is predicted to increase linearly with  $V$  as

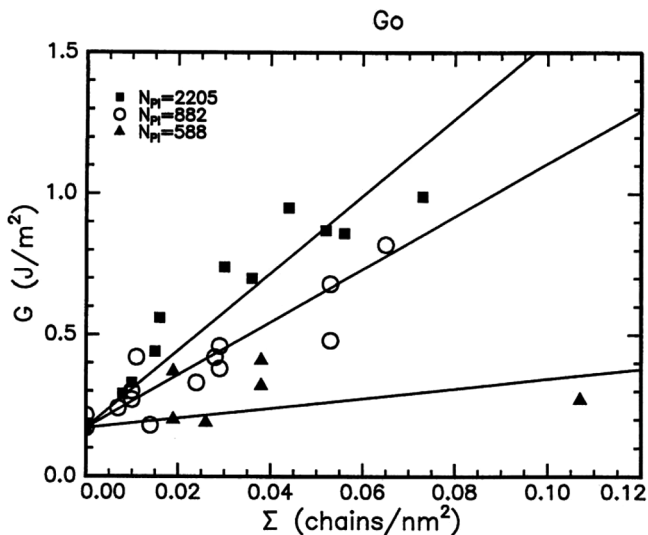
$$\frac{dG}{dV} \approx \frac{G_o}{V^*}$$

The effects of connector chain aggregation have been examined theoretically and found to modify the predictions at high values of  $\Sigma$  [27].

The actual toughness values predicted by this model are very small, typically of the same order as the work of adhesion. The model's predictions have been compared with experiment by a number of authors [28–31] using the JKR technique. In this test an elastomer lens is pressed against a flat substrate and the contact area studied as a function of the load. Using polyisoprene [28,29],  $G_o$  was found to vary with both the density and length of the connector chains as predicted (see Figure 6). The values of  $G_o - W_A$  obtained were consistent with the model but the value of critical velocity  $V^*$  was found to be very low. More recently  $G_o - W_A$  has been measured using polydimethylsiloxane (PDMS) lenses and results obtained that are again consistent with Equation (10) [32].

An important issue in consideration of connector chains in cross-linked networks is whether the connector chains will go into the networks. Penetration requires that the network swells and so at first sight would appear to be thermodynamically unfavorable, but full penetration also removes an interface between the connector chain layer and the network and so there is a free energy term favouring





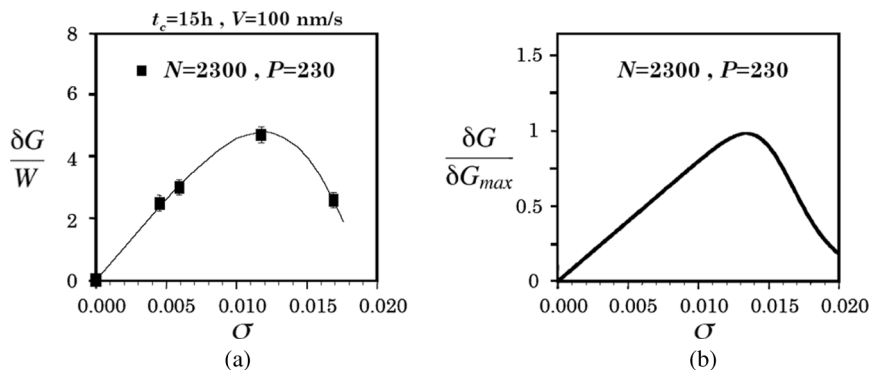
**FIGURE 6** The variation of  $G_0$  with  $\Sigma$  for three different molecular weight polyisoprene tethered chains in a cross-linked polyisoprene lens. Reprinted with permission from [27]. Copyright 1994 American Chemical Society.

penetration. Vilmin *et al.* have shown that full penetration is expected at low connector chain concentration  $\Sigma$ , while connector chain penetration goes to zero at high  $\Sigma$ . A model based on this idea has been shown to agree well with experimental results obtained in PDMS [32,33] (see Figure 7).

### Chain Scission

The classic model that describes chain scission in elastomers was proposed many years ago by Lake and Thomas [34]. The aim of the model is to calculate the energy dissipated in breaking all the polymer strands that have adjacent cross-links on either side of the crack plane. The basic assumption of this model is that all the main chain bonds in any strand that breaks must be strained to the dissociation energy of a main chain bond. It is assumed that this energy in the strand is dissipated when the chain fractures. If a strand has a degree of polymerization  $N$  and each monomer unit contains  $n$  main chain bonds then

$$G_o = \Sigma N n U \quad (11)$$



**FIGURE 7** The left pane shows the experimental variation of the toughness of a siloxane network (degree of polymerization between crosslink points  $P$ ) and a substrate covered with end tethered siloxanes chains (degree of polymerization  $N$ ) at an area density of  $\sigma$  per  $\text{nm}^2$ . The right pane shows the theoretical prediction [30,31].

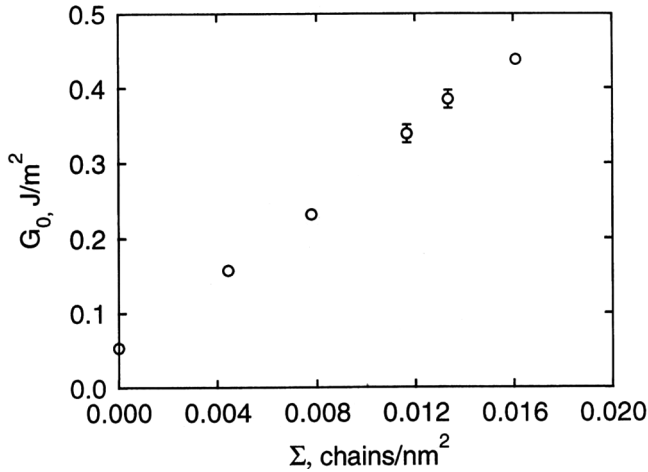
where  $U$  is the dissociation energy of a main chain bond. For cohesive failure

$$\Sigma = v_x d / 2 = A v_x N^{0.5} = B N^{-0.5} \quad (12)$$

where  $d$  is the mean distance between adjacent cross-links on a strand and  $v_x$  is the number of cross-links per unit volume and  $A$  and  $B$  are known constants depending on the flexibility of the polymer chain and its density. Combining these two equations demonstrates immediately that  $G_o$  is predicted to vary as  $N^{0.5}$ .

The Lake-Thomas model is specifically applicable for the threshold toughness, that is to say the toughness as the crack speed tends to zero, as there are expected to be viscoelastic contributions to the toughness at finite crack growth rates.

The predictions of the Lake-Thomas model have been compared with measurements of cohesive toughness obtained at high temperatures and low crack growth rates, often in materials swollen in a solvent. Good agreement between experiment and the model is normally found [35]. The model has also been found to be consistent with the use of an end-linkable siloxane connector chain between a PDMS lens and a substrate [36,37] (see Figure 8). In this work the length of the strand between crosslinks was much greater than the length between entanglements and the relevant strand length was  $\sim 2N_e$ .



**FIGURE 8** The variation of the threshold toughness  $G_0$  with  $\Sigma$  when an end-reactive PDMS chain was coupled into a PDMS network. Reprinted from [35] with permission from Elsevier SAS.

### Interface Slip

When an elastomeric material adheres to a rigid substrate, the huge elastic mismatch causes considerable shear stresses to occur at the interface. Chaudhury and coworkers [38,39] have demonstrated that these shear stresses can cause failure mediated by interfacial slip. The toughness of the interface was shown to be controlled, not by the work of adhesion but by the shear stress that the interface could withstand. The existence of the slip was demonstrated explicitly by placing fluorescent beads in the material close to the interface and observing their motion. In the original work the process was modelled as a dewetting and the energy assumed to be dissipated within a wetting wedge. However, recent experiments, where the distortions of the elastomeric film have been observed in more detail, have shown that the energy dissipation can be explained by simple viscoelastic distortion within the elastomeric adhesive [40].

### CONCLUSIONS

At the scale of polymer repeat unit or chain, failure tends to occur by the detachment of simple van der Waals bonds, by chain pullout or by chain scission. All these processes can be found at both glassy and

elastomeric polymer interfaces. The energy dissipated by these processes is very small; so toughness, either of a material or at an interface, requires that the chain scale processes couple into processes that occur in a larger volume and so dissipate more energy. For a glassy polymer, the large scale process is normally crazing whilst in an elastomer it is viscoelastic deformation. A quantitative understanding of failure and toughness hence requires an understanding of coupling between the processes that occur at different length scales. The understanding is good for simple coupling chains at glassy polymer interfaces, but more work is required to obtain a quantitative understanding of other situations in glassy polymers or failure in elastomeric or many semicrystalline systems.

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