Load History Dependence of Fracture in Rubber-Toughened Epoxies

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ABSTRACT

The most common toughening mechanisms in structural adhesives are viscoelastic processes which means that the fracture energies for bulk adhesive specimens and bonded joints vary with loading history. Although this is well known, relatively few studies have examined this effect in detail. The work here explored this issue by measuring fracture energies for bulk specimens at a wide range of constant cross-head speeds and a series of more complex loading histories. The results for the constant cross-head speed experiments were consistent with previous studies in that decreasing the loading rate produced an increase in toughness. For most rates, the behavior was approximately linear elastic with little or no r-curve behavior. Below a critical rate, however, there was a transition to ductile failure with a very high fracture energy, a large r-curve, and significant permanent deformation that clearly violated the linear elastic approximation. With the more complex loading histories, the toughness increased with the time a sample was held at high loads prior to fracture. This was attributed to growth of the crack-tip deformation zone before the failure point was reached.

INTRODUCTION

The technology to toughen a cross-linked resin, without undue sacrifices in the other mechanical and thermal properties, is well known [1,2]. Moreover, there have been numerous studies on the mechanisms of toughening in such systems [1,2]. It is now generally agreed that most toughening mechanisms are viscoelastic in nature so they depend on loading history. Despite this knowledge, however, there have been relatively few detailed studies of rate effects in these materials. The work that has been done was usually limited to changing the cross-head speed in a constant cross-head speed experiment [2]. The research here seeks to address this issue by conducting tests over a wide range of cross-head speeds and a series of more complex loading histories. The specific histories examined were selected because they are relatively simple extensions beyond the constant cross-head speed tests.

EXPERIMENTAL PROCEDURE[a]

Two different toughened epoxies were used. For the constant cross-head speed tests, the samples were made with acrylic-rubber particles (copolymer of 2-ethylhexyl acrylate and glycidyl methacrylate) generated as a dispersion in an liquid epoxy resin (Dow Tactix 123 LER, a diglycidyl ether of bisphenol A {DGEBA}-type epoxy resin). Details of this material, which was developed by Dow Chemical Co., are given in the literature [3]. The dispersion was diluted with the epoxy give a rubber particle to epoxy mass ratio of 0.200 and piperidine was added as a curing agent to give a piperidine to epoxy mass ratio of 0.050. For the experiments with more complex loading histories, a second system was used because these tests required larger amounts of material than were available with the acrylic system. This second system used carboxyl-terminated poly-butadieneacrylonitrile (CTBN) and DGEBA cured with piperidine. In this case, the CTBN to epoxy mass ratio was 0.188 while the piperidine to epoxy mass ratio was 0.050. Although the concentrations of constituents were different in the two systems, the volume fraction of the rubbery phase was similar (about 20 %), and this is often cited as the most important parameter [3,4]. Plates were molded with the two systems, and fracture tests were conducted with compact tension specimens cut from the plates. Details of the sample preparation and testing are given elsewhere [3-5].

Two types of fracture tests were conducted. The first type used a constant cross-head speed to load the samples until failure. The cross-head speeds ranged from 2 cm/min to 0.005 cm/min. For selected specimens, a grid was marked on the side of the sample, and the crack growth was monitored throughout the test. For the very low speed experiments, where stable crack growth was observed, a video microscope was used to follow this growth. The standard uncertainties in the crack length measurements were ± 0.5 mm without the microscope and ± 0.1 mm with the microscope.

[a] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the items are the best available for the purpose.

The second type of fracture test performed here involved more complex loading histories. Four different loading histories were examined but space limitations restrict the discussions here to the first three procedures. **Procedure A** served as a starting point for the more complex procedures that follow and involved constant cross-head speed experiments like those described previously. Samples were loaded to failure using either a slow (0.05 cm/min) or a fast (5 cm/min) speed. The average fracture energies at the slow speed, G_{ICS}, and the fast speed, G_{ICF}, were taken as reference points in the remaining experiments. **Procedure B** involved tests where the cross-head speed was changed during the course of the experiment. The specimens were loaded at the slow speed, but before the failure load was reached, the cross-head motion was shifted to high speed. A series of such experiments were conducted, and the independent variable was the transition point between speeds. This transition point was quantified by calculating the strain energy release rate using the crack length and load at the transition point and describing the result as a fraction of the reference value, G_{ICS}. A transition point of 100 % meant that the sample was loaded all the way to failure at the slow speed while a transition point of 0 % corresponded to loading to failure at high speed. Thus the results in procedure A are the limits in procedure B. The question of interest is how the behavior changes from one limit to the other as the transition point is shifted from 0 % to 100 %. **Procedure C** was similar to procedure B except that the transition involved a hold time as well as a speed shift. The samples were loaded at the slow speed to a load below the failure point. The cross-head was stopped, and the displacement on the samples was maintained for a specified hold time, t_1, before the samples were loaded to failure at the fast speed. Only one transition point was used, and it was selected based on the results from Procedure B. The independent variable in the tests was the hold time, t_1.

For all of the fracture experiments, the fracture energies, G_{IC}, were determined according to ASTM E-399. For the constant cross-head speed tests, the relative standard uncertainty in the fracture energies was ± 6 % while the relative standard uncertainty for the more complex histories was ± 10 %.

RESULTS AND DISCUSSION

Figure 1 shows a typical example of fracture energy as a function of crack growth for different loading rates in the constant cross-head speed experiments (type one tests). The initial studies examined speeds from 0.01 cm/min to 2.0 cm/min, and over this range, the behavior was similar to what has generally been reported in the literature for such materials; i.e. little or no r-curve behavior [1,2]. By r-curve behavior we mean that the resistance to crack growth increases as the crack propagates down the specimen so that there is a measurable region of stable crack growth with an increasing fracture energy. This continues until the crack growth becomes unstable or a plateau is reached where propagation occurs at a relatively constant fracture energy. Although a recent publication has reported a large r-curve effect in such materials [6], the initial results here gave only small r-curves at the lower loading rates. Nevertheless, the trend was towards such behavior as the loading rate was decreased. Consequently, experiments were conducted at even lower loading rates, and a video microscope was used to improve the detection of crack growth. For these tests, a transition to ductile failure with a large r-curve was found (0.005 cm/min curve in Figure 1). The change in behavior was very sharp; decreasing the rate by 200 fold from 2 cm/min to 0.01 cm/min produced only very modest changes in behavior, but a further 2 fold decrease to 0.005 cm/min altered the response totally. This sudden transition may be one reason why some authors have seen the r-curve behavior while others have not. It should be noted that at the slowest rate there was significant permanent deformation in the material so that the application of linear elastic fracture mechanics is probably not valid.

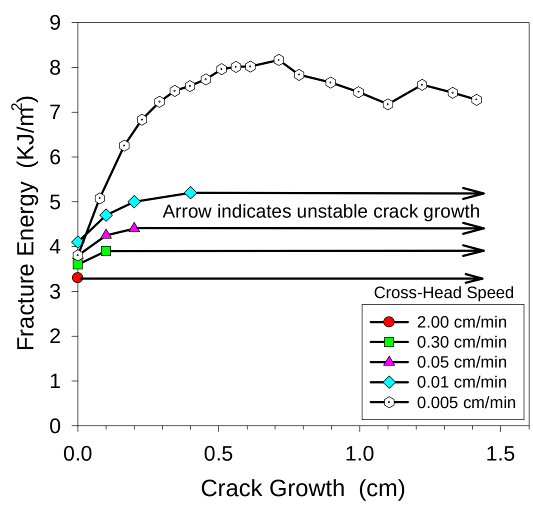

Figure 1: Fracture energy as a function of crack growth for different cross-head speeds (type one tests). The relative standard uncertainty in the fracture data is ± 6 %.

More complex loading histories were examined with the second type of fracture experiment. The data from **Procedure A** (constant cross-head speed to failure) gave baseline fracture energies of (1.86 ± 0.11) KJ/m^2 for the fast speed, G_{ICF}, and (2.27 ± 0.14) KJ/m^2 for the slow speed, G_{ICS}. This is not a large difference, but it is clearly outside the experimental uncertainty indicating a loading rate dependence of fracture energy like that seen above. The results from tests with **Procedure B** (shift from slow speed to high speed during experiment) are shown in Figure 2. The transition point indicates the fraction of the loading (in terms of strain energy release rate) conducted at slow speed before shifting to the high speed. Consequently, the limiting values, 0 % and 100 %, were the constant cross head speed results, G_{ICF} and G_{ICS}, respectively. For reference, these values are shown in the Figure as horizontal lines as well as points at 0 % and 100 %. The Figure shows that as long as the change in cross-head speed was below 80 % (or $0.8*G_{ICS}$), the final fracture energy was G_{ICF}. This was true if the cross-head speed below $0.8*G_{ICS}$ was all fast, all slow, or a combination of slow then fast. Only when the transition point was above $0.8*G_{ICS}$ did the final fracture energy increase significantly above G_{ICF}. This indicates that the last part of the loading curve was most important in determining the final behavior. Based on this result, the transition and hold point in Procedure C was taken as $0.95*G_{ICS}$.

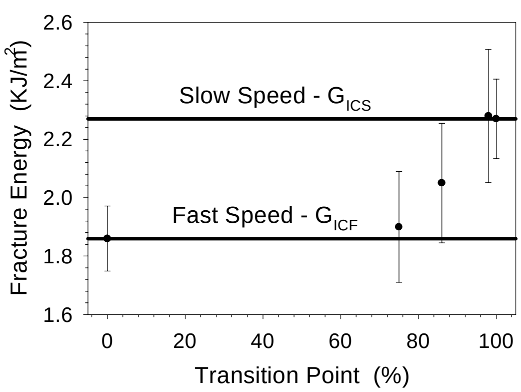

Figure 2: Fracture energy as a function of the transition point between slow and fast cross-head speeds. The horizontal lines indicate the limiting values at 0 % and 100 % (G_{ICF} & G_{ICS}). The bars indicate the relative standard uncertainty in the data.

Results for **Procedure C** (slow speed-hold-fast speed to failure tests) are shown in Figure 3 as a function of hold time. The zero hold time experiment was equivalent to Procedure B with a transition point of $0.95*G_{ICS}$ and that gave a fracture energy of G_{ICS}. This is shown in Figure 2 and 3 as the "Slow Speed" line. When there was a hold time between the change of speeds, the fracture energy increased above G_{ICS}. Initially, increasing the hold time increased G_{IC}, but all of the increase occurred within the first hour. Beyond that time, the fracture energy was constant. As a result, there was no transition to ductile failure as was seen in the first type of test conducted in this study even with hold times of 50 h. This may be because the material used in the complex history experiments (CTBN system) has a lower toughness than the acrylic system, but another contribution factor may be that the hold time in the experiments was at constant displacement not constant load. As a result, during the hold time, the load decreases thereby lowering the driving force for further deformation. For all the experiments conducted here, however, the fracture energy was a strong function of the loading history. The results are consistent with the idea that toughness depends on the size of the crack-tip deformation zone and both time and load can promote zone growth.

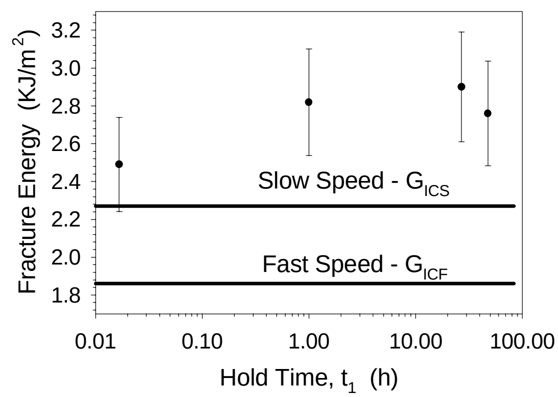

Figure 3: Fracture energy as a function of hold time at $0.95*G_{ICS}$. The error bars represent the standard error for the data while the lines represent the average fracture energies for slow and fast cross-head speeds (G_{ICS} & G_{ICF}).

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