Fracture and Toughening Mechanisms in Polymer Alloys

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ABSTRACT

The fracture behavior of alloys of rigid polymers is examined. The toughening effect of the dispersed phase is studied via model systems. In all cases cavitation of or caused by the toughening phase is found to precede plastic shear deformation. The evidence points strongly to the need for cavitation before the plastic shear deformation can occur. The experimental results are compared to a recent theoretical model. The role of elastomeric tougheners is discussed.

KEYWORDS

Polymer alloys; Polymer blends; Toughening; Fracture; Impact modification; Epoxy; Rubber toughening; Poly(phenylene oxide); Nylon.

INTRODUCTION

In recent years a number of high performance polymer alloys have become available. These alloys differ from conventional polymer blends in that at least two of the major components possess high (for polymers) modulus, and together they form a multiphasic structure. When properly compounded, these alloys, like their metallic counterparts, often possess desirable mechanical, chemical and processing properties not found in the individual component polymers. The development of new polymer alloys of this type has therefore become an important focus in many laboratories. Unfortunately, when two arbitrarily chosen rigid polymers are blended together, the result is usually a material with little mechanical integrity, much less toughness. This is due to a lack of adhesion at the interface. However, these problems can be overcome by the use of chemicals or copolymers that promote good dispersion of one polymer phase in another and at the same time provide some strength at the interface. These problems belong in the realm of chemistry and chemical engineering and do not concern us directly here. Nevertheless, the morphological and interfacial properties do have a most significant influence on the mechanical strength and fracture toughness of these alloys, and the interpretation of the deformation mechanisms must be in the context of a given set of these properties.

Alloys of rigid polymers, even when the dispersion is uniform and the interfacial strength is high, are usually quite brittle, though some slight synergism has occasionally been observed

(Koo *et al.*, 1985). The most successful examples of these alloys which possess high toughness all contain varying but quite small amounts of elastomers. Presumably, the presence of the elastomer is critical for the high toughness of the material. The elucidation of the role of the elastomer in the deformation process, which is not well understood, is essential for the successful development of these important new materials. A comprehensive model that specifically quantifies the role of the elastomeric toughener has been proposed by Evans *et al.* (1986). The purpose of the present paper is to describe these events in toughened plastics and alloys in some detail, and to examine the applicability of Evans' model in light of our results. The hope is that once the role of the elastomer is understood, then we will be able to make polymer alloys with optimal toughness.

In a recent paper (Sue and Yee, 1988) we described the fracture mechanisms in one polymer alloy consisting of nylon 66 [PA] and poly(phenylene oxide) [PXE] with a dispersion of an elastomer in the latter phase. Without the elastomer, this alloy is quite brittle (Shibuya *et al.* 1987). These fracture mechanisms and the sequence in which they occur are depicted in Fig. 1.
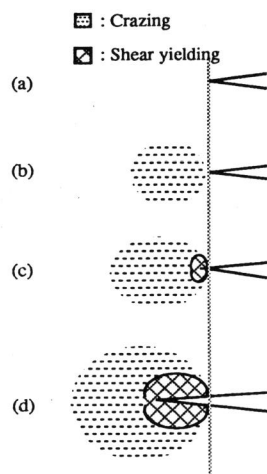

Fig. 1 : A sketched sequence of the toughening mechanisms in PA/PXE blend. (a) the initial starter crack; (b) the formation of a crazed zone in front of the crack tip as the specimen is initially loaded; (c) the formation of initial shear yielded zone around the crack tip as the hydrostatic tension is relieved due to the formation of crazes; (d) the shear strain energy builds up which causes the growth of the plastic zone and, at a critical value, the crack propagates in a stable fashion.

A TEM micrograph of the crack tip region is shown in Fig. 2a. Among other observations we found that a dilatant zone consisting of a massive amount of micro-crazes has formed well ahead of the propagating crack. The crazes appear to be nucleated by the elastomeric phase (see Fig. 2b). Near the crack tip the material undergoes significant plastic deformation by shear. However, a zone of micro-crazes completely surrounds the plastic shear zone. In the latter zone, some of the micro-crazes are collapsed by the large shear deformation. This observation shows that cavitation in the form of crazing precedes plastic shear deformation. Plastic shear deformation, when it occurs, has the effect of decreasing the dilatation rather than enlarging the crazes. In the wake of the crack no bridging particles are found. The process described suggests that the toughness has intrinsic and extrinsic contributions. The intrinsic contributions come from crazing and plastic shear deformation which dissipate energy. The precise amount of this contribution can, in principle, be calculated by the area under the loading-
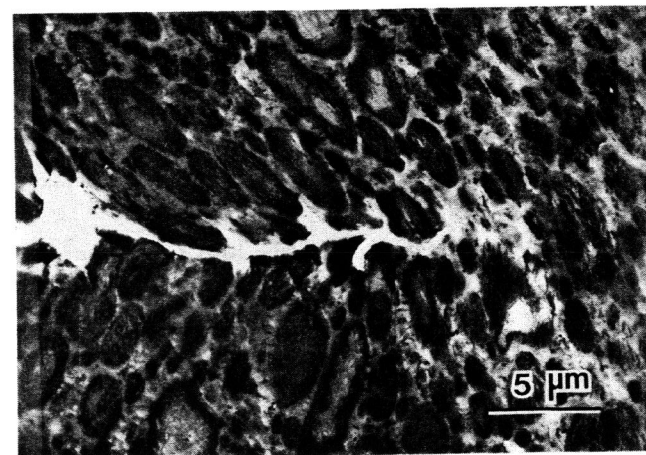

Fig. 2a : A TEM micrograph of the crack tip of a PA/PXE blend.
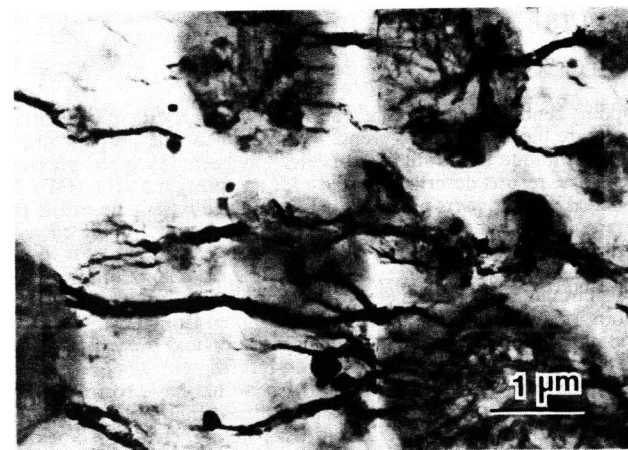

Fig. 2b: A TEM micrograph of a region beyond the crack tip (in the dilatant zone).

unloading curve for the appropriate stress state integrated over the volume of the process zone. The extrinsic contributions stem from the modification of the stress intensity factor by the plastic deformation processes: the crazing and the plastic shear deformation change the load bearing capability of the material ahead of the crack tip, thus providing a crack shielding effect by reducing the stress intensity factor. At the crack tip, the large plastic deformation of the dispersed particles has the effect of blunting the crack, thus reducing the stress intensity further. Finally, the dilatation and the unloading of the material in the wake of the crack must reduce the stress intensity still further. Some important questions remain unanswered. For example, how much does each mechanism contribute to the total toughness? Are the mechanisms multiplicative rather than additive as suggested by Evans *et al.* in 1986? Is there one overriding

mechanism among all that have been observed? To answer these questions, we need to know not only the *sequence* of events, but also the *causal relationship*, if any, between these events. This information can be obtained from experiments on simpler model systems. The results from these experiments are described in the following paragraphs. Data on some of the properties of these materials are presented in Table 1.

TABLE 1: Fracture Toughness values for several polymers and their alloys.

Matrix:	Fracture Toughness J_{Ic} (G_{Ic}) in kJ/m^2		
	Neat Resin	Rubber-Modified	Rigid-Modified
Polyamide 6, 6	5.0	21.0[a]	9.3[b]
DGEBA / piperidine	0.5	3.0[c]	1.0[d]

Notes: (a) modified with ca. 20% rubber. (b) modified with ca. 50% PXE.
(c) modified with ca. 10% rubber. (d) modified with 10% PXE.

RESULTS

Rubber-Toughened Epoxy

We used a four-point-bend fracture specimen that has two nearly identical starter cracks on the tensile edge to capture the deformation events occurring near the propagating crack tip. The application of this technique to the study of plastics has been described previously elsewhere (Sue et al., 1988). The results described here are for an epoxy material (DER 331 cured with piperidine) toughened with 10 parts of a carboxyl-terminated butadiene-nitrile [CTBN] rubber. The CTBN forms a dispersion approximately 2 microns in diameter in the epoxy matrix. Fig. 3 is a transmitted light optical micrograph of a polished section taken from the center of a specimen with an arrested crack. A large, faint, circular zone emanating from the crack tip can be observed. This circular zone in turn envelopes a smaller, elliptical but intensely dark zone. Both zones are observable due to the presence of cavitated rubber particles. The contrast in intensity is due mainly to the difference in the concentration and the extent of cavitation of the particles. This elliptical region is also known to be birefringent when viewed using crossed-polarized light. The birefringence is due to shear bands that have formed in the epoxy. The size of this shear-banded zone is both shorter and slimmer than the zone containing the more intensely cavitated rubber particles. Since the stresses are highest at the crack tip but diminish gradually away from it, these results demonstrate unequivocally that the cavitation of the rubber particles *precedes* the formation of the shear bands. This contradicts assumptions by others that the cavitation of the rubber particles is the *result* of plastic shear deformation (Evans et al., 1986; Kinloch et al., 1979; and Dekkers et al., 1988). Having clarified this important point, we hasten to add that the plastic shear deformation does, in this case, enlarge and elongate the voids near the crack tip. Finally, in the wake of the crack, no bridging rubber particles are found.

We now address the question of whether the cavitation of the rubber particles is necessary. These epoxies are quite brittle without the rubber phase (Yee and Pearson ,1986). If, however, solid, highly cross-linked rubber particles that are resistant to cavitation are added to the epoxy, little toughening effect is found (Riew). Clearly, then, the cavitation is necessary both to the development of the shear bands (at the crack tip) and to the achievement of high toughness. This conclusion also contradicts that of Dekkers and co-workers (1988), who view the cavitation as an undesirable by-product of the shear banding process. We will show more support for our conclusion in a subsequent section on epoxy/PXE.
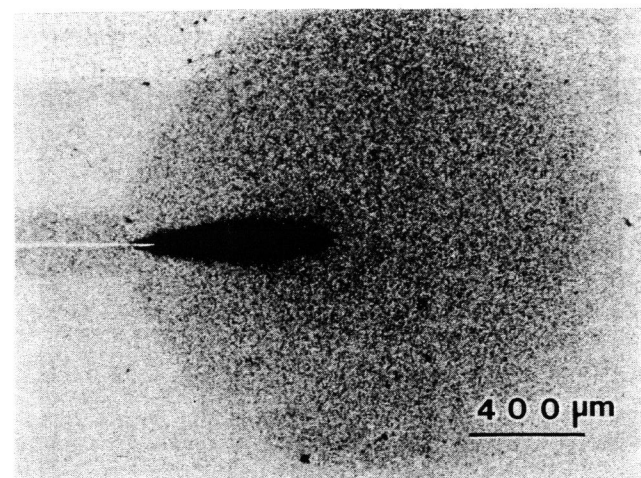

Fig. 3 : An optical micrograph, taken in transmission, of the plastic zone in a rubber toughened epoxy

PXE-modified Epoxy

We now return to a model material consisting of an alloy of two rigid polymers. A concept that has gained a certain degree of acceptance is that toughening can be effected if the toughening phase can generate stress concentrations, thus nucleating more shear bands (Kinloch et al., 1979; Dekkers et al., 1988; Yee 1987). We have recently determined the relative properties of the phases that would satisfy the requirements of the foregoing concept (Sue, 1988). Yet, the experimental results presented thus far shows that the cavitation that occurs in the toughening particles has a causal relationship with the subsequent formation of shear bands. The toughening phase must then be capable of cavitation in addition to being able to generate stress concentrations. We now show results on a system where the dispersed phase is quite resistant to cavitation -- epoxy/PXE. The preparation and other details relevant to this system will be presented elsewhere (Pearson). Briefly, the PXE is initially dissolved in DGEBA epoxy, but is precipitated out of the solution as a fine dispersion about 1 micron in diameter during the curing of the epoxy. Fig. 4 is a transmission optical micrograph of a thin section taken from an epoxy/PXE specimen tested in tension to yield. The plane of the section is parallel to the tensile direction. The profusion of shear bands attests to the effectiveness of the PXE, which has a lower modulus than epoxy, to enhance their formation. Fig. 5 is a transmission optical micrograph of a thin section taken from a epoxy/PXE specimen containing two blunt notches and fractured in four-point bending. This section shows that the deformation ahead of the unbroken blunt notch consists of a slip line field around the notch tip. Near the tip of the slip line field, a few cracks are visible. With very sharp starter cracks there are only a few cracks present at the crack tip and only a very limited amount of plastic shear deformation. PXE does toughen epoxy (Table 1)-- a result also found by Raghava (1988) and Sun (1988) on similar thermoplastic-modified epoxies. However, the toughening mechanism in this case seems to be the generation of secondary cracks . The conclusion we can draw from these results is that the ability of a dispersed particle to nucleate shear bands does not guarantee toughening effects by enhancing plastic shear deformation when the stress state has a high hydrostatic component, such as that near a crack tip. A recent calculation (Sue, 1988) shows that if the particles are capable of cavitating, then the hydrostatic tension around each particle would be reduced, and the effective (octahedral) stress concentration would be increased by ca. fivefold. Experiments are underway to verify the toughening effects of a PXE particle that can cavitate.
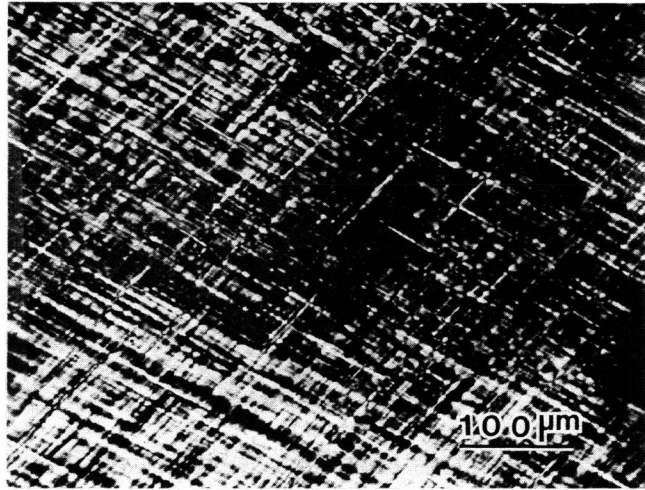
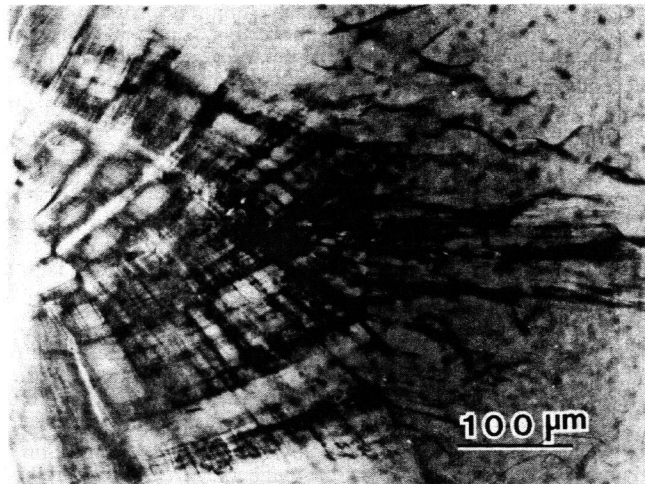Fig. 4 : An optical micrograph showing shear bands in a deformed tensile specimen of a Epoxy/PXE blend.

Fig. 5: An optical micrograph of the deformed region at a notch tip (taken from a DN-4PB specimen of Epoxy/PXE).

DISCUSSIONS

The results presented here are consistent with our previous results on CTBN-toughened epoxies Yee and Pearson, 1986) and PXE-toughened nylon (Sue and Yee, 1988). The sequence of events and the causal relationships between the various deformation mechanisms have been studied in some detail in this work. In all the cases studied, the cavitation event (which includes crazing), if it occurs, takes place before shear banding. We have also shown strong evidence that the cavitation is *necessary* for the formation of shear bands if the stress field has a high hydrostatic component. However, it is important to note that not all the cavitation has led to the formation of shear bands. This is evident from the fact that the cavitation zone is always larger than and indeed envelopes the shear-banded zone. We can infer from this that there must be a critical effective (octahedral) stress value for the formation of shear bands which must be reached soon after the cavitation event. In none of the cases have we observed evidence of particle bridging in the wake of the crack.

A model of rubber toughening in plastics, proposed by Evans *et al.,* (1986), has been formulated to take into account the contributions of specific deformation events. This model is particularly relevant to the present work because of the clear roles assigned to the rubber phase. Specifically, the rubber particles are said to initiate cavities in the matrix *because* the matrix is undergoing plastic flow. Plastic hole growth then contributes further to the toughness. Furthermore, the rubber particles may stretch across the crack planes. The stretching and tearing of the rubber particles dissipates energy, thus enhancing the toughness. The rubber particles that bridge the crack planes in the wake of the crack would increase the toughness even more. The authors are careful to point out that the model is preliminary in nature and that more experimental results are necessary to verify it. In this model, the toughness of the composite J_c has two components: J_0, the fundamental toughness, and ΔJ_c, the additional toughness contribution from the tougheners. That is,

$$J_c = J_0 + \Delta J_c \tag{1}$$

The additional toughness scales with the width of the plastic zone h, i.e.,

$$\Delta J_c = \beta h \tag{2}$$

where

$$h = E J_c g / \sigma_y^2 \tag{3}$$

β and g are numerical parameters, σ_y is the yield stress, and E is the modulus. By substituting Eqs. 2 and 3 into Eq. 1, we get -

$$J_c = J_0 / [1 - \beta g E / \sigma_y^2] \tag{4}$$

According to Eq. 4, the final toughness J_c scales with the fundamental toughness J_0. Process zone effects are thus said to be multiplicative.

We now examine the Evans model in light of the experimental results. We note that the plastic zone size is related to the final toughness by Eq. 3. The validity of this equation depends on two assumptions, viz., that the plastic zone is formed by shear yielding, and that the final toughness J_c involves shear yielding mechanisms only. Following this, if we now equate h with the width of the plastic zone corresponding to the bounds given by the cavitated zone, Eq. 3 would not be valid, since not all of the zone involves shear yielding. If, on the other hand, we equate h with the width of the plastic zone corresponding to the bounds given by the shear-banded zone, Eq. 1 would not be valid, since the contributions from cavitation mechanisms would be neglected. Since the conditions assumed by Eqs. 1 and 3 cannot be simultaneously

satisfied, Eq. 4 is invalid. However, it is important to point out that if the cavitation were a *consequence* of the shear banding associated with the particles, then the difficulties with the assumptions noted above would be obviated. Questions about the crack bridging mechanism are moot since no bridging particles are found. We plan to perform in-situ experiments in the scanning electron microscope to discover if bridging particles exist during crack propagation.

The results and discussions presented above give clues to the desirable properties of toughening rubber particles. Had the Evans model been shown to be correct, then the rubber particles should be tear- and cavitation-resistant. This could best be accomplished by using rubber with high molecular weight and a fairly high level of cross-linking. On the other hand, our results indicate that the principal role of the rubber particles appear to be that of cavitating at the "right moment", i.e., just before the brittle fracture stress of the matrix is reached, taking into consideration the stress concentration effect of the rubber particle itself. For this, the cross-link density of the particles must not be too high. The exact cross-link density could be estimated if its relationship to cavitational resistance is known.

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