

Fracture Toughness of an Epoxy System

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Synopsis

The fracture toughness of epoxy used in the bulk and adhesive form was measured by a previously developed technique. The uniform double cantilever-beam specimen, which was described earlier, was modified to a tapered beam, which simplified the experimental procedure and calculations for obtaining toughness measurements. By varying the ratio of hardener to resin and post-cure temperature on a single epoxy system (DER 332-TEPA), it was found that the toughness of the epoxy used in either bulk or bond form varied by a factor of approximately five. A particular combination of composition and post-curing temperature generally yielded higher toughness in the bulk than in the bond form. This was not always the case, however. At high post-cure temperatures, where the bonds were very tough, their toughness exceeded that of the bulk material. Hence, it does not appear possible to predict joint toughness from bulk toughness measurements. The toughness of joints was found to be a single-valued function of tensile modulus. For the bulk material, on the other hand, the toughness obtained on the epoxy having a specific modulus depended on the combination of composition and post-cure temperature. Joint toughness for any combination of composition and post-cure temperature depended only on the cracking rate. If the epoxy was the type that caused cracks to jump rapidly, the epoxy was tough and vice versa. For a particular epoxy system, toughness was increased by driving the crack at an increasing rate.

INTRODUCTION

Fracture mechanics is a relatively new discipline which relates the fracturing behavior of flawed bodies to applied loads. By its concepts, one defines a quantity, the fracture toughness, which has the same importance in brittle failure that yield strength has in ductile failure. In a ductile material, the load at which deviations from elasticity occur is associated with the yield point. In a cracked body the load that causes a stationary crack to propagate rapidly is associated with the fracture toughness (for initiation). The load that causes a running crack to stop is associated with an arrest toughness. Hence, the fracture toughness of a material is seen to be a measure of its ability to resist extension of a pre-existing crack. Whether it is evaluated for initiation or arrest, it can be defined either in terms of a critical stress intensity factor, K_{Ic} , or by the strain energy release rate, G_{Ic} . These two are related by Young's modulus E and Poisson's ratio ν , as shown in eq. (1).

$$G_{Ic} = (K_{Ic}^2/E) (1 - \nu^2) \quad (1)$$

When a load is applied to a cracked or flawed body, an initial crack will either not expand or expand slowly when the loads are less than those required to attain K_{Ic} or G_{Ic} . When the load is high enough to exceed these values, the crack extends catastrophically.

An evaluation of K_{Ic} requires a stress analysis at the crack tip which is not available for heterogeneous systems. On the other hand, G_{Ic} can be measured by energy methods. These are applicable to any system and thus fracture toughness in this paper is described in terms of G_{Ic} . The strain energy release rate is defined as:

$$G_{Ic} = (P_c^2/2b) (\partial C/\partial a)$$

where P_c is applied load at instant of fast crack extension, b is specimen thickness, C is specimen compliance = δ/P (δ is the displacement through which load P travels), and a is crack length.

A previously described procedure for measuring the fracture toughness of adhesive joints¹ has made it possible to investigate the influence of processing variables on toughness. Some preliminary studies carried out prior to the ones discussed in this report indicated that the chemical variables, i.e., post-cure temperature and ratio of hardener to epoxy, exert a far greater influence on toughness than the mechanical variables, adherend surface finish, or bond thickness. On the basis of these preliminary tests, the present study was undertaken to more completely define the influence of these two chemical variables.

A single epoxy system, Dow epoxy resin (DER) 332 and a room temperature curing amine hardener, TEPA, was used. The adherend for the joint specimens was the aluminum alloy 2024-T4.

The earlier report on toughness of joints also described two types of fractures: center-of-bond, and interphase. Since the latter fractures are difficult to analyze, possibly because of a poor definition of the crack front, only data obtained on center-of-bond failures are discussed. The combinations of post-cure temperatures and compositions that tend to produce interphase fractures were avoided whenever possible.

The techniques of fracture mechanics apply equally well to bonds and bulk material. Hence it was possible to compare the toughness of the epoxy when used in bulk versus adhesive form. The comparison was made by determining the influence of a particular variable, either post-cure temperature or ratio of hardener to resin, when the epoxy was used in the two different applications.

To compare tensile properties with fracture toughness, all values of bulk toughness obtained by any combination of composition and post-cure temperature were plotted as a function of modulus for identically produced tensile specimens. The same technique was used for comparing joint toughness and tensile modulus.

No attempt was made to find mechanisms for rationalizing the differences or relationships in properties; the report is concerned only with mechanical behaviors.

SPECIMEN PREPARATION AND TESTING PROCEDURE

Tensile Specimens

Tensile tests were used to characterize the mechanical properties of the epoxy system. The test specimens were cast rather than machined to avoid the introduction of residual machining stresses. The casting technique was designed to develop a thermal history identical with that used for both joint and bulk toughness specimens. Although both the DER 332 and TEPA were kept as free from extraneous materials and deterioration as possible, neither was filtered prior to use. The TEPA was refrigerated between the time of arrival and use, however.

Specimens were prepared by heating the desired epoxy-hardener mixture to 110°F., thoroughly mixing, and then casting the charge into warmed

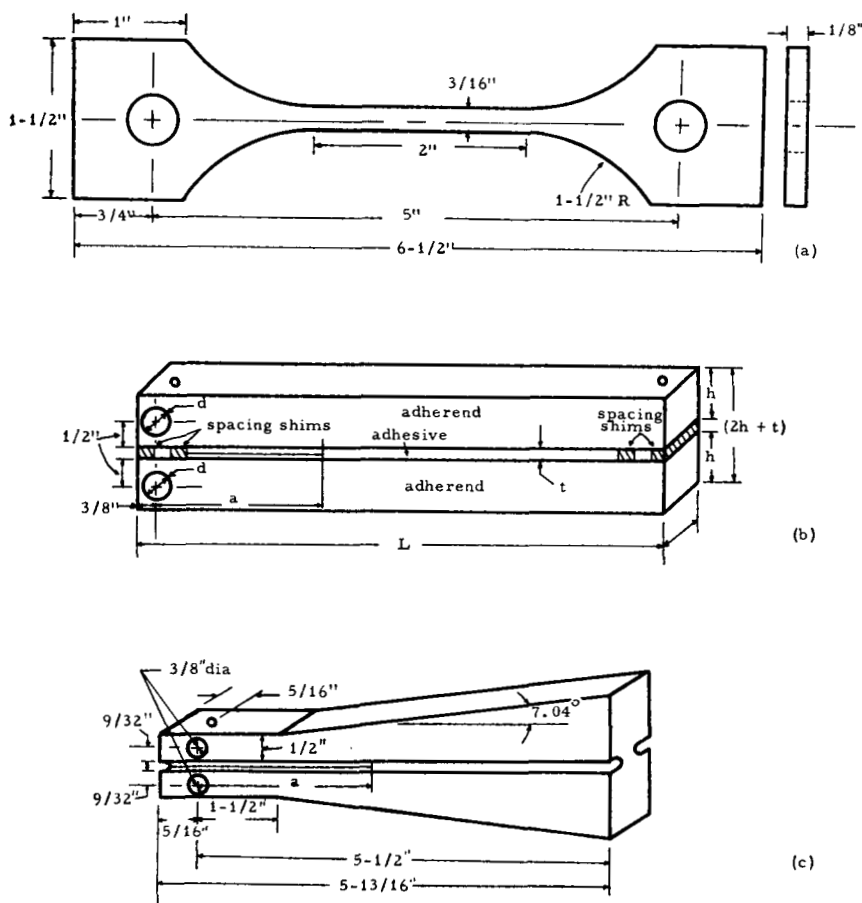


Fig. 1. Schematic diagrams: (a) tensile specimen; (b) uniform double cantilever-beam specimen; (c) tapered double cantilever-beam specimens (side grooves were needed only for bulk specimens).

silicone rubber specimen molds which had been spray-coated with a non-silicone parting agent (Surfak, Gibraltar Industries, Inc., Chicago, Illinois). The specimen cross section over the 2-in. gage length was slightly less than $\frac{3}{16} \times \frac{1}{8}$ in. Loading was by pin grip holes provided in the dumbbell ends of the specimen, as shown in Figure 1a. The mold temperature was maintained at 150°F. during curing to duplicate gelation conditions of the joints. Since the minimum specimen thickness was $\frac{1}{8}$ in. and the total weight of epoxy only 30 g., no serious problem was expected with exotherm. There was a temperature rise of approximately 25°F. at the dumbbell end of the specimen for the highest hardener contents (15–25 phr TEPA), however. This exotherm was evidenced by a slight yellowing of the ends of the specimens, but since the center test section was still quite light, it was assumed that the temperature rise in this volume was negligible. After hardening, the specimens were removed from the mold and post-cured in an air oven, on glass, at the desired temperature.

After post-curing, any rough edges around loading holes and at the corners of the test section were sanded smooth with 600 grit paper. Tensile tests were made on an Instron testing machine fitted for pin grips. Displacement, measured with a standard LVDT extensometer attached directly to the specimen with knife edges and rollers, was plotted against the load on an X-Y recorder. Since total extension to fracture was small, the entire load extension curve could be obtained with the sensitive extensometer used to determine elastic modulus.

Bulk Epoxy Specimens

Tapered double cantilever-beam specimens of the type shown in Figure 1c were used for measuring the toughness of bulk epoxy. This specimen shape was developed in order to obtain a relationship between load and toughness that was independent of crack length. The tapered specimen has the added advantage that a constant crack velocity occurs over the length of the specimen so long as the crack speed follows the constant machine crosshead rate. This characteristic and other details of the tapered specimen are described in the Appendix to this report. In order to maintain the crack in the desired plane of extension, however, it was necessary to groove the two sides of the specimen so only the center half of the specimen thickness was left in the test section. It was expected that the side notch geometry and particularly the radius at the notch bottom might influence the measured toughness values so that the geometry was varied for a number of identically produced specimens. The test data, however, indicated that variations in the side grooving over the range of investigation produced identical toughness values.

Because the bulk epoxy specimens were large compared to the tensile specimens, it was expected that these might exhibit an exotherm during curing, particularly when the specimen molds were held at 150°F. To evaluate this temperature rise some samples were cast in a water-cooled aluminum mold and compared with others cast in hot (150°F.) and warm

(100°F.) specimen molds. Thin thermocouples were buried in the castings and the epoxy temperature recorded over the full cure period. It was found that even with high hardener contents there was no temperature rise with the aluminum or warm silastic molds.

A few test samples were also prepared in which DER-TEPA was cast between epoxy adherends in order to duplicate the bonds made with aluminum adherends. It was not possible to maintain the crack extension within the cast material, however, so that this phase of the study was discontinued.

Joint Toughness Specimens

The aluminum adherends were prepared by milling as described elsewhere.² This produced a finish on the bond surface of $25 \pm 5 \mu\text{in}$. Cleaning solutions and procedures were of a standard type for epoxy joints.³

Specimen geometries used for the joint study consisted of both the uniform double cantilever-beam type (Fig. 1b), characterized and described in the previous report¹ and the tapered double cantilever beam discussed above and in the Appendix to this report.

Once the adherends were cleaned, they were bolted together separated only by shims of the size required to obtain the proper bond thickness. The bolted assembly was then Teflon-taped to provide a casting dam for the epoxy, and to protect the loading holes from being filled. Once taped, the specimen was placed on a 150°F. hot plate. Resin and hardener, mixed at 110°F., was poured into the joint starting at one end, and moving slowly to the other, after the adherends had attained the hot plate temperature. Due to the high adherend temperature, the epoxy mixture became quite fluid so that most bubbles poured in the joint cavity rose and were eliminated. Once pouring was completed, all but a small part of the excess epoxy on the surface was removed with a glass rod drawn over the joint. (The thin layer of epoxy on the surface was needed for measuring crack rate as described below.) Gelation was complete in 1 hr. or less, depending on the epoxy composition, after which the hot plate was turned off, and the specimen allowed to slowly cool to room temperature. The tape was then removed and a 5-hr. post-cure effected. All handling, after initial cleaning of the adherends, was with non-porous treated nylon gloves. The post-cured specimens were tested in the Instron tensile machine using the loading holes provided. Deflection, measured with an LVDT placed on the loading fixture was plotted versus load on the X-Y recorder as was done for the tensile specimens.

Measurement of Strain Rate

Three methods were available for measuring cracking rates: two for coarse, average values and one for fine-scale measurements. Average crack length versus time could be obtained by noting specimen compliance change with time. This, however, requires accurate measurement of the slope of the modulus line versus time which is difficult. An alternative

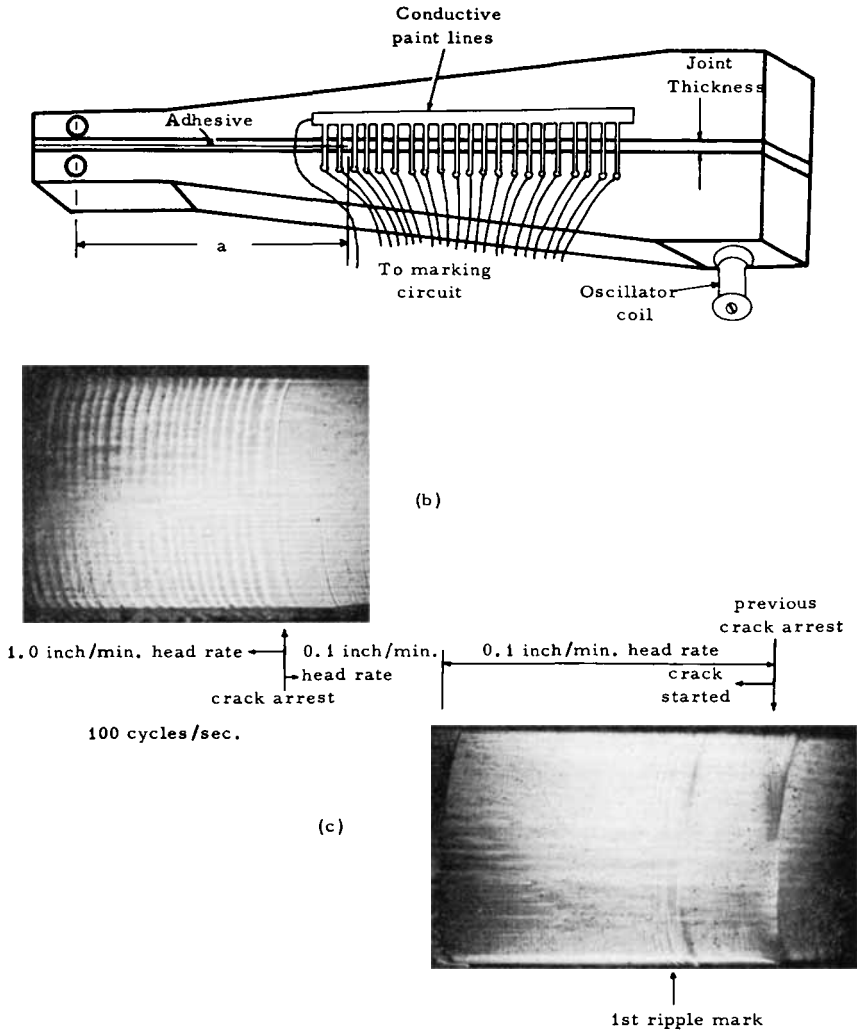


Fig. 2. (a) Schematic diagram of conductive paint lines and bell coil attached to tapered double cantilever-beam specimen for measuring strain rate; (b) ripple pattern for slow running crack; (c) ripple pattern for fast (jumping) crack.

method was used to locate the position of the crack front with time by placing a number of equally spaced conductive paint lines on the epoxy coated side of the joint specimens or on either side of the bulk toughness specimen. These lines were then connected through a resistance bank into either an operational amplifier or a battery operated circuit. When the crack passes through one of the lines a step appears on the oscilloscope plot of voltage versus time of this circuit. To measure crack velocity on a fine scale, a marking technique which was a modification of the Kerkhof method suggested by P. Mast of the Naval Research Laboratory, was

used. The markings appear as a result of oscillations supplied by a signal generator through a bell coil and magnet assembly coupled mechanically to the specimen. A schematic drawing of a specimen used for crack rate studies is shown in Figure 2a. Distinct ripple markings of the type shown in Figures 2b and 2c have been observed for applied frequencies of 50–1000 cps. Calculated crack velocities obtained by using the ripple-pattern marking, were verified by the breaking tapes. Velocities have been observed in aluminum joints from approximately 0.01–50 ft./sec. and up to 35 ft./sec. in bulk epoxy. Opening displacements and loads are plotted simultaneously on the oscilloscope so that correlations between crack velocity and toughness could be made. All toughness tests were made such that the time to fracture, i.e., time to go from zero load to fracture load, t_c , was between 5 and 15 sec., unless otherwise noted.

TEST RESULTS AND DISCUSSION

Tensile Properties

The tensile properties for post-curing at 150 and 200°F. are shown in Figure 3 as a function of hardener content. Although there is consider-

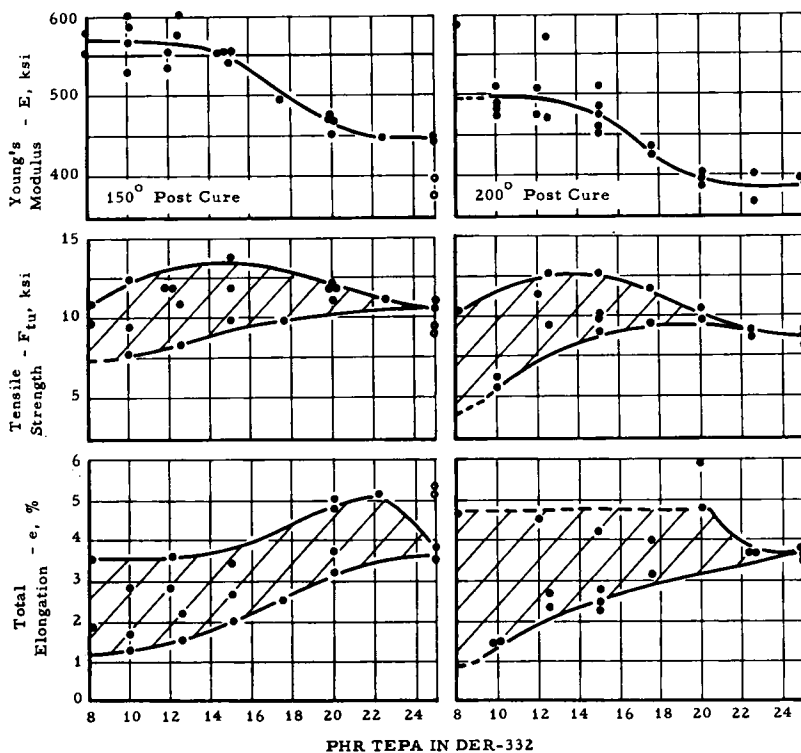


Fig. 3. Tensile properties of epoxy as a function of composition for two post-cure temperatures. Specimen cross section $1/8 \times 3/8$ in. on a 2-in. gage length; post-cure time 5 hr.

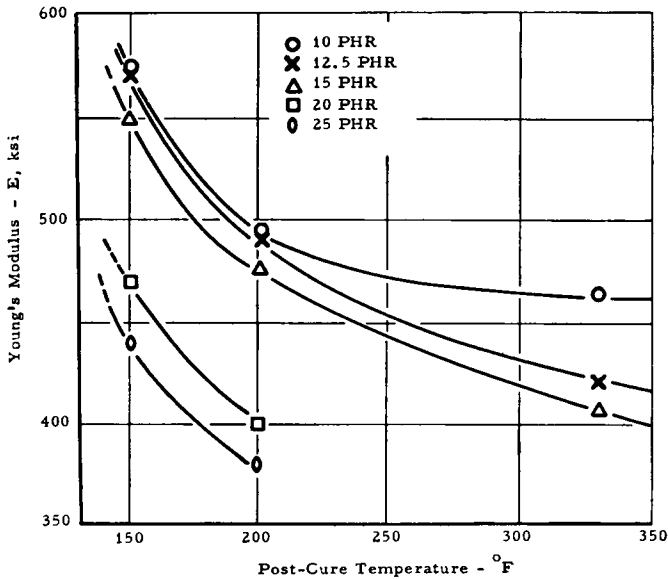


Fig. 4. Young's modulus of epoxy as a function of post-cure temperature for several compositions. Post-cure time 5 hr.

able scatter, the modulus curves are reasonably well defined. The stiffness of the material remains relatively constant from low hardener contents (8 phr) to the stoichiometric ratio (15 phr). Further increases in the amount of hardener causes a fast decrease in modulus up to 20 phr, after which the stiffness again remains constant. The difference in level between the high and low hardener content is approximately 20%. (The two low modulus points for 150°F. post-cure and 25 phr shown as open circles are probably due to an exotherm and hence were ignored in drawing the curve.)

The modulus measurements are essentially independent of flaws, eccentric loading, etc., since this property is measured at small strains. The ultimate tensile strength and elongation, on the other hand, are fracture properties and because the epoxies are extremely brittle, the measured value of both of these is depressed by imperfections in the samples or erratic testing procedure. The "least flaw" or idealized test for these properties is given by the top of the scatter band, so this upper boundary is considered the proper property-composition curve. For both curing temperatures, the tensile strength appears to be highest for the stoichiometric composition. The elongation-composition curve for the lower post-cure temperature is a mirror image of the modulus curve excepting for the very highest hardener content. Although this inverse relationship between ductility and modulus is expected, it was not found for the 200°F. post-cure hardener contents between 14 and 16 phr.

The effect of post-cure temperature on modulus is shown in Figure 4. As the temperature is raised, the modulus decreases in a smooth fashion.

This loss of modulus with increasing post-cure temperature was unexpected since the higher post-cure was expected to increase crosslinking and, as a consequence, increase stiffness.

Toughness of Bulk Epoxy

The resistance of bulk epoxy to crack propagation as measured by G_{Ic} was determined for a series of hardener contents at one post-cure temperature (150°F.) (Fig. 5), and for the stoichiometric composition (15 phr), as a function of post-cure temperature (Fig. 6).

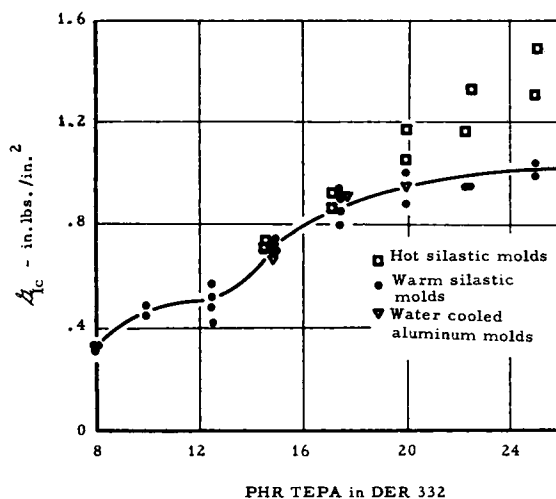


Fig. 5. Bulk toughness as a function of composition for three types of molds. Tapered double cantilever-beam specimens, $\frac{1}{4}$ in. wide, grooved $\frac{1}{16}$ in. on each side; 150°F., 5-hr. post-cure.

Since crack toughness involves the propagation of a macroscopic crack, the effects of randomly distributed small flaws were negligible so that less scatter was expected in fracture toughness than in tensile fracture properties. Scatter that did occur, up to 0.1 in.-lb./in.², was primarily a result of material inhomogeneity and, to a lesser extent, a result of testing inaccuracy.

In some of the initially cast bulk specimens, the specimen molds were heated to 150°F. to corresponded to the adherend temperature used in the preparation of aluminum-epoxy-aluminum specimens as described above. With this mold temperature, even a modest amount of exotherm caused curing to occur at a temperature that exceeded the subsequent 150°F. post-cure (Fig. 5). To avoid this occurrence, the mold temperature was reduced to approximately 110°F. The cooler specimens had a reduced toughness when the hardener content was high (Fig. 5), and this lower value represents the properties of bulk epoxy having a thermal history close to that of the joint material.

That an exothermic reaction did not contribute appreciably to the shape of the curve in Figure 5 is seen by the fact that the specimens cast in water-cooled aluminum molds yielded identical results with those cast in the 110°F. specimen molds. Further, no rise was found in the temperature versus cure-time curves obtained on the warm specimen-molded 15-25 phr specimens. As discussed above, thin thermocouples were buried in these castings for recording temperature during the complete cure.

Figures 5 and 6 show a general increase of toughness with increase in hardener or post-cure temperature. Although the phenomenon is complex, both curves have a positive slope suggesting that increasing hardener content and increasing post-cure temperature produces similar changes on a

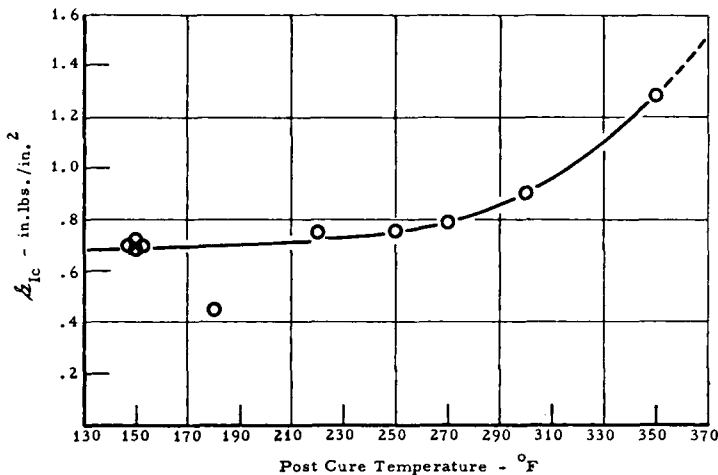


Fig. 6. Bulk toughness vs. post-cure temperature for the 15 phr TEPA-DER 332 system. Tapered double cantilever-beam specimens grooved $\frac{1}{16}$ in. on each side; post-cure time 5 hr.

submicroscopic scale, perhaps by knitting a tighter structure through added crosslinking. (Such a conclusion is not consistent with the decreasing modulus versus post-cure temperature curve, however.)

The ripple-marking technique, as discussed above, could not be used on the bulk epoxy specimens without influencing the values of measured toughness because the weight of the attached bell coil and pull of the magnet disturbed the very low load readings. In spite of this difficulty the speed of a free running, or jumping, crack was found to be approximately 30 ft./sec. when the crosshead speed was made equivalent to a crack traveling at 0.1 ft./sec. Velocity versus distance profiles of the jumping crack showed that the maximum velocity was attained very near the previous crack arrest point, as in Figure 2c. As the crack progressed it continually slowed until the next arrest point was reached. Decreases in toughness of the order of 20 per cent were measured between crack initiation and crack arrest.

Toughness of Joints (Aluminum Adherends)

The effect of composition on the toughness of joints is shown in Figure 7 and the influence of post-cure temperature in Figure 8. As was the case with bulk properties, toughness was generally found to increase with either

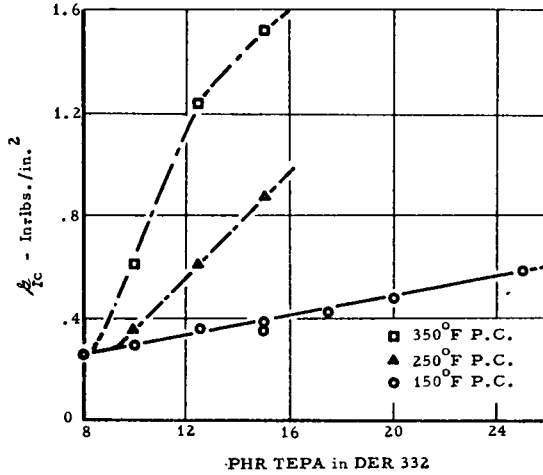


Fig. 7. Joint toughness as a function of composition for three post-cure temperatures. Post-cure time 5 hr.

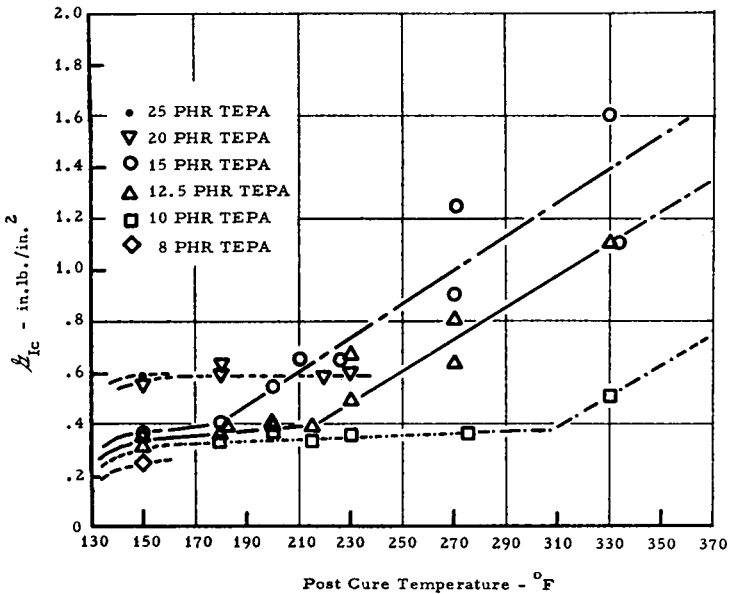


Fig. 8. Joint toughness as a function of post-cure temperature for several compositions. Tapered and uniform double cantilever-beam specimens, 1/2 in. wide; post-cure time 5 hr

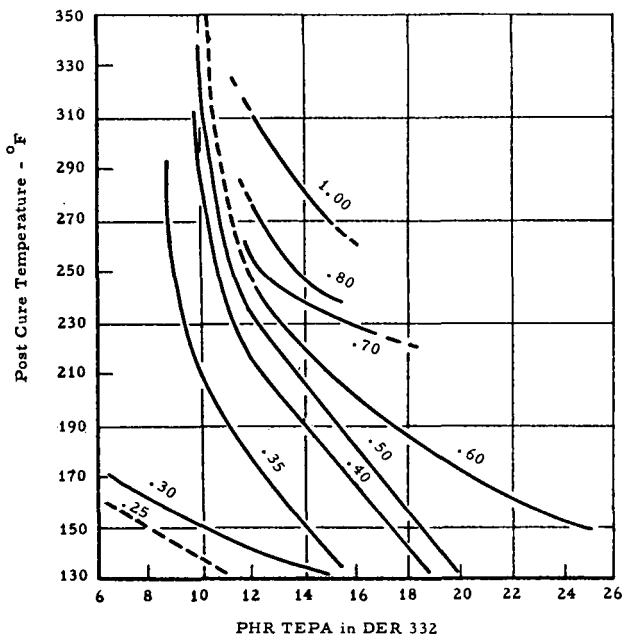


Fig. 9. Contour map of toughness as a function of post-cure temperature and composition. Post-cure time 5 hr.

increasing hardener content or increasing post-cure temperature. The plateau found between 10 and 12.5 phr for the bulk epoxy on post-curing at 150°F. (see Fig. 5) was not found for the joints. As the post-cure temperature is raised, the slope of the toughness-composition curve becomes increasingly steep (Fig. 7).

The shape of the toughness versus post-cure temperature curves (Fig. 8) are similar for compositions of 10, 12.5, and 15 phr. In all three cases, there is a plateau of toughness up to some specific post-cure temperature after which there is an approximately linear rise in toughness with increase in temperature. The temperature at which the rise in toughness begins is decreased as the amount of hardener increases. For the 20 phr composition, center-of-bond fractures were not obtained above 230°F. post-cure so that this portion of the curve could not be defined. Nevertheless, if this epoxy system were to show a consistent behavior with the three lower hardener compositions, the beginning of the fast toughness rise should have occurred in the vicinity of 150°F. which is the lowest post-cure temperature used.

If there were an influence of residual stresses produced by the difference in coefficient of thermal expansion of the aluminum adherend and the epoxy adhesive, one would expect a toughness decrease with increased post-cure temperature. Since the opposite is found, it must be assumed that residual stresses exert an influence that is far less important than the chemical changes produced by the increased post-cure temperature.

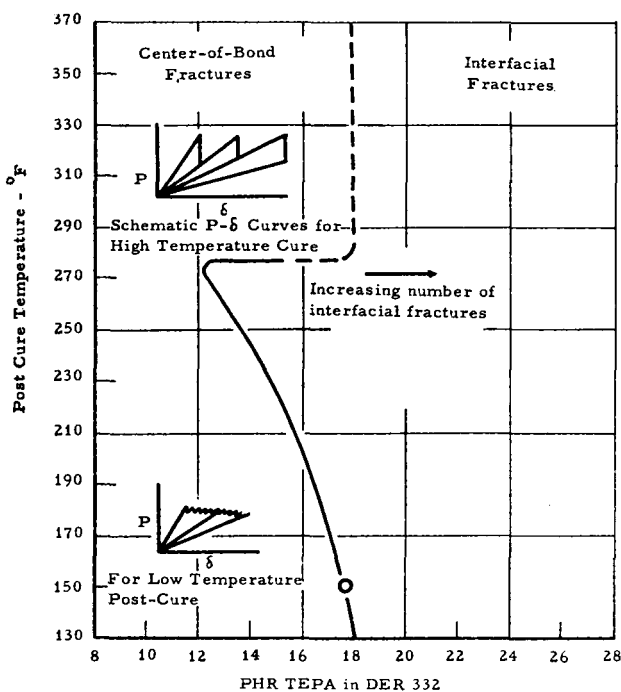


Fig. 10. Fracturing behavior of joint specimens as a function of composition and post-cure temperature. Note shape of $P-\delta$ curves of specimens in two states. Post-cure time 5 hr.

To relate the dependence of toughness on post-cure temperature and composition, a contour map of toughness as a function of these two independent variables is shown in Figure 9. The slope of the model is slight for low hardener compositions even at high post-curing temperature; however, for high post-cure temperatures and hardener contents the contour is very steep, resulting in very high toughnesses for high post-cure temperature and high hardener combinations. For the latter, toughnesses are of the order of four times as high as they are when the temperature and hardener content are both low.

All of the data presented in this report are based on center-of-bond fractures. A considerable number of interphase fractures, however, did occur in the course of the investigation. These always occurred when the amount of hardener was excessive, say, greater than 20 phr, whereas, they never occurred for hardener contents less than approximately 12 phr. The tendency for interphase fractures was also dependent on post-cure temperature as shown schematically in Figure 10. This tendency for the crack to run near one adherend was greatest when post-curing was of the order of 230–270°F. Although the shape of the curve, as presented in Figure 10, is thought to be realistic, a complete analysis of type of fracture was only made for the post-cure temperature of 150°F. The top of the

curve is shown dashed because specimens with more than 15 phr TEPA were not post-cured above 230°F. At 230°F. and 15 phr TEPA, the fractures were at the interphase, and a black deposit formed on the adherend.

When center-of-bond fractures occurred above the nose (Fig. 10), the toughness and cracking rate were both very high. Center-of-bond fractures below the nose were generally typified by low toughness and slow cracking. This difference in fast and slow cracking is apparent from the load-opening curves for the fast and slow running cracks. On high temperature curing, the load-deflection curve has a pronounced sawtooth pattern. Cracks propagate longer distances per jump and outrun the head velocity cracking rate by several orders of magnitude. Crack velocities approached 50 ft./sec., and the fracture surfaces were extremely rough on a fine scale. At low post-curing temperatures the load versus opening curve is again sawtoothed, but the amplitude of the teeth is small and the frequency high. For these cases the crack velocity approached that dictated by the head speed, i.e., 0.01 ft./sec. These two types of $P-\delta$ curves are shown schematically in Figure 10.

Comparison of Bulk and Bond Toughness

The relationship between the toughness of epoxy in bulk form, as compared with its use in a bond, is extremely complex. It might be assumed that the toughness of bulk epoxy is representative of very thick joints. If this is the case, the effect of bond thickness for low post-cure temperature (150°F.) as a function of composition can be ascertained from Figure 11. For low hardener contents of, say, stoichiometric and below, the effect of bond thickness is modest. As the amount of hardener is increased, however, this effect becomes more pronounced. In all cases, however, it can be assumed that increasing bond thicknesses result in an increased toughness.

Using the stoichiometric composition and varying post-cure temperatures

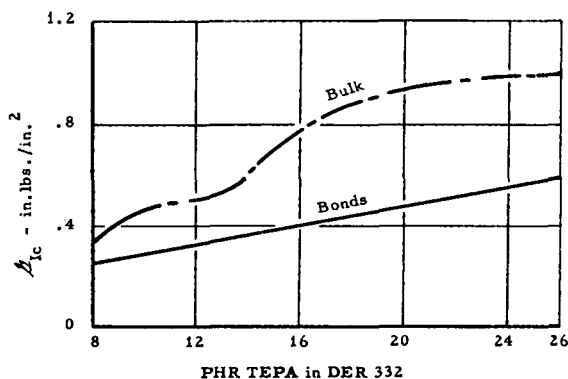


Fig. 11. Toughness comparison of bulk and bonds with varying content of TEPA in DER 332. Post-cure at 150°F. for both specimen types.

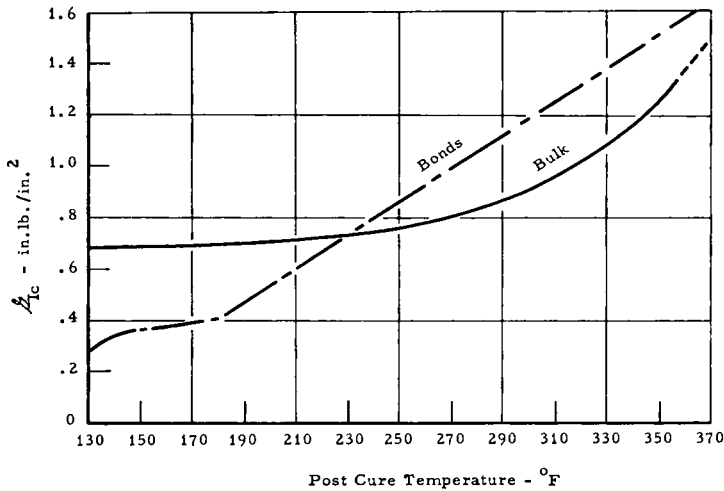


Fig. 12. Toughness comparison of bulk and joints for 15 phr TEPA as a function of post-cure temperature. Post-cure time 5 hr.

produces a much more complex behavior, as shown in Figure 12. When the post-cure temperature is low, i.e., less than 230°F., the bulk epoxy is tougher than the bond; above this temperature the reverse is true, i.e., the bonded epoxy is tougher than the bulk. If one assumes that the toughness of bulk epoxy is identical with that of very thick bonds, the effect of bond thickness can be ascertained from this figure. At postcuring temperatures less than 230°F., thick joints would be expected to be tougher than thin ones. Above 230°F., on the other hand, the reverse behavior would be expected, whereas, at 230°F. post-cure, one would expect no influence of bond thickness, whatsoever. This crossover of bond and bulk epoxy is probably a velocity effect in the bonds. As stated above, below 230°F. post-cure center-of-bond fractures were slow, and the jump length was small. Above 230°F., the fractures were fast, rough, and jumped long distances.

Comparison of Bulk and Joint Toughness with Tensile Modulus

The relationship between the bulk toughness and tensile properties was obtained by plotting G_{Ic} versus Young's modulus for all of the bulk samples for which both types of data were available (Fig. 13). It is apparent in this figure that various combinations of composition and post-cure temperature that yield a given value of modulus do not produce identical values of toughness, i.e., the latter is not a single-valued function of the former.

A similar plot of joint toughness versus Young's modulus, however, Figure 14, shows that these two are, indeed, related by a single curve. Low elastic moduli produce high toughness, and as the modulus is increased the toughness continuously drops. When the elastic modulus exceeds ap-

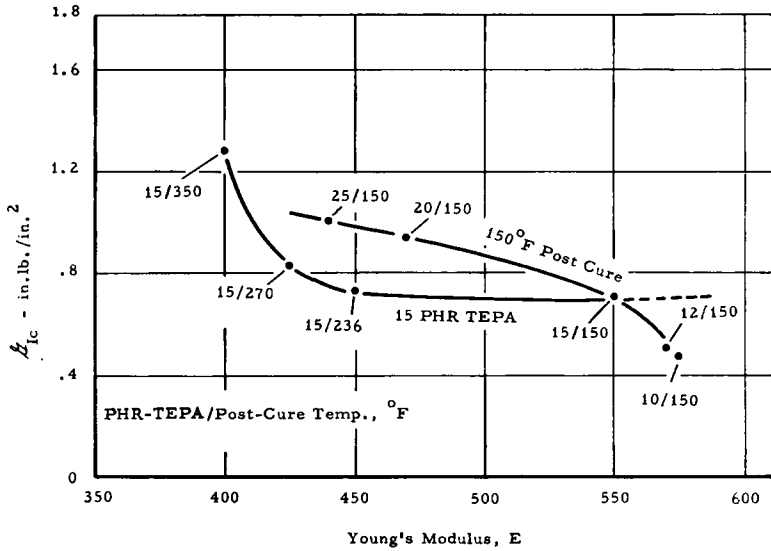


Fig. 13. Bulk toughness vs. bulk modulus for one composition and one post-cure temperature. Post-cure time 5 hr.

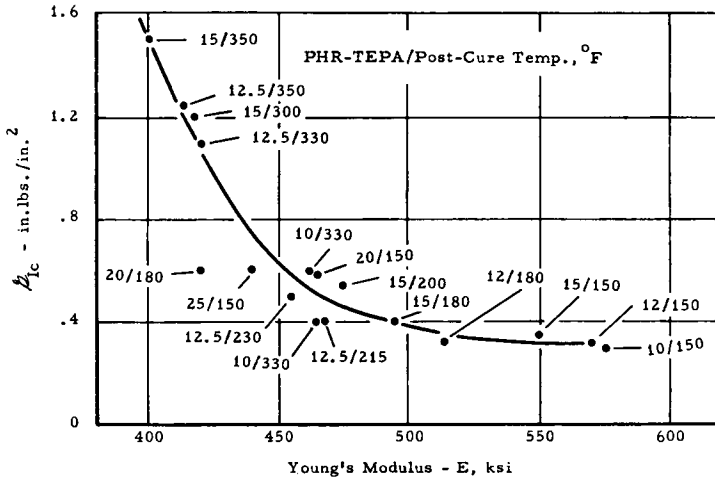


Fig. 14. Joint toughness vs. bulk modulus for various compositions and post-cure temperatures. Post-cure time 5 hr.

proximately 0.5×10^6 psi, however, additional increases in modulus do not produce a further drop in toughness.

Dependence of Toughness on Cracking Rate

The ripple-marking technique as discussed above makes it possible to measure essentially instantaneous values of cracking rate from initiation to arrest. Similarly, the $P-\delta$ curve yields values from which G_{Ic} can be

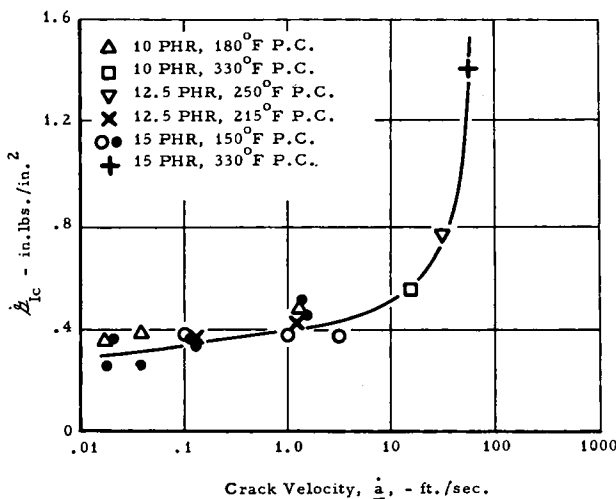


Fig. 15. Dependence of toughness on crack velocity.

calculated for each value of P as the crack extends so that it is possible to obtain a G_{Ic} value for each crack velocity over the complete event of a crack jump. The toughness discussed in this report, however, was based on calculations involving the maximum load which occurs at the end of the elastic portion of the P - δ diagram (see inserts in Fig. 10) and is associated with the crack velocity close to the instant of reinitiation. Hence, the velocity obtained by measuring the period of the first ripple mark (see Fig. 2) is an average value for the G_{Ic} presented in this report.

When the toughness values were plotted as a function of initial crack velocity, Figure 15, a G_{Ic} versus v curve was obtained that was independent of the chemical variables that produced the given toughness. Apparently the difference in toughness of joints which show center-of-bond fractures results from the difference in velocity at which the crack starts to run. In Figure 15, points to the right of 10 ft./sec. are all jumping cracks whose velocity far exceeds that of the cross head travel. The open circles to the left of 10 also represent free running or jumping cracks whereas all other points between 0.01 and 10 ft./sec. propagated at a rate that was a reflection of the crosshead travel of the test machine.

CONCLUSIONS

The conclusions presented below were based on a single epoxy system, DER 332 with TEPA as the hardener, and must be considered applicable to only this system.

Smooth Tensile Properties of Epoxy

The elastic modulus of this epoxy system is relatively constant for hardener contents between 8 and 15 phr, as well as between 20 and 25 phr

for a constant post-cure temperature. With the lower hardener contents, however, the level of the modulus curve is approximately 20% higher than it is with the higher hardener content. As post-cure temperature is increased, the room temperature modulus decreases for any given hardener content. The latter behavior was surprising, since the higher temperature would be expected to increase crosslinking and hence stiffness.

The tensile strength for both of the investigated post-cure temperatures, 150 and 200°F., appears to exhibit a maximum at the stoichiometric composition, although this composition has no special significance for other properties.

The tensile fracture properties, i.e., tensile strength and elongation, exhibit a large amount of scatter presumably due to randomly distributed flaws and erratic testing procedure. The elastic modulus which is measured at low strains is not affected by these variables, and hence, shows less scatter.

Toughness of Bulk and Joint Epoxy

The toughness of epoxy used either in the bulk form or as a joint generally increases with increasing hardener content or increasing post-cure temperature. Joint toughness increases rapidly with hardener content after high post-cure temperatures and slowly after low post-cure temperatures. The rate of toughness increase with post-cure temperature is fastest when the temperature is high and when the composition is in the range of stoichiometric.

The type of fracture experienced by joints is also a function of post-cure temperature and composition. Very high hardener contents lead to interphase fractures for all post-cure temperatures investigated. As the hardener content is decreased, center-of-bond fractures occur, and the toughness and cracking rate is very high after high post-cure temperatures, but low for low post-cure temperatures.

Dependence of Toughness on Smooth Tensile Properties

Bulk toughness of epoxy is not a single-valued function of Young's modulus, but depends on the combination of composition and post-cure temperature used to obtain the specific value for the elastic property. On the other hand, joint toughness does appear to be a single-valued function of the modulus with low values of modulus producing high toughness with a continuous decrease in toughness as the modulus increases. Modulus values above approximately 0.5×10^6 psi, however, produce an essentially constant toughness.

Comparison of Bulk and Joint Toughness

It is not possible to predict joint properties from bulk toughness. Although for most combinations of hardener content and post-cure temperature the bulk toughness is higher than that of the joints, this is not always

the case. For example, for the stoichiometric composition, bulk epoxy is tougher than joints for low post-cure temperatures, but the joints are tougher after high post-cure temperatures. This relationship is opposite to what would be expected if residual stresses were a major factor in determining the toughness of joints.

Dependence of Joint Toughness on Cracking Rate

By using the ripple-marking technique, it was possible to relate toughness with essentially instantaneous cracking velocity. By this procedure it was shown that joint toughness was a single-valued function of cracking rate, independent of the combination of composition and post-cure temperature used to obtain the given toughness.

APPENDIX

Selection of Sample Shape for Opening Mode Toughness Measurements

The previous papers^{1,2} discuss in some detail the double cantilever-beam specimen shown in Figure 1b used for determining opening mode toughness G_{Ic} for adhesives. For this specimen the experimentally determined expression of G_{Ic} was:

$$G_{Ic} = (P_c^2/2b) (2/3EI) [3(a + 0.6h)^2 + h^2]$$

where P_c is the load at instability, b is specimen width, h is specimen height, E is the modulus of elasticity, I is moment of inertia, and a is crack length, measured from the point of load application.

An accurate determination of G_{Ic} thus required either a knowledge of a or compliance, $1/M$, which is a function of a . The problem of determining crack length or compliance accurately is compounded when measurements are to be made at higher strain rates (faster fracture times, t_c) than those used in the test series, i.e., $t_c \cong 10$ sec.; $\delta \cong 0.1$ in./min. For a constant head velocity the crack will be driven at a continually slower rate using this specimen type. Additionally, since a constant G_{Ic} results in a continually decreasing load, measurements of $1/M$ or a must still be made very accurately at the higher rates in spite of velocity effects. A number of methods have been used successfully to measure crack length at these higher rates. Among these are a ripple-marking system and a series of painted lines which give a signal when broken by the running crack. These techniques are described in the text.

In order to avoid the experimental difficulties in measuring $1/M$ or a and to use a constant head rate for constant driven cracking rate, a tapered specimen of the type shown in Figure 1c was developed. For this specimen the analytical expression for G_{Ic} on the basis of only simple beam theory is:

$$G_{Ic} = (P^2/2b_n) (24/Eb) (a^2/h^3)$$

where b_n is the specimen width in the plane of crack extension.

For adhesives $b_n = b$, while for bulk material, grooved 25% on each side, $b_n = b/2$. Since the specimen taper is such that (a^2/h^3) is constant, G_{Ic} is a function of load alone for a specific material and geometry. In practice (a^2/h^3) represents a curve which can be approximated by a straight line over relatively long distances for specimen making purposes.

Any rate studies on the specimen are greatly reduced in measurement complexity since changing load means changing toughness. High and low strain rate studies as well as those on bulk material are simplified because crack length or compliance need not be measured. Additionally, constant head velocities produce constant driven crack velocities.

The authors acknowledge the many helpful suggestions made by Mr. Charles Bersch, Professor H. T. Corten, and Dr. R. L. Patrick. Permission to publish this work from the Bureau of Naval Weapons is also gratefully acknowledged.

References

1. E. J. Ripling, S. Mostovoy, and R. L. Patrick, *Mater. Res. Std.*, No. 3, **64**, 129 (1964)
2. E. J. Ripling, S. Mostovoy, and R. L. Patrick, *ASTM Spec. Tech. Publ.*, No. **360**, 5 (1963).
3. I. Skeist, *Epoxy Resins*, Reinhold, New York, 1962.

Résumé

On a mesuré la résistance à la cassure de résines époxy utilisées en masse ou comme adhésifs à l'aide d'une technique développée précédemment. La barre uniforme à deux points d'appui, qui était utilisée comme échantillon dans des études préalables, a été modifiée et remplacée par une barre d'épaisseur variable, ce qui simplifie le processus expérimental et les calculs pour obtenir la mesure de la dureté. En variant le rapport durcissant résine ainsi que la température du traitement thermique on a trouvé dans le cas d'une seule résine époxy (DER 332-TEPA) que la dureté de la résine utilisée en masse ou comme adhésif variait dans une proportion de 5 à 1. On constate en général que la dureté de la résine en masse est meilleure que la dureté de la résine utilisée comme adhésif. Il existe cependant des exceptions; lorsque la température de traitement est élevée, on trouve que la dureté de l'adhésif est supérieure. Par conséquent, il n'est pas possible de prédire la dureté de l'adhésif à partir de la dureté du matériel en masse. On a trouvé que la dureté des adhésifs dépendait seulement du module de Young. Pour le matériel en masse, la dureté dépend, pour une même valeur du module, de la composition de la résine et de la température du traitement. A n'importe quelle composition et quelle que soit la température du traitement, on a trouvé que la dureté des joints dépendait de la vitesse de propagation des fissures. La dureté d'une résine époxy dépend du mode de propagation des fissures. Si ces fissures confluent rapidement, on trouve que la résine époxy a une grande résistance aux chocs. Pour un système époxy particulier, on augmente la résistance aux chocs, lorsqu'on favorise la propagation des fissures en augmentant la vitesse.

Zusammenfassung

Die Bruchzähigkeit von Epoxidharzen in Stückform und als Klebstoff wurde nach einem früh entwickelten Verfahren gemessen. Die Probengestalt wurde von der früher beschriebenen Form eines gleichförmigen Doppelauslegerbalkens in die eines sich verjüngenden Balkens abgeändert, wodurch die Versuchsmethodik und die Berechnung zur Zähigkeitsdaten vereinfacht wurde. Durch Variation des Verhältnisses Härter zu Harz und der Nachhärtungstemperatur bei einem einzelnen Epoxysystem (DER 332-

TEPA) wurde eine Variierung der Zähigkeit des verwendeten Epoxydharzes in Stückform oder als Bindemittel um einen Faktor von etwa 5 erreicht. Eine bestimmte Kombination von Zusammensetzung und Nachhärtungstemperatur lieferte in allgemeinen in Stückform eine höhere Zähigkeit als in Bindemittelform. Dies war jedoch nicht immer der Fall. Bei hohen Nachhärtungstemperaturen, wo die Bindungen sehr zäh waren, überstieg ihre Zähigkeit diejenige eines Materials in Stückform. Es scheint daher nicht möglich zu sein, aus Zähigkeitsmessungen an Stücken die Zähigkeit von Verbindungen vorherzusagen. Die Zähigkeit der Verbindung erwies sich als eindeutige Funktion des Zugmoduls. Für das Material in Stückform hängt andererseits die für das Epoxydharz mit einem spezifischen Modul erhaltene Zähigkeit von der Kombination von Zusammensetzung und Nachhärtungstemperatur ab. Die Verbindungszähigkeit bei einer beliebigen Kombination von Zusammensetzung und Nachhärtungstemperatur hing nur von der Rissgeschwindigkeit ab. Wenn das Epoxydharz von demjenigen Typ war, der ein rasches Springen der Risse verursachte, war das Epoxydharz zäh und umgekehrt. Bei einem bestimmten Epoxydsystem wurde die Zähigkeit durch Vortreiben des Risses mit steigender Geschwindigkeit erhöht.

Received November 19, 1965

Revised February 6, 1966

Prod. No. 1350