Adhesion between polymers

by H. R. Brown

This paper is concerned with recent work that relates to the adhesion between nonreacting polymers. Advances in the understanding of cracks at bimaterial interfaces are considered, with particular emphasis on their implications in the interpretation of adhesion tests. An interpretation of the peel and blister tests is then discussed. Consideration is given to mechanisms of polymer failure as they relate to adhesion, with an emphasis on the distinctions between the properties of glassy and elastomeric materials. Polymer self-adhesion and its relation to interdiffusion are reviewed and compared with the adhesion of miscible polymers. In considering the adhesion between immiscible polymers, emphasis is given to the use of copolymers as coupling agents at the interface.

Introduction

Adhesion is an immensely complicated area concerned with the strength of the coupling that can occur between any pair of materials. It is also a subject of wide-ranging utility with a steadily increasing importance in many technologies. In this paper we restrict the subject to just the adhesion between pairs of polymeric materials. Consideration is also restricted, in the main, to adhesion that is *not* caused either by reactive chemical systems forming bonds across the interface or by mechanical keying between the materials due to roughness of the interface. The main subject of this paper is the adhesion between nonreactive polymers.

The adhesion between nonreactive polymers is itself a broad area in which it is necessary to consider a number of different cases. We first examine self-adhesion of thermoplastics and some polyimides and then consider the adhesion between different materials. The large difference in the mechanical properties between elastomers and thermoplastics makes it necessary to consider different mechanisms of adhesion in these two groups of materials.

The adhesion between two identical noncrosslinked elastomers, normally referred to as *tack*, is very important in rubber technology, particularly in the building of complex structures such as car and truck tires. Tack is caused both by dispersive forces across the interface (requiring wetting) and by interdiffusion of the long chain molecules across the interface. The equivalent adhesion between glassy or semicrystalline polymers is created by heating the materials above their glass transition temperature to permit interdiffusion, and is referred to as *welding* or *crack-healing*. The main distinction between the tack of elastomers and the welding of thermoplastics is not in the joining mechanism, which is polymer interdiffusion in both cases, but in the separation or fracture mechanics. Fracture toughnesses are controlled by the local mechanisms and the mechanical properties of a material. Consequently, fracture toughnesses tend to differ significantly for elastomers and thermoplastics [1].

The adhesion between two different nonreacting polymers is controlled by the entanglement between the two materials. If the materials are essentially insoluble in each other and the interface between them is very narrow, low adhesion can be expected. However, if the materials have a broad interface, they normally adhere strongly. There are two exceptions to this rule. First, the adhesion between the two polymers can be greatly increased if a third polymer that is miscible in both polymers is present at the interface and entangles with both polymers. Second, if at least one of the two polymers is elastomeric and has a mechanical energy loss spectrum such that energy is lost by viscoelastic processes in crack propagation, then, for finite crack propagation rates, considerable adhesion can be measured with essentially zero interdiffusion. This latter case demonstrates that broad generalizations have not yet been found in the area of adhesion that are valid across material types.

Tests of adhesion are essentially fracture tests and, like the cohesive or bulk fracture of a material, they require an understanding of the mechanics that occurs close to the crack tip and of the material deformations caused by this mechanical situation. At an atomic scale, the forces that actually cause the formation of new surfaces are due to, and are themselves influenced by, the continuum deformations that occur close to the crack tip. Models that attempt to ignore the complex crack-tip processes and thereby directly relate the results of some ill-defined mechanical test to a chemical property at an interface are inevitably restricted to showing some correlations across only a limited range of systems.

In this paper we describe some recent work on the mechanics of interfaces and then consider the interpretation of adhesion tests. The recent theoretical and experimental work on polymer–polymer adhesion is then reviewed. We first discuss adhesion of glassy polymers, considering both bare interfaces and interfaces in the presence of diblock and random copolymers. The final part of the review is concerned with the situation in which the material on one side of the interface is elastomeric. Much of the work described here involved the use of a thin layer of a copolymer, often a diblock copolymer, at the interface between two bulk homopolymers. [A diblock copolymer is a material in which each polymer chain consists of two homopolymer chains (blocks) that are joined together at one point.] The diblock copolymers are useful because they permit the formation of well-defined interfacial structures. They are also directly useful in some blends and additives.

Tests to measure adhesion

Most of the recently developed adhesion tests are based on fracture mechanics. Adhesion fracture mechanics tests are crack propagation tests with the requirement that the crack must propagate close to or along the interface. Such tests are not normally specific to particular material types; even if one is concerned only with polymer–polymer adhesion, tests that are developed for other materials are often useful. In fracture mechanics tests, the results are given as either G_c, the critical value of G, the strain energy release rate (or fracture toughness), or K_c, the critical stress intensity factor. Since G_c is a measure of the energy dissipated per unit crack area formed, it has units of surface energy. Numerically, it is normally orders of magnitude larger than both thermodynamic surface energies and the energies necessary to break chemical bonds and form a new surface in a polymer. The vast majority of the energy that G_c measures goes into the necessary plastic or viscous processes that occur round a crack tip in loading the actual tip to the breaking point.

In the fracture mechanics of bulk materials [2], there are three possible independent modes of deformation at the crack tip: the opening mode I, described by K_I and G_I, a shear mode II in the plane of the sample, K_{II} and G_{II}, and an out-of-plane shear mode III, K_{III} and G_{III}. In general, in cohesive failure of bulk materials, only the opening mode is important, since cracks normally travel in a direction that maximizes the opening mode, ensuring that the contributions of the other modes are insignificant. The only case where shear modes are significant is in materials with grossly anisotropic fracture properties, such as in fiber-reinforced composites. In adhesion we are concerned with interfaces between two different materials. This introduces two extra complexities to the situation. First, the crack is constrained to follow the interface rather than find its own path, so there is considerable opportunity for the crack to propagate in mixtures of modes I and II. Second, modes I and II are not, in principle, separable at interfaces between materials of different elastic properties, although in modeling an approximate separation is often useful.

The difficulties in the continuum elasticity analysis of the problem of a crack at a bimaterial interface have been recognized for many years [3]. The solution for the case of a traction-free crack at a bimaterial interface gives a nonphysical result that oscillates close to the crack tip in such a way that the two materials must occupy the same points in space. In reality the crack surfaces are not traction-free; they must touch and push against each other. A second problem is that the stress and deformation fields given by the elasticity analysis, unlike the situation for a crack in a single material, cannot be separated into the three independent modes, since the apparent ratio of opening to shear mode depends on the distance from the crack tip. In practical terms, both the oscillations and the mode mixing often occur very close to the crack tip, where the linear elastic solutions are no longer valid. Very close to the crack tip, the stresses are high, so the deformations are caused partly by viscoelastic or plastic processes. These processes are highly nonlinear in the stresses, so the oscillations and scale effects that are predictions of linear elasticity are normally ignored, permitting the use of the classic modes I and II. A stress pattern around a crack tip at a bimaterial interface can be described by a complex K^*. As the elastic constant difference between the two materials is reduced to zero, K^* can be related to the normal K's so that $K^* = K_I + iK_{II}$ [4]. The ratio of the two modes is then described by the phase angle Ψ of the complex K^*. Rice [3] has emphasized that, for materials of significantly different elastic properties, a large change in crack length can change the phase angle of K^* without any change in the ratio of tension to shear loading.

Recently Williams and coworkers [5, 6] have proposed a new scheme for the analysis of mixed-mode failure that they suggest applies to materials in which the plastic zone is relatively large, as is often the case in polymers and polymer composites. They point out that the approach described in the previous paragraph is based on the assumption that the stress around the crack tip outside the plastic zone can be described by a dominant singular elastic stress field of the form $r^{-1/2}$. When the plastic zone is large this assumption is no longer true, and they suggest an analysis based on a global (rather than local) approach and the partitioning of a globally obtained G so that $G = G_I + G_{II}$. Using their experimental results, Williams et al. compared their global model with a local model of Hutchinson and Suo [7] and concluded that the former scheme results in a more consistent interpretation of the data.

Interfacial failure is really the only situation in isotropic materials where crack propagation can occur in a situation other than pure mode I (opening mode). There exists therefore very little information on the effect of phase angle Ψ on cracking. However, a number of tests have recently been developed and characterized specifically to obtain such information [8, 9]. These tests are basically asymmetric fracture mechanics tests where Ψ has been calculated as a function of the crack length and modulus ratio of the two materials. In the systems studied by Cao and Evans [10], Ψ did not have massive effects on the crack resistance, though, as expected, the critical K is always lowest for $\Psi = 0$.

The effect of Ψ has been found to be very large in some interfaces between glassy polymers, and in particular, in the interface between polystyrene (PS) and polymethylmethacrylate (PMMA). The toughness of this interface was found to be about 200 J/m^2 when measured using geometrically symmetric compact tension, double torsion or double cantilever beam samples [11, 12]. However, the measured toughness dropped to about 12 J/m^2 when an asymmetric double cantilever beam sample was used [12]. The asymmetric sample was stiffened on the PS side to cause a K_{II} component that would tend to push the crack into the PMMA. Optical observation of the fracture surfaces showed that this large drop in the measured toughness came about because, in the symmetric samples, the crack tip crazes tended to propagate from the interface into the PS (PS has a lower crazing resistance than PMMA). Since these crazes were suppressed in the asymmetric samples, the crack propagated at much lower G_c. A similar but weaker effect can be observed by using a wedge-opened double cantilever beam, where there is considerable compressional stress in the direction of crack propagation. Wool [1] measured a toughness of 45 J/m^2 for the PS/PMMA interface using such a test. This effect of phase angle has been observed in a number of other glassy polymer pairs such as PMMA/polyphenylene oxide (PPO), PS/styrene acrylonitrile (SAN), PS/polycarbonate,[1] and PS/poly 2-vinyl pyridine (PVP) [13], though in these four cases the effect is not as large as it is with PS/PMMA. In each system the lowest interfacial G_c is found when the K_{II} component is chosen to drive the crack into the material with higher craze resistance. Hence, it seems possible that the effect comes from the different crazing properties of the two materials rather than their different elastic properties.

There is considerable interest in the adhesion between materials that are in the form of thin films. The adhesion of thin films is most commonly measured using peel tests, though such tests work only when one of the materials is reasonably ductile. Peel tests work very well in measuring weak adhesion, but their interpretation becomes problematic when the adhesion is strong. This problem occurs because strong adhesion causes high peel forces and hence, for thin strips, the deformation in the peeled strip ceases to be entirely elastic. A considerable amount of the peel energy then goes into yielding the peeled strip in bending rather than going into crack tip processes. There are two basic approaches to overcome the yielding problem; one can either calculate and correct for this extra plastic work, or redesign the test to decrease the plastic work. Attempts to calculate this plastic work have mainly considered two regimes. Gent and Hamed [14] developed a model for very thin peeled strips where the bending curvature was controlled by the strip thickness: Essentially, the bending radius could not be less than the strip thickness. They showed that the plastic work, and hence peel energy, increased with increasing strip thickness. Kim and Aravas [15] considered the alternative regime where the bending curvature was greater than about four times the strip thickness. Within this regime the plastic work of bending decreased with increasing strip thickness. Kim's approach, when it applies, gives a "universal peel diagram" that permits the extraction of the real joint toughness from the peel force. Williams [16] has developed a model that spans the whole thickness range and predicts a maximum in peel energy at an intermediate

[1] H. R. Brown and K. Char, unpublished data.

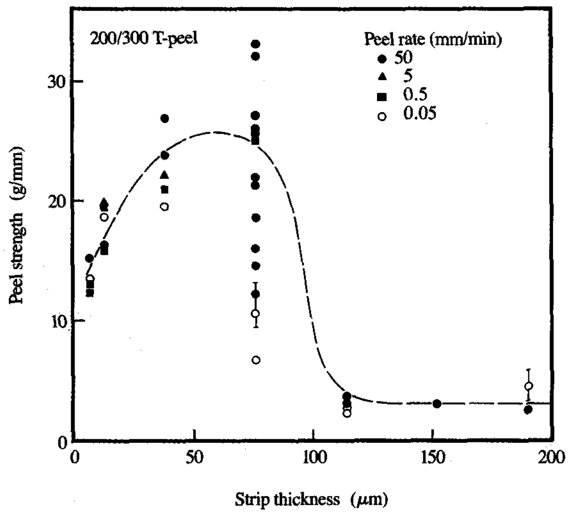

Figure 1

Peel strength vs. strip thickness for a joint made by curing a polyimide layer at 200°C, depositing a second layer from solution, and curing the pair at 300°C. The position of the maximum is clearly dependent on the peel rate. Reproduced from H. R. Brown and A. C. M. Yang, *J. Adhesion Sci. Technol.* **6**, 333 (1992), with permission.

thickness. An example of this maximum is shown in **Figure 1**.

The problems in peel testing are caused by the sample yielding during bending. One approach to circumventing this difficulty, which has been taken by Gent and Kaang [17], is to decrease the peel angle. They have shown that a reduction of the peel angle from the standard 90° to 45° or 30°, and preferably an extrapolation to zero peel angle, is a sensible approach. Williams' analysis described above has been used to correct for the bending plastic work; hence, it has been shown [18] that the G_c of a polyethylene–PET joint is independent of peel angle over a wide range of angles between 30° and 150°. This result is perhaps surprising, as one might have thought that the mode mixity, and hence toughness, would change with peel angle. However, it has been shown that Ψ, when calculated by classical elastic techniques or by global analysis, changes very little with peel angle [19].

There is considerable interest in using blister tests rather than peel tests to measure the adhesion of thin polymer films. Allen and Senturia [20] have advocated an island blister geometry where there is a small attached circle in the center of a detached annulus. Pressurizing the annular blister propagates the interface crack and so decreases the radius of the inner circle. This test has been analyzed in comparison with both the normal blister test [21, 22] and a peninsular blister test in which the blister has a rectangular outline with a long central attached strip. It has been shown that the circularly symmetric normal and island blister tests are not greatly different from peel tests with the usual problems of plastic bending; however, the peel angle can be small. The peninsular blister tests appear to have a genuine advantage in suppressing the bending plastic work. Another way of decreasing the plastic bending work is to greatly increase the thickness of the film to be detached so that its deformation is only elastic. The "inverted blister test" described by Fernando and Kinloch [23] is a way to realize this aim while still studying the adhesion of a thin film adhered to a thick substrate. The top surface of the thin film is glued down to a second rigid substrate, and then a blister is formed between the thin film and the original substrate. Because the interface being studied must be weaker than the interface between the thin film and the top substrate, this technique is probably most useful in situations when the film is very thin or fragile.

Adhesion between homopolymers

• *Self-adhesion and adhesion between miscible polymers*
When two pieces of an amorphous polymer are brought into contact at a temperature above their glass transition temperature, the chains from the two sides interdiffuse. This interdiffusion causes the strength of the interface to increase with time until it reaches the cohesive strength of the material. The main concerns in this area are to understand the diffusion processes at the interface and the relation between the diffusion-controlled interpenetration and the strength or toughness of the interface. The diffusion processes always occur when the material is above the glass transition temperature T_g, but the mechanical adhesion tests are normally done at ambient temperature. Hence, considerable differences would be expected between the tack of elastomers and the welding of glassy polymers, since failure properties are very different above and below T_g.

The diffusion of long chain polymers has been a subject of intense research activity in the last decade, with the result that most of the processes are now well understood [24]. Chains move primarily along their contour length by the process of reptation, because motion in other directions is limited by entanglement with other chains. When two blocks of material are brought into contact, there are, of course, no chains crossing the interface. Initially sections of chains cross the interface until they hit entanglement constraints. However, the main process by which chains cross the interface is reptation, in which, for each chain, a chain end must cross the interface first. The chain end can be visualized as dragging the rest of the chain behind it. Clearly the number and length distribution of the chains that cross the interface in a time t less than the reptation time (the time for a chain to completely leave its tube) are controlled by the molecular weight of the chains and distribution of chain ends close to the original interfaces.

A range of models have been proposed to relate the interdiffusion across an interface to the strength or toughness of the interface [1, 25–27]. These models differ in their assumptions of what molecular parameters are relevant in the control of strength or toughness. For example, in some models the important parameter is assumed to be the number of loops across the interface; in others, it is assumed to be the average contour length of the diffused chains. A range of other assumptions also exist in the literature. Any model that claims to operate over a wide range of joint toughnesses and, in particular, up to the point when the interface is as tough as the bulk material, must also be a model of bulk toughness. Hence, one approach to finding which molecular parameters are relevant involves comparing the theoretical predictions with experimental results for both the annealing time dependence of joint strength and the molecular weight dependence of bulk strength [1]. In the author's opinion, this problem is not yet solved, since the current models of welding and bulk toughness are not consistent with what is known about the micromechanics of failure by crazing.

From the large difference in failure properties of polymers above and below T_g, one might expect that welding of glassy polymers is very different from tack of elastomers. However, a remarkable feature of the experimental situation is that in both classes of materials [1, 27, 28], failure stresses vary as the joining time $t^{1/4}$, and failure energies vary as $t^{1/2}$. These power laws fit the experimental data over a wide time range in glassy polymers but over a rather restricted range in elastomers. The experimental situation for the molecular weight dependence of healing rate is not so clear. However, for both polystyrene and polymethylmethacrylate, it has been shown that the healing rate drops only slowly with increasing molecular weight [1]. In most experiments, it would appear that bulk strength or toughness is obtained when the interdiffusion distance is approximately a coil size.

The adhesion between polyimide films has been a subject of considerable interest in the electronic and computer industries, since polyimides are frequently used as dielectrics. Polyimide thin films are normally formed by laying down a polyamic acid layer from solution and then curing it to the imide form. The T_g of the polyimide layer is at least as high as the curing temperature. The main concern is the adhesion between a cured first layer and a second layer deposited on it and then cured. Although the layers are made of the same material, they are never both above their T_g's. During curing of the second layer, while it is mainly polyamic acid, it is above its T_g but not necessarily miscible with the polyimide underlayer, which meanwhile is below or close to its T_g. Not surprisingly, the adhesion between such layers of polyimides is frequently poor.

One technique to improve the adhesion between polyimide layers is to cure the first layer only partially. By using this technique it has been shown that the adhesion between layers increases with the amount of interdiffusion, but a surprisingly large interdiffusion distance is required to give good adhesion [29]. Two techniques have been described to increase the interdiffusion and hence the adhesion. Swelling the cured polyimide in a solvent before depositing the second layer can cause a modest increase in adhesion [30]. Much greater adhesion increases can be obtained by converting a thin top layer of the imide back to the polyamic acid by wet chemical techniques before coating on the second layer [31, 32]. Excellent adhesion has been demonstrated with a number of polyimides as long as the converted polyamic acid layer was at least 20 nm thick.

• *Adhesion between immiscible polymers*

The equilibrium width of an interface between homopolymers of high molecular weight is controlled by the balance between a repulsive enthalpy of mixing of the two materials, normally described by their Flory–Huggins interaction parameter χ and mixing entropy. The interaction parameter is defined so that it is positive when the interaction between the materials is repulsive (the normal case). Helfand and Sapse [33] showed that the width of the interface w is given by

$$w = \frac{2a}{\sqrt{6\chi}}, \qquad (1)$$

where a is the size of a statistical segment. The variation of concentration of the two materials (the segment density profile) through the interface was shown to follow a hyperbolic tangent profile.

Interfacial widths and profiles can be measured using neutron reflection [34]. This technique, which has been developed primarily in the last few years, is particularly useful if there is a considerable gradient of neutron scattering length across the interface. The neutron scattering length of hydrogen is very different from that of deuterium, so the gradient can be obtained by using a deuterated material at one side of the interface. Initially there was some surprise because the measured interfacial widths were considerably broader than those predicted by Helfand's theory. However, it has recently been realized that the interfaces are not entirely flat because they contain capillary waves. When allowance is made for the capillary wave broadening to the measured segment density profile, good agreement between experiment and theory is found [35, 36].

Interfacial strength is by no means as well understood as interfacial structure. As polymers gain their strength from entanglement of chains, and entanglement between the materials on either side of the interface is bound to increase with increasing interfacial width, it is to be expected that both interfacial strength and toughness will increase with interfacial width. De Gennes [37] has suggested in an approximate theory that interfacial strength should vary as $\exp(\chi^{-1/2})$, but there are no suitable data sets to test this theory. In a recent paper [38], Willett and Wool measured both χ and the interfacial toughness between polycarbonate (PC) and a series of styrene–acrylonitrile copolymers. They showed that χ went through a minimum and the interfacial toughness went through a maximum at a copolymer composition of about 23% by weight of acrylonitrile. This experiment helps to confirm the qualitative expectation that toughness decreases with increasing χ, but a quantitative understanding must wait for the development of a theory that incorporates both the relation between toughness and entanglement and the relation between interfacial width and entanglement.

Diblock copolymers at glassy polymer interfaces

If an A–B diblock copolymer is chosen so that block A is miscible with polymer C and block B is miscible with polymer D (the pairs A and C and also B and D can be of the same material), a thin layer of the diblock is expected to organize at the interface between C and D so that block A is dissolved in C and block B in D. Density profiles of the different components can be calculated using mean field theory [35] and can be measured by both neutron reflection and secondary ion mass spectroscopy (SIMS). Russell and coworkers have found good agreement between experiment and theory when a polystyrene–polymethylmethacrylate (PS–PMMA) copolymer was placed between PS and PMMA homopolymers [39].

When there is an attractive enthalpy of mixing (negative χ) between a block and a bulk polymer, that block has been shown to stretch away from the interface. For the case in which the block was PS with a molecular weight of about 140 000 and the bulk polymer was polyphenylene oxide (PPO), the block was stretched by about a factor of 3 in agreement with a simple theory of enthalpy-induced brush stretching [40].

Many polymer–polymer interfaces are mechanically weak because there is little chain entanglement across the interface. An organized layer of a diblock copolymer can toughen the interface if each block entangles with one of the bulk polymers. In essence, each molecule of the diblock copolymer forms a single stitch across the interface. The effectiveness of the diblock in this situation therefore depends on the strength of the coupling between it and the bulk polymers. If the diblock molecules are short, interfacial failure causes them to pull out from one side of the interface. If the diblock molecules are long, they are more likely to break than to pull out [41]. The criteria that determine whether pull-out rather than chain scission takes place have been examined by the use of partially deuterated diblock copolymers, in which one of the blocks is deuterated. A technique such as SIMS is used to detect the presence of deuterium on the fracture surfaces. It has been shown that the molecular weight between entanglements, M_e, for each block in the relevant polymer, controls the transition between pull-out and chain scission. If at least one of the blocks of the copolymers is shorter than M_e, the diblock will pull out [13, 42]. If the molecular weights of both the blocks are much larger than M_e, the diblock will break close to its junction point [41]. Some deuterium depth profiles that demonstrate this chain scission situation are shown in **Figure 2**. The precise block molecular weight that controls the transition seems to depend on the mode of failure, but it always seems to occur in the range between 1 and 4 M_e.

The maximum stress that the interface can sustain can be assumed to be a product of the pull-out or failure force of a diblock molecule f_s with the number of diblock molecules per unit area of interface, Σ. When Σf_s is small, the stress is not sufficient to cause crazing, the most common form of nonelastic deformation in a glassy polymer, and so the interface tends to show little toughness. Xu et al. [43] have proposed a model for the pull-out energy in which they predict that the interface fracture toughness G_c should be of the form

$$G_c \sim N^2\Sigma, \qquad (2)$$

where N is the degree of polymerization of the pulled-out chains. Washiyama et al. [44] have demonstrated that this relation is a good fit to the data that they obtained in the pull-out regime where there was no crazing. Wool has proposed an alternative relation for chain pull-out based on assumptions of unstable failure and a particular form of energy transfer at the crack tip. In this way he predicts that G_c varies as $N\Sigma$.

When the stress that the interface can sustain becomes large enough to initiate a crack tip craze, i.e., when $\Sigma f_s > \sigma_c$, where σ_c is the craze stress, the vast majority of the failure energy is dissipated in the growth of the crack tip craze. Hence, G_c is essentially a measure of the energy of formation of this crack tip craze. The current author proposed a model [45] for this energy based on the realization that the stress concentration at the crack tip in the craze increases with craze width. The crack is assumed

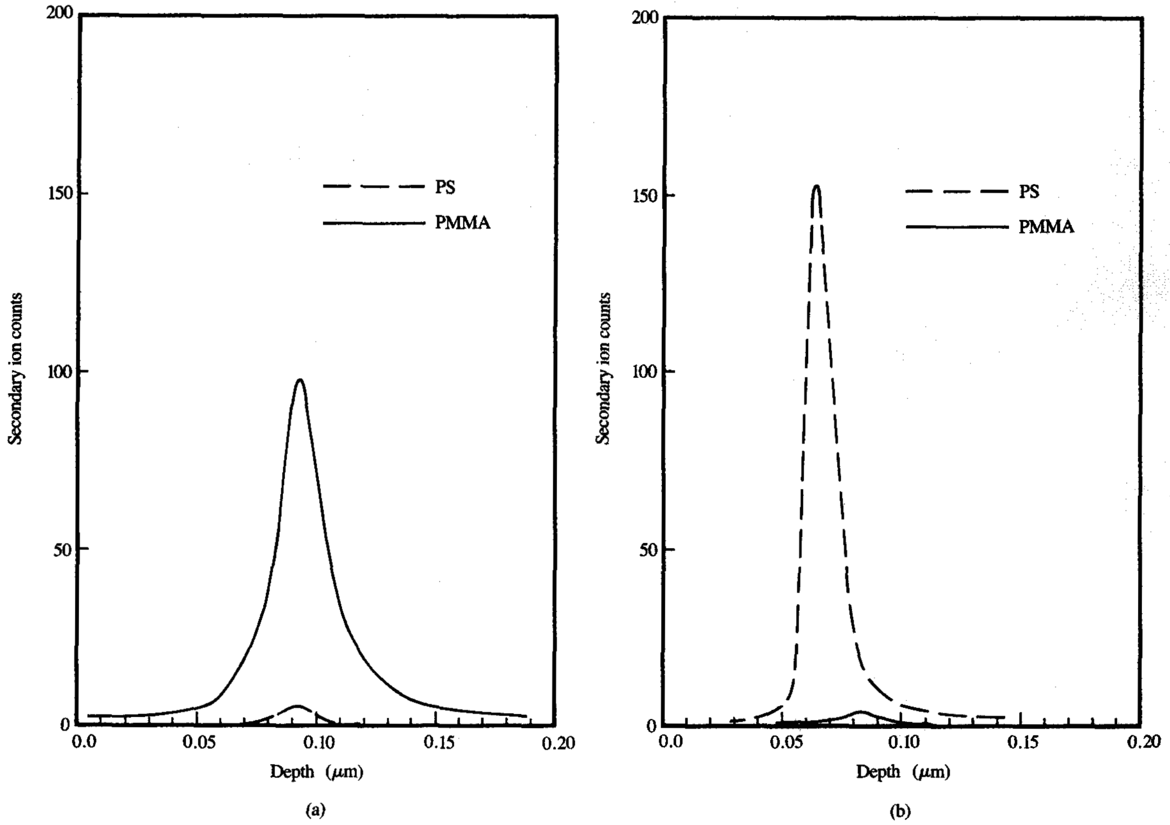

Figure 2

SIMS deuterium depth profiles under the fracture surfaces when a PS–PMMA copolymer is used between PS and PMMA homopolymers: (a) PMMA fracture surface; (b) PS fracture surface. The dashed and solid lines in the figures refer respectively to the situations in which the PS half and the PMMA half of the copolymer were deuterated. The fracture surfaces were covered with a thin layer of hydrogenated material before analysis. From [49], reproduced with permission.

to propagate when the force on the diblock chains in the craze fibril at the crack tip reaches f_s. This model predicts that

$$G_c \sim f_s^2 \Sigma^2 D/\sigma_c \,, \tag{3}$$

where the craze is described by the mean fibril diameter D and the craze stress σ_c. In the pullout regime f_s might be expected to vary linearly with N, while it should be constant, independent of N, when the chains fail by scission. The predictions of this model, and in particular the prediction that, in the scission regime, G_c depends on Σ^2 and is independent of diblock molecular weight, have been compared with experimental results for a series of symmetric PS–PMMA diblocks between PPO and PMMA homopolymers [46]. The comparison, shown in **Figure 3**, confirms the validity of the model. These results have been used to obtain estimates of the force needed to break a polymer chain. The value obtained, about 2×10^{-9} N, compares well with estimates of the chain breakage force obtained by other techniques [45, 47].

As diblock copolymers are used as coupling agents between components of a blend, there is bound to be concern about the optimum value of the diblock molecular weight. It is evident that if the diblock molecular weight is very low, the interface will fail by chain pull-out with a low toughness. If, on the other hand, the diblock molecules are very large, the maximum value of Σ at saturation will be relatively low, again giving low toughness. There is an optimum diblock molecular weight that occurs at a value about equal to the molecular weight at the transition from chain pull-out to scission, so it is

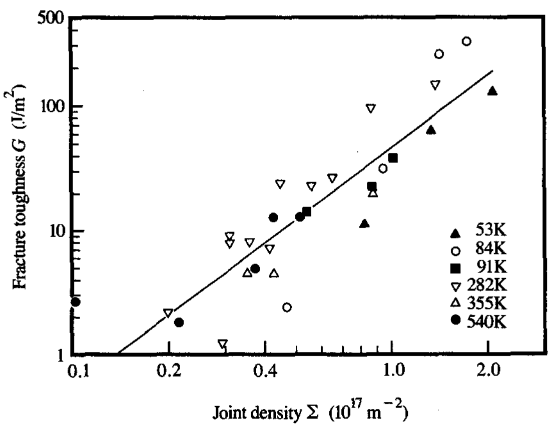

Figure 3

Variation of fracture toughness with number of PS–PMMA copolymer molecules per unit area at an interface (labeled as joint density). The line is drawn with a gradient of 2. From [46], reproduced with permission.

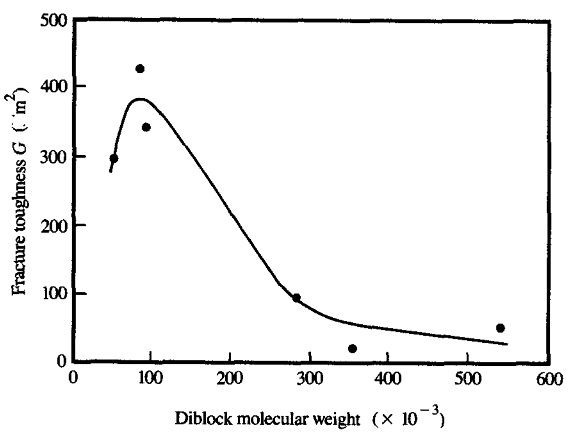

Figure 4

Maximum fracture toughness obtainable with a thin layer of PS–PMMA diblock between PS and PPO homopolymers as a function of the diblock molecular weight. The optimum molecular weight would appear to be about 100 000. From [46], reproduced with permission.

between 1 and 4 M_e per block [46, 48]. The behavior is shown in **Figure 4**.

Random copolymers at interfaces

An effective coupling agent at a polymer–polymer interface must be a material capable of entangling with the bulk materials on either side. Diblocks are not the only copolymers that are capable of entangling in this way, and it is not obvious that they have the optimum geometry. A different, much cheaper, copolymer geometry that has also been shown to be effective in this way is a random copolymer. As can be seen from **Figure 5**, a random PS–PMMA copolymer has been shown to be a very effective coupling agent between PS and PMMA and also to work between PS and PPO [49]. Random copolymers have also been shown to be effective between PS and poly 2-vinyl pyridine (PVP)[2]. It is presumed that the random copolymer functions by forming loops on both sides of the interface in a manner consistent with the theory of Balazs et al. [50, 51].

Chain pull-out in elastomers

If one or both of the polymers on either side of the interface are in the elastomeric state at the testing temperature, the whole issue of interfacial adhesion or toughness is profoundly changed. The deformation around the crack tip is bound to be mainly in the elastomer, and much of the energy loss in failure occurs, not close to the crack tip, but by viscoelastic deformation in a broad region around the crack tip. The viscoelastic deformation losses appear as a temperature- and rate-dependent factor that multiplies the crack-tip energy losses G_I. The main concern of this review is these crack-tip processes that contribute to G_I.

A number of models of chain pull-out have been proposed, particularly by de Gennes and coworkers [52–54]. They predict that G_I increases linearly with crack growth rate, V, from a threshold value at zero rate. The threshold is predicted to be the sum of the surface and stretching energies involved in the formation of the single chain fibrils that are assumed to be necessary for pull-out. The rate of increase of G_I with V is expected to vary linearly with the effective chain friction. Until recently, it was assumed that the chain friction was just given by $N\zeta_0$, where ζ_0 is the monomer friction coefficient. However, Rubinstein et al. [55, 56] pointed out that the relevant relaxation time is that of an end-tethered chain in a network, so the chain friction coefficient is actually much larger than $N\zeta_0$.

Measurement of G_I is complicated by the viscoelastic dissipation discussed earlier. However, this extra energy loss becomes insignificant at very low crack velocities and also when the specimen volume is small. One way to make measurements with small specimens is to use the Johnson–Kendall–Roberts (JKR) technique, together with

[2] E. J. Kramer, Cornell University, private communication.

the small lenses introduced by Chaudhury and Whitesides [57, 58]. In this technique, a lens-shaped elastomer is loaded against a flat substrate for a time to allow a bond to form at the interface. The sphere is then unloaded, and the interfacial crack slowly propagates, driven by the stored elastic energy in the crosslinked elastomer lens. The basic idea is shown in **Figure 6**.

The JKR technique has been used to study chain pull-out when a crosslinked polyisoprene (PI) lens was coupled to a PS substrate by a layer of PS–PI block copolymer [59, 60]. The results were found to be qualitatively consistent with the pull-out models. The threshold value of G_c was found to increase with diblock copolymer coverage Σ and also with the molecular weight of the PI part of the diblock. The apparent chain friction observed was much higher than the simple friction $N\zeta_0$ and was consistent with the value predicted by the recent model of Rubinstein.

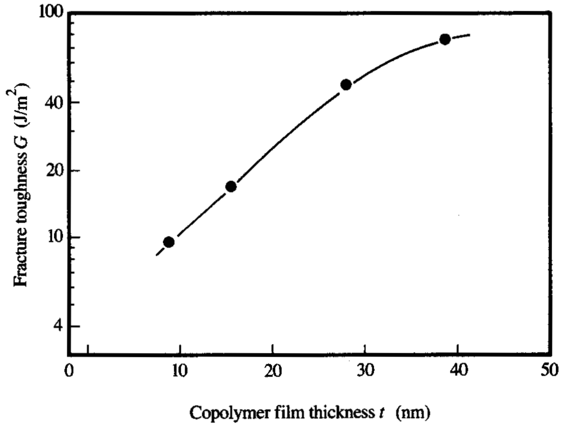

Figure 5

Variation of the fracture toughness of an interface between PS and PMMA homopolymers with the thickness of a layer of random PS–PMMA copolymer at the interface. From [49], reproduced with permission.

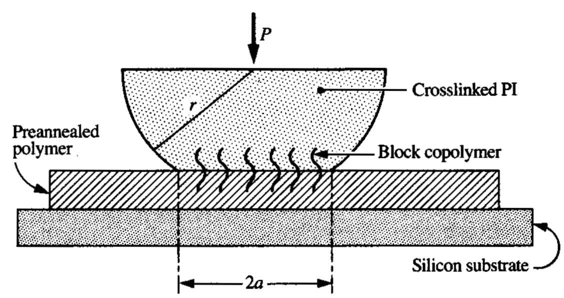

Figure 6

Geometry of the JKR experiment. The load P is applied to join the polymer at the interface, then removed to start the crack propagation.

Conclusions

There have been considerable advances in the understanding of polymer–polymer adhesion in the last few years. The subject of adhesion involves the relation between the physico-chemical processes that occur at a molecular scale and the micro- and macro-mechanical processes that occur during fracture. Hence, the improved understanding of adhesion has required improved mechanical analysis and fracture tests, improved micromechanical analysis of crack-tip processes, and new techniques for the study of molecular scale processes at the crack tip. It is hoped that in the future these techniques can be extended to the more difficult situations where there is chemical reaction at the interface.

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