

The Fracture Toughness and Stress Corrosion Cracking Characteristics of an Anhydride-Hardened Epoxy Adhesive

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Synopsis

The toughness and stress corrosion cracking characteristics of an epoxy resin (DER 332) hardened with hexahydrophthalic anhydride (HHPA) were investigated. The epoxy was studied in both the bulk and bond form, and its properties were compared with an amine-hardened (tetraethylene pentamine, TEPA) system. The toughness, G_{Ic} , of the anhydride system varied less as a function of ratio of hardener-to-resin content and postcure temperature than it did in the TEPA-hardened system. Like the latter, however, its toughness in the bulk and bond forms could not be correlated, but G_{Ic} of the joints was dependent on tensile modulus and/or yield strength of the bulk epoxy. Both systems were also toughened in the vicinity of the crack tip by water for short-time loading, but their long-time load carrying capability was reduced by a water environment. The anhydride hardened system was more sensitive to strength loss in water than the amine system. The fracture morphology for the two systems was the same, i.e., fast cracking occurred cohesively near the center of the bond, and slow cracking occurred at the interface.

INTRODUCTION

The failure of adhesive joints in service is thought to result from the extension of preexisting crack-like flaws, such as bubbles, dust particles, or unbonded areas, that are introduced into the joint during manufacturing. The techniques of fracture mechanics make it possible to measure the strength of structural members in the presence of such flaws, and methods for applying this discipline to adhesive joints have been developed by this laboratory.^{1,2} The preexisting flaws may extend rapidly to cause a complete separation in times less than a millisecond, or they may grow slowly, so that complete separation requires hours, days, or more. Most typically, service fractures occur in two steps: first, the crack grows slowly over the time period required for it to attain a critical size, after which rapid fracture completes the failure. The two extremes of such fracturing are cracking under sustained, comparatively low loads, in which case essentially all the separation occurs slowly, and short-time overloads where rapid fracturing predominates. Hence, defining the mechanical properties of joints requires a description of both their short-time and long-time load-carrying capabilities.

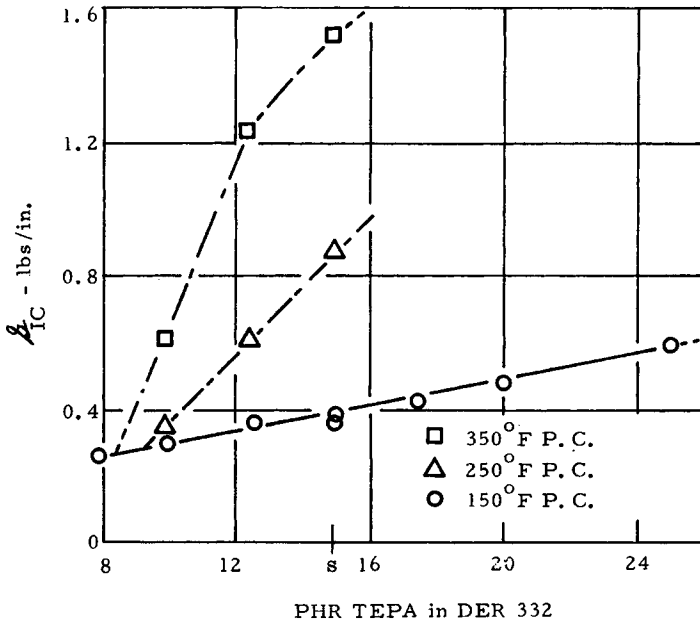


Fig. 1. Joint toughness as a function of ratio of TEPA hardener to resin content (DER 332) for three postcure temperatures. Postcure time, 5 hr.³

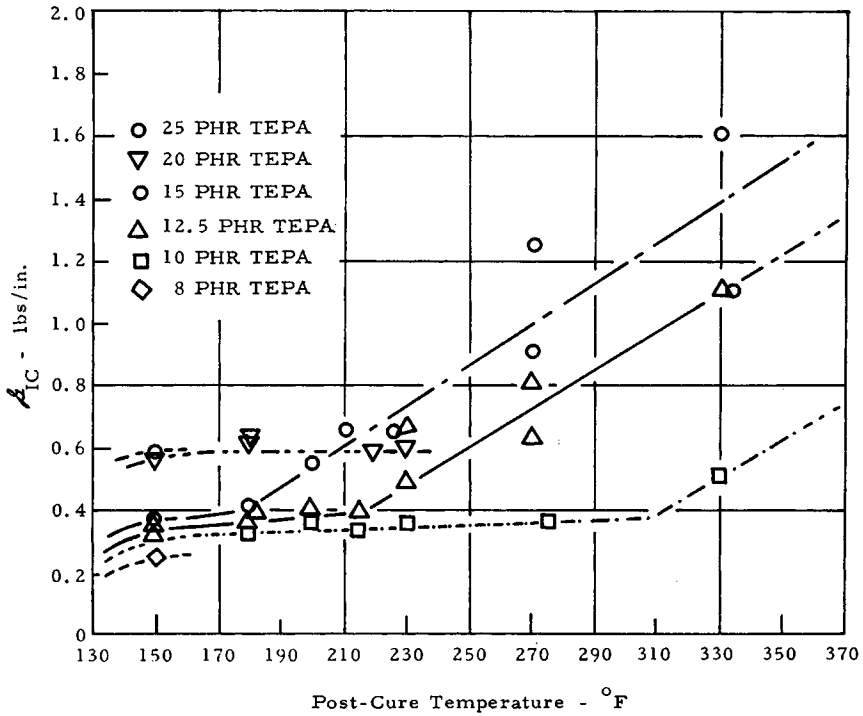


Fig. 2. Joint toughness as a function of postcure temperature for several ratios of TEPA to DER 332. Postcure time, 5 hr.³

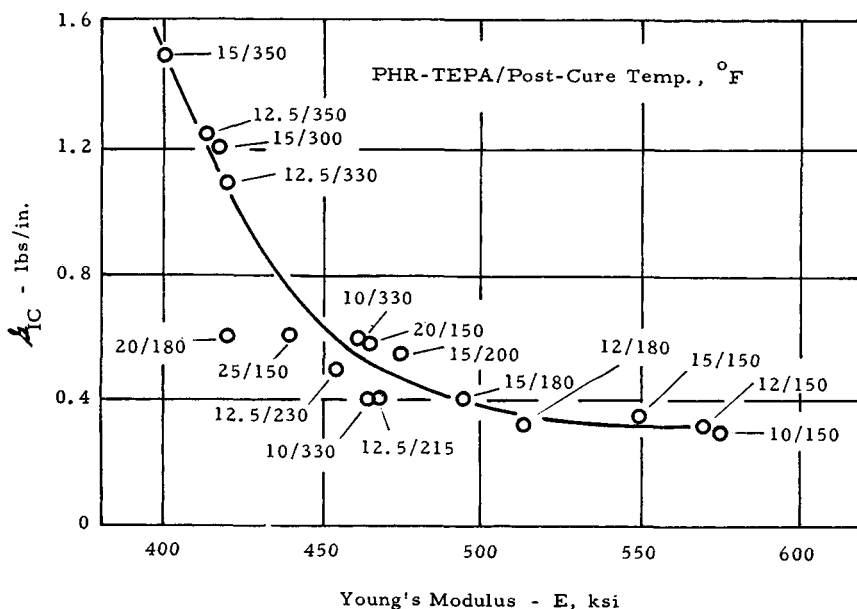


Fig. 3. Joint toughness vs. tensile modulus of the bulk epoxy for various combinations of composition and postcure temperature. Postcure time, 5 hr.³

Fracture mechanics is concerned with both these types of cracking. The measure of resistance to crack extension is the strain-energy release rate, or crack extension force, G_i , having units of pounds per inch in the British system. The short-time behavior is described by the fracture toughness, G_{Ic} , the critical value of G_i , at which a stationary or slow-moving crack accelerates to a high velocity. The long-time behavior, which is a measure of the stress corrosion cracking (SCC) resistance of the joint, requires two values for its description: (1) G_{Isc} , the threshold value of G_i below which crack extension will not occur in a particular environment, within a specified period of time, and (2) the dependence of cracking rate \dot{a} on G_i when $G_i > G_{Isc}$ for the environment of interest. A more complete description of the importance of these properties and the manner in which they are measured is given in refs. 1 to 4.

Both the toughness and stress corrosion cracking behavior of 5-mil thick epoxy joints using the room temperature curing amine hardener, TEPA (tetraethylene pentamine), have been studied in some detail.^{3,4} The joint toughness was found to increase with increased hardener content or postcure temperature, as shown in Figures 1 and 2. It was also found that the toughness of the joint was a single-valued function of Young's modulus of the bulk epoxy (Fig. 3) and that the latter property decreased with postcure temperature or hardener content (Fig. 4). These relationships suggest that the modulus of the bulk epoxy determines its toughness when it is used as an adhesive.

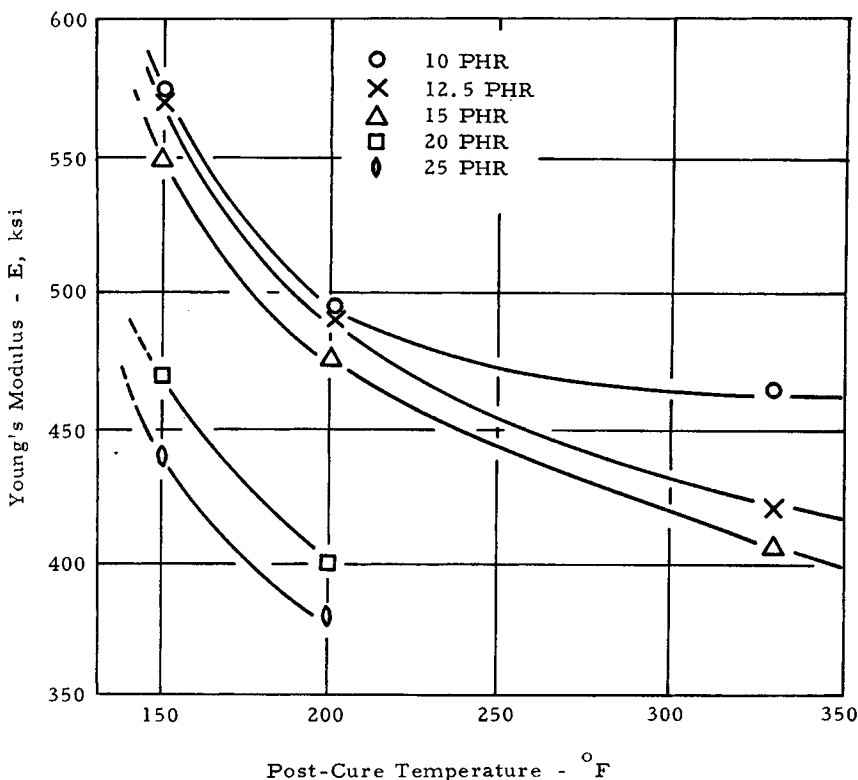


Fig. 4. Young's modulus of bulk epoxy as a function of postcure temperature for several compositions. Postcure time 5 hr: (○) 10 phr; (×) 12.5 phr; (△) 15 phr; (□) 20 phr; (◇) 25 phr.

Although the toughness of the amine-hardened system was investigated over a broad range of compositions⁵ and postcure temperatures, its stress corrosion cracking (SCC) characteristics were studied for only two systems: 10 phr of TEPA in DER 332 resin (Dow epoxy resin designation, mol. wt. 172-178), postcured at 180°F; and 12.5 phr of TEPA, postcured at 270°F, both for 5 hr. The SCC environment used was water in both the vapor and liquid form. For both adhesive systems, G_{ISCC} was found to decrease with increasing relative humidity, approaching as a limit the value of G_{ISCC} in liquid water with 0.05% Kodak Photo-Flo (proprietary wetting agent of Eastman Kodak) to serve as the wetting agent. This limiting value of G_{ISCC} for 10T/180 was approximately $G_{Ic}/4$, while for 12.5T/270 it was $G_{Ic}/2$. Adhesive systems are identified as follows: first number indicates parts per hundred of resin (phr) of hardener; letter indicates hardener system, T = TEPA and H = HHPA; number after slash indicates postcure temperature (°F). (The calculated stoichiometric compositions are indicated on the figures by an "s": 14.7 phr for TEPA in DER 332, and 82.4 phr for HHPA in DER 332.)

The present program was undertaken in order to compare the fracturing characteristics of an anhydride-hardened system with the amine-hardened one. The anhydride-hardened resin was selected because its modulus in the bulk form (unlike that of the amine-hardened one) was reported to increase with hardener content.⁵ Further, the two systems would be expected to display different levels of sensitivity to water since unreacted anhydride is more hygroscopic than unreacted amine.

EXPERIMENTAL

The methods used for testing and analyzing the data on this program were identical to those used for the amine-cured system.^{3,4} Specimen preparation was somewhat modified, however, since the characteristics of the anhydride and amine hardeners are different. The former, being solid at room temperature, was weighed out and melted just prior to combining with the resin. The melting temperature is a measure of water absorption, and when the melting point was too high, i.e., 140–150°F, a new batch of hardener was used. Because of the sluggishness of the reaction, a small amount (2 phr) of the accelerator, DMP-30 (Rohm & Haas Corp., Philadelphia, trade name for 2,4,6-tri-(dimethylaminomethyl)phenol), was added prior to mixing.

Tensile, Bend, and Toughness Testing of Bulk Epoxy

Tensile properties of the cast materials were measured on specimens having pin-grip ends, on a reduced section approximately $\frac{3}{16}$ sq. in. in size and having a 2-in. gauge length (Fig. 5a). Whereas the amine-hardened tensile specimens were cast to shape in order to minimize the volume of resin and hardener being reacted, it was possible to cast plates of the anhydride-hardened materials because the exothermic reaction for this system is far less severe. Plates $\frac{3}{16}$ in. thick were produced by casting mixed and degassed epoxy of each composition over a liquid mercury bed in a mold which allowed good temperature control during curing. Tensile or bend specimens were machined from the plates. After machining, all cut edges and sharp corners were sanded to the best finish possible using 600-grit emery paper. Specimens having sharp nicks or casting defects in the gauge length were discarded.

The 5-hr postcuring was done at 212°F (100°C), 311°F (155°C), and 365°F (185°C) after machining so that both casting and machining residual stresses were eliminated by the heat treatment.

Tensile testing was done in a screw-driven tensile testing machine at a cross-head rate of 0.05 in./min. Selected tensile specimens were checked during testing with a polariscope to assure axial alignment. Modulus and total elongation were measured using a spring-loaded elastic extensometer. Pressure exerted on the specimen by this device was kept to the lowest level necessary to keep it from losing contact during the test. Load-displace-

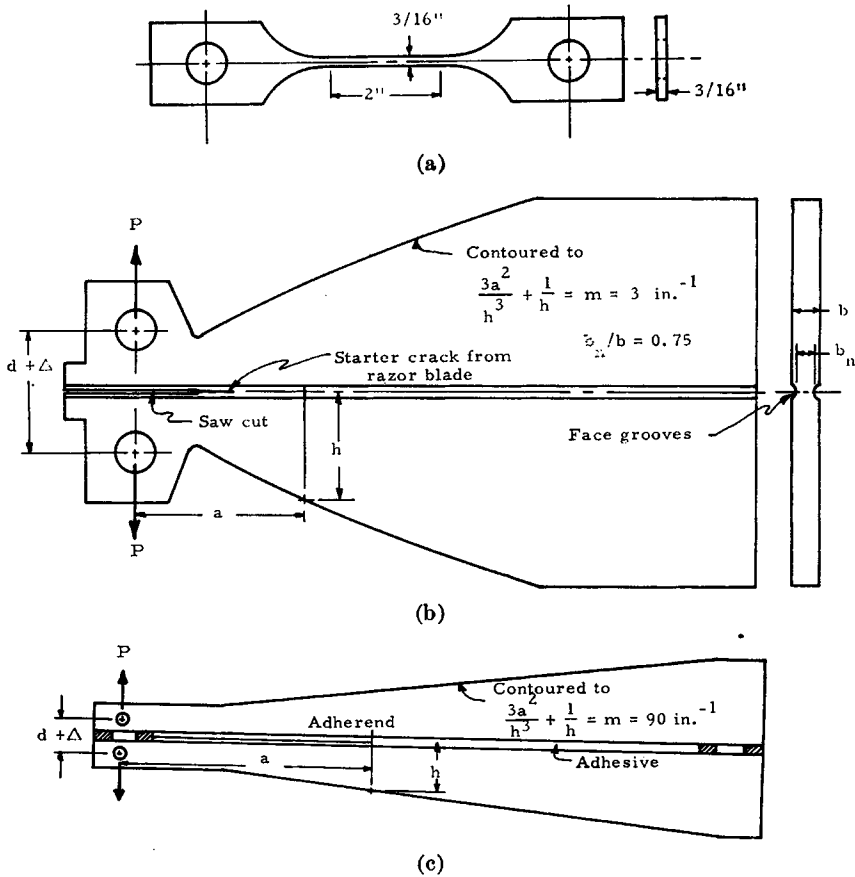


Fig. 5. Schematic diagrams: (a) tensile specimen; (b) tapered double-cantilever beam specimen ($m = 3$) (bulk specimen); (c) tapered double-cantilever beam specimen ($m = 90$) (joint specimen).

ment records ($P-\Delta$) were made on all specimens using an X-Y recorder set for the appropriate ranges of load and extension expected from these tests.

Modulus in bending was determined in four-point loading using the fixture shown in Figure 6. Young's modulus E for such a beam is

$$E = 3Pdl^2/4bh^3\Delta$$

where P = load, d = distance between outside and inside pin, l = span between inner pins, b = specimen width, h = specimen height, and Δ = deflection.

The large deflections associated with bending made it possible to obtain well-defined load-displacement records so that accurate slope measurements could be made.

Manufacture of specimens for measuring bulk toughness of the HHPA-hardened DER 332 epoxy resin was similar to that used for tensile and bend

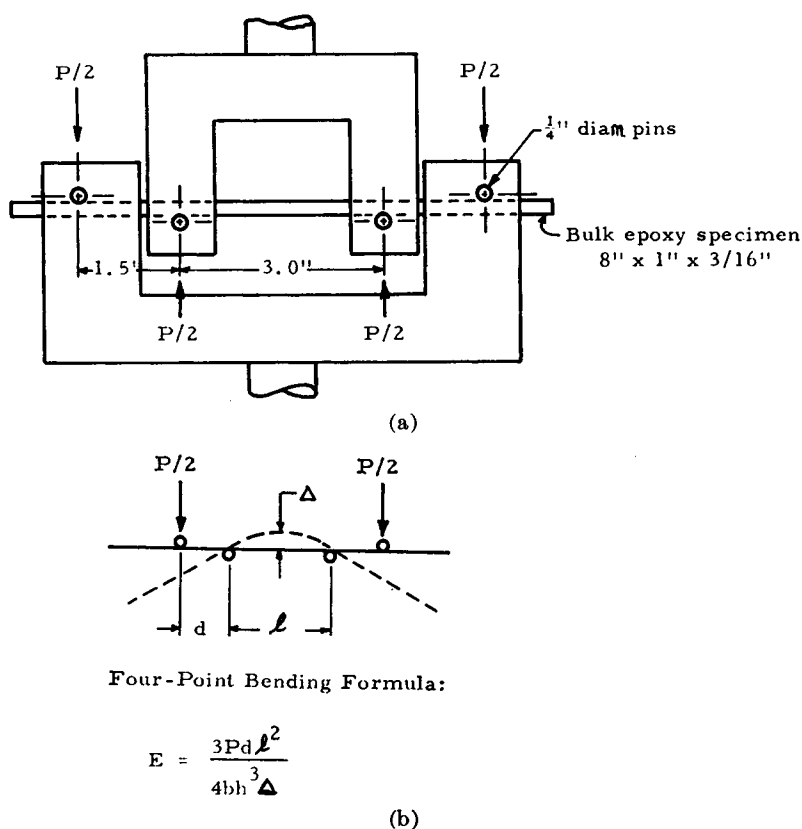


Fig. 6. (a) Fixture used for four-point bending of bulk epoxy specimens; (b) schematic and formula.

specimens. Again, plates of each composition were cast on the temperature-controlled mercury bed, with gelation occurring at 150° to 180°F in about 1 hr after pouring. In this case the castings were approximately $\frac{3}{8}$ in. thick rather than the $\frac{3}{16}$ in. used for tension and bending. In the earlier study of the TEPA plus DER 332 system, the bulk toughness specimens were contoured to a gradually sloping contour ($m = 90 \text{ in.}^{-1}$). To minimize bending stresses and hence arm break-off (see ref. 2), the contour angle for the HHPA specimens was made much steeper, to $m = 3 \text{ in.}^{-1}$ ($m' = 4.75 \text{ in.}^{-1}$), as shown in Figure 5b. The face grooves needed to contain the crack in the desired plane of extension were always the same shape: $b_n/b = 0.75$, with a root radius at the bottom of the groove of 10 mils.

Postcuring was again done after machining to relieve the machining and casting residual stresses. After postcuring, a saw cut was made to the point where the taper began, and a razor blade was used to tap in a crack. The crack from the razor blade was not generally sharp enough to be a "natural crack." Consequently, data were only collected on specimens after a crack was "popped in" by tensile loading.

Calculation of bulk toughness was made using the formula from ref. 2:

$$G_{Ic} = \frac{4P_c^2}{Eb_n b} m'$$

where P_c = fracture or critical load, in lb; E = modulus of elasticity of bulk material, in psi; b_n = crack width at notch plane ($b_n/b = 0.75$); b = specimen width ($\cong 3/8$ in.); $m' = 4.75$ in.⁻¹ for $m = 3$ in.⁻¹; $m = (3a^2/h^3) + (1/h)$, in in.⁻¹; a = instantaneous crack length, in in.; and h = instantaneous height from crack plane to taper, in in. Hence

$$G_{Ic} = 360 \times 10^{-6} P_c^2 \text{ lb/in.}$$

Toughness and Stress Corrosion Cracking of Adhesive Joints

The type of specimen, the specimen preparation, and the testing method used to collect toughness and stress corrosion cracking data in the adhesive joints were identical to those previously used on the amine systems.^{3,4} The specimen shape is shown in Figure 5c.

RESULTS AND DISCUSSION

Tensile Properties

Young's modulus in bending and tension, as a function of the composition and postcure temperature, is shown in Figure 7. The scatter in tensile modulus for the anhydride-hardened system was greater than had been found for the amine-hardened one.³ It was for this reason, and the importance attributed to modulus, that this property was also measured in bending. The difference in shape between the tensile and bending curves as a function of composition cannot be readily rationalized. In any event, there is less difference in modulus as a function of composition for either test than previously reported in ref. 5 for the TEPA-hardened resin.

The yield strength is defined as the stress at 1% total strain. For the two lower postcuring temperatures, fracturing occurred prior to reaching this strain for the specimens made with 120 phr of hardener.

Toughness of Bulk Epoxy

The toughness of bulk HHPA-hardened epoxy was measured on specimens prepared with the same combinations of hardener contents (viz., 50, 70, and 120 phr) and postcuring temperatures (212°, 311°, and 365°F) that was used for the tensile test specimens. The load (P) versus displacement (Δ) curves obtained on the bulk material were "peaked," or saw-toothed, so that two instability points were identified; a high one, associates with the toughness or energy needed to cause a slow-moving or stationary crack to abruptly jump ahead at a high velocity, and a lower one that is associated with the toughness at which a running crack will stop. Both of these points

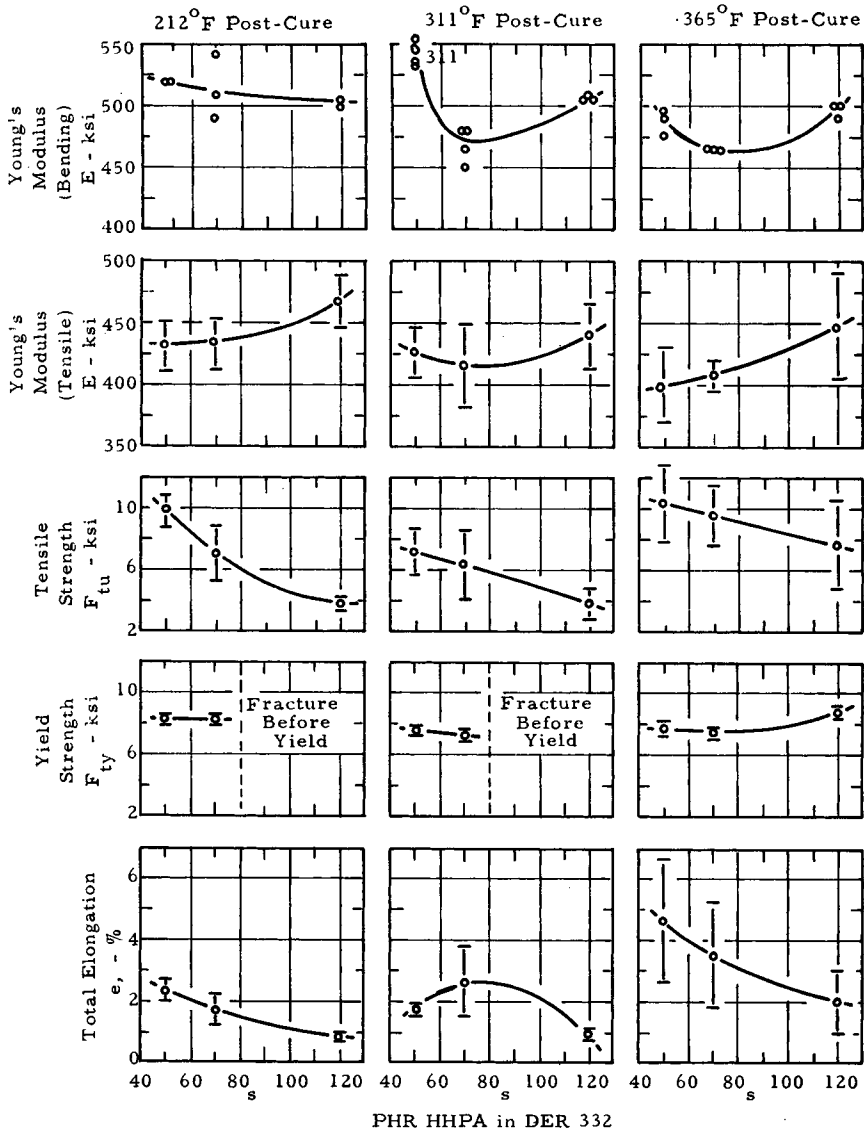


Fig. 7. Mechanical properties of bulk epoxy as a function of composition for three post-cure temperatures. Postcure time, 5 hr.

are identified in Figure 8, in which the toughness of bulk epoxy hardened with HHPA is shown as a function of composition, for each of the three postcure temperatures. For some of the specimens, the difference between initiation and arrest was large, while for others it was essentially zero. The large increase in toughness found as the amount of TEPA hardener was increased from approximately one-half to twice the stoichiometric composition was not found with the HHPA-hardened one. On the other hand, the

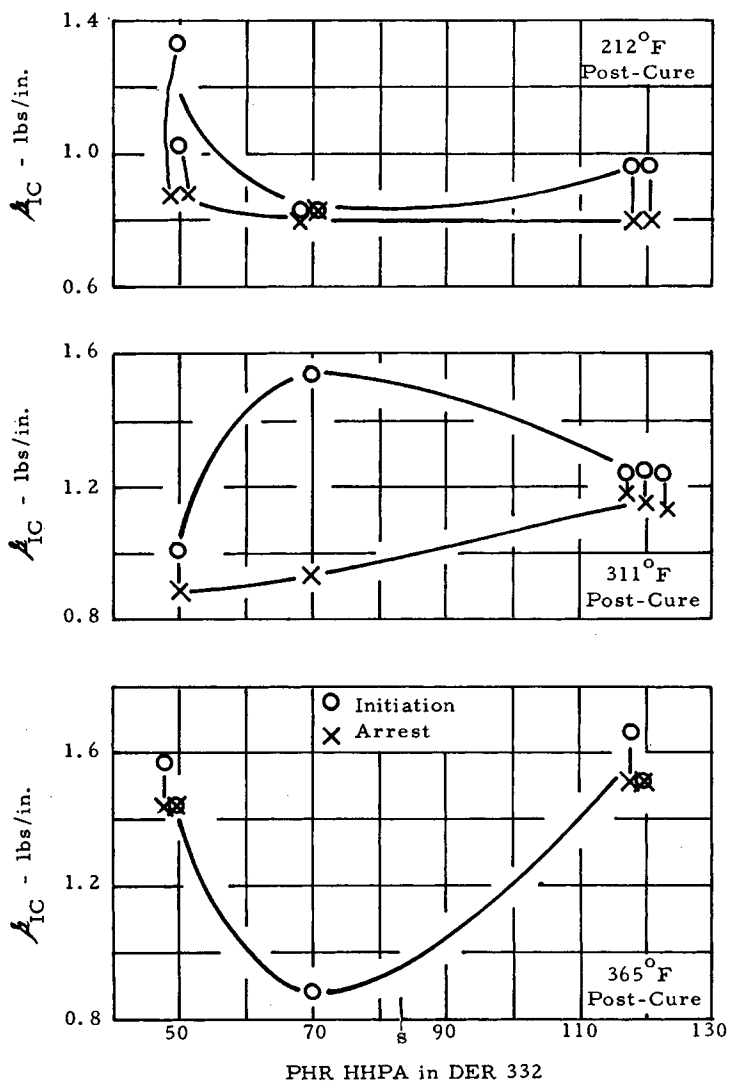


Fig. 8. Toughness of HHPA-hardened bulk epoxy as a function of composition for three postcure temperatures. Postcure time, 5 hr: (O) initiation; (X) arrest.

toughness of the latter did increase with postcure temperature (Fig. 9), which was consistent with the TEPA system.

Toughness of Joints

The effect of composition and postcure temperature on the toughness of 5-mil-thick joints of the HHPA-hardened epoxy system is shown in Figures 10 and 11. Variations in either the hardener-to-resin ratio or postcure temperature, over the ranges investigated, were found to have only a

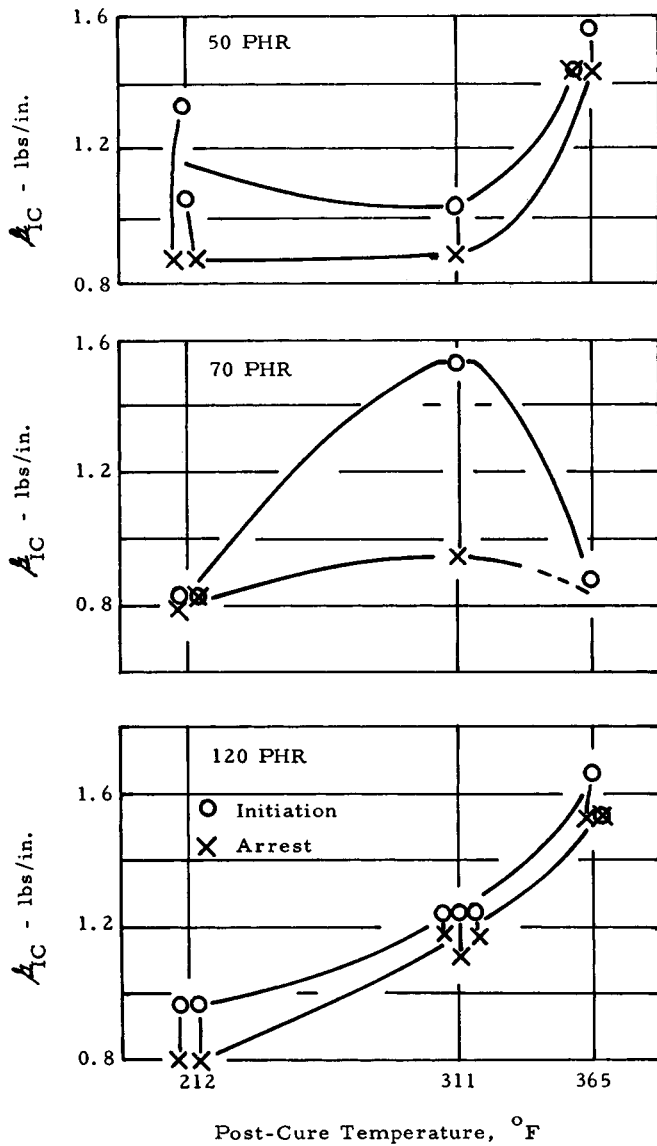


Fig. 9. Toughness of HHPA-hardened bulk epoxy as a function of postcure temperature for three compositions. Postcure time, 5 hr: (O) initiation; (X) arrest.

modest effect on toughness. This behavior is also quite different from that found for the amine-hardened system. For the latter, changes in these manufacturing variables caused a fourfold change in joint toughness.

Further, increasing the postcure temperature for amine-hardened joints for all hardener-to-resin ratios caused a larger increase in initiation than in arrest toughness. This toughening was shown to be associated with an

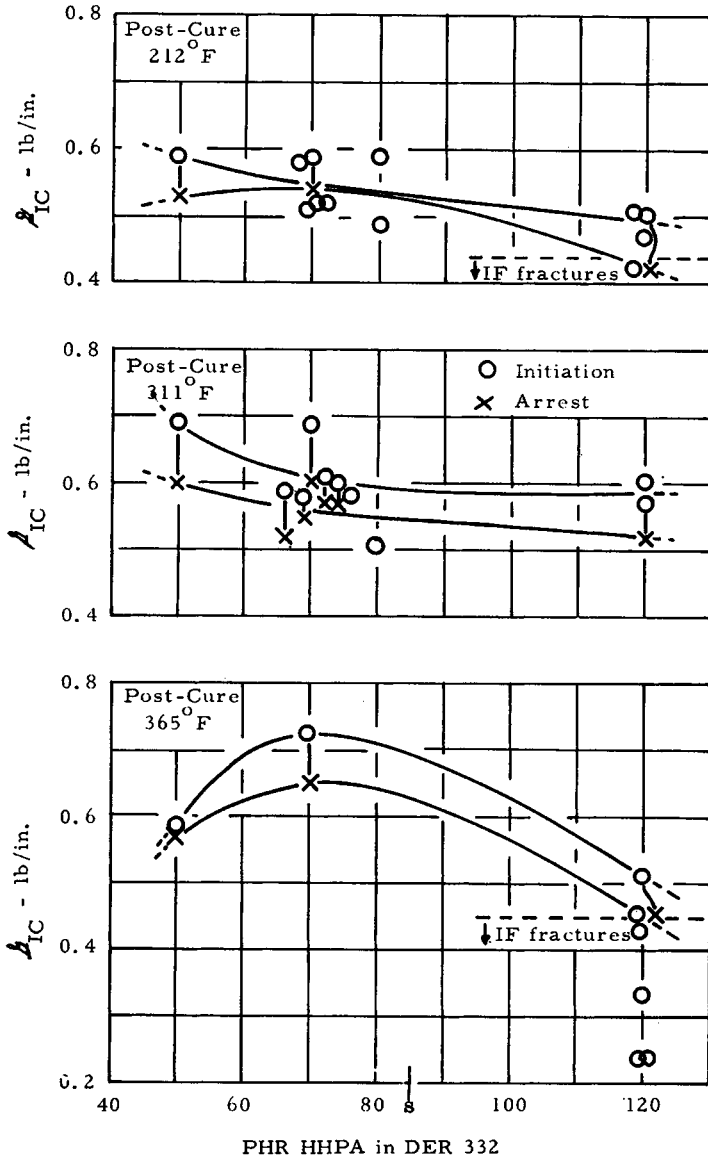


Fig. 10. Toughness of HHPA-hardened epoxy 5-mil adhesive joints as a function of composition for three postcure temperatures. Postcure time, 5 hr: (○) initiation; (×) arrest.

increased crack velocity at initiation for specimens postcured at high temperatures. The difference between initiation and arrest toughness for the anhydride-hardened joints, on the other hand, was always small, implying that increased postcure temperatures did not force the crack to extend at higher velocities.

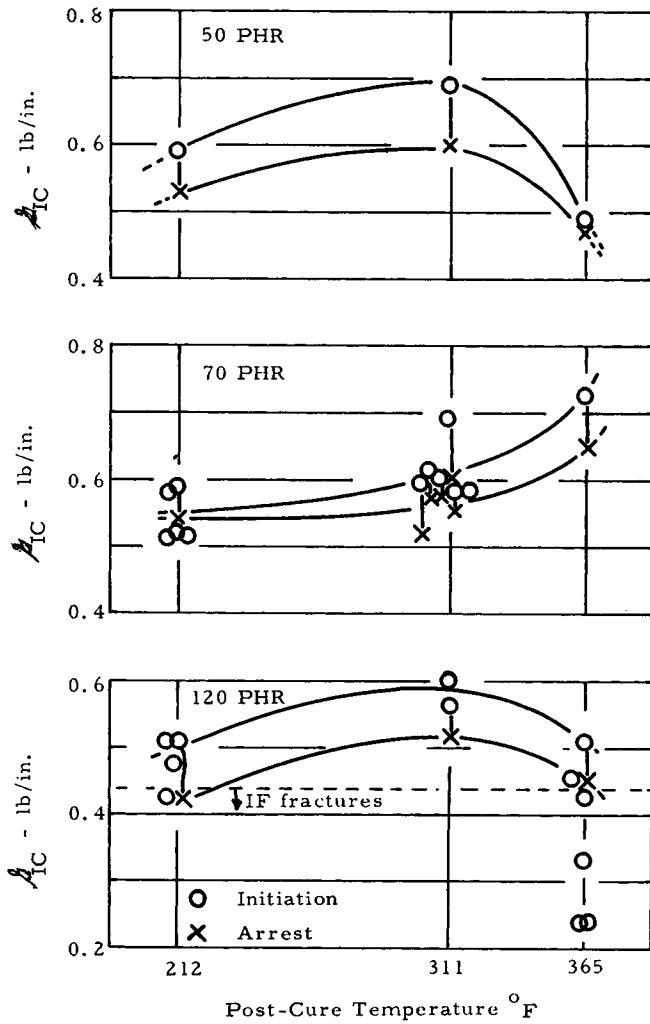


Fig. 11. Toughness of HHPA-hardened epoxy 5-mil adhesive joints as a function of postcure temperature for three compositions. Postcure time, 5 hr: (O) initiation; (X) arrest.

In the study of the amine-hardened system, the initiation toughness of joints was shown to be a function of Young's modulus of the bulk epoxy. In order to find whether or not the bulk or bond toughness was related to any of the smooth specimen properties, the initiation and arrest toughnesses were plotted as a function of modulus (both bend and tensile), tensile strength, yield strength, and elongation. As found with the amine-hardened system, the toughness of the bulk epoxy could not be correlated with any uncracked specimen property: nor could the toughness of bonds and bulk be correlated. The initiation and arrest toughness of the joints, on the

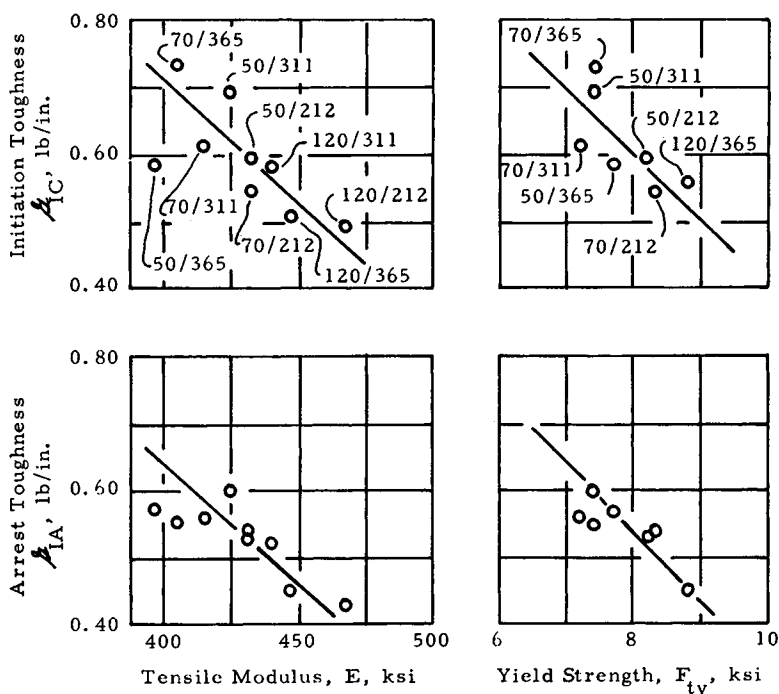


Fig. 12. Dependence of joint toughness on tensile modulus and yield strength of bulk epoxy.

other hand, did show a dependence on tensile modulus and yield strength (Fig. 12). Because of the manner in which the yield strength was defined, i.e., stress at 1% total strain, both the yield strength and tensile modulus would be expected to show similarly shaped curves as a function of any material processing or testing variables. This relationship between tensile modulus and yield strength would, of course, be true for any other material including the amine-hardened epoxies. Hence, the toughness of joints for both the amine- and anhydride-hardened systems were seen to correlate with tensile modulus and yield strength. In the study of amine-hardened joints, the crack velocity was found to increase with decreasing modulus. Yet cracking velocity would be expected to be directly, rather than inversely, proportional to a function of E , specifically $\dot{a} \propto E^{1/2}$. This would suggest that the toughness of the joints actually depends on the yield strength of the epoxy, and the previously reported dependence on tensile modulus is a result of the close correlation between modulus and yield strength of the epoxies.

The fracture morphology of the TEPA- and HHPA-hardened systems was similar. For most compositions and postcure temperatures, fractures extended cohesively near the center of the bond (CoB). When the amount of hardener was in excess of 120% to 150% of stoichiometry, however, the

preferred cracking position for both systems was near or at the interface (IF) (see Figs. 10 and 11).

Stress Corrosion Cracking of Joints

The sensitivity of adhesive joints to water was shown to manifest itself in two ways in the study of the amine-hardened system. For crack extension that occurred under the action of increasing load tests, where the total loading time was of the order of 1 or 2 min or less, water strengthened the joint; while long-time exposure to water caused a severe loss of strength. To determine the influence of water on short-time loading for the HHPA system, one adhesive (70H/311) specimen was tested as follows: (a) fractured dry to establish \mathcal{G}_{Ic} , (b) soaked 10 min in water with a wetting agent and tested, (c) soaked 2 hr and tested, and (d) finally, soaked 20 hr and tested. The P - Δ diagram for the specimen is shown in Figure 13.

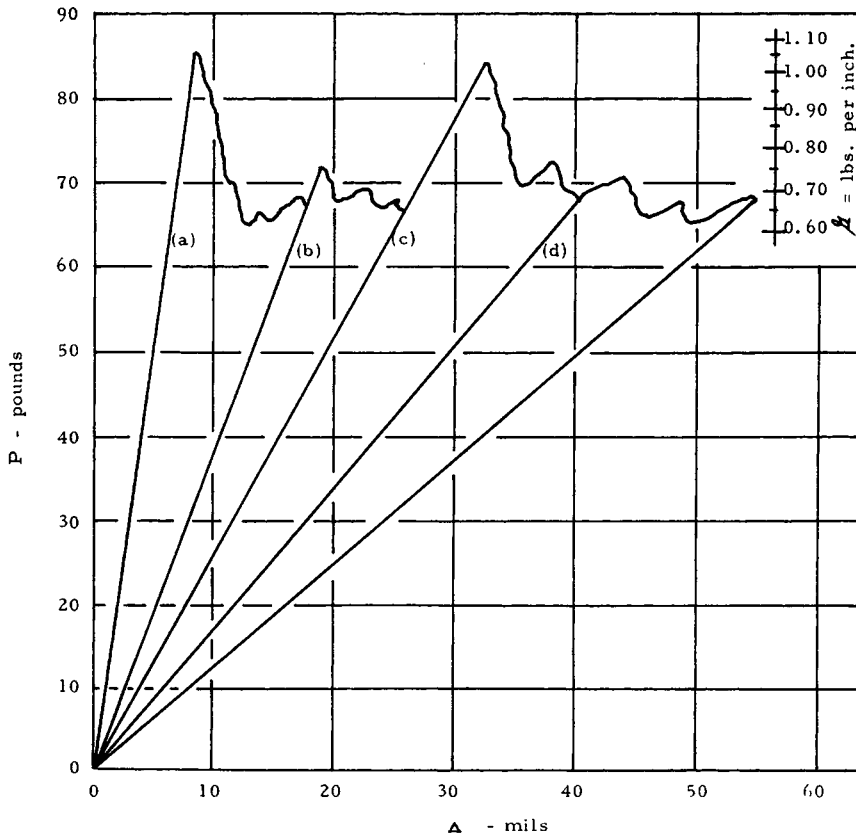


Fig. 13. Load-extension diagrams for 70H/311 adhesive specimen tested: (a) dry from blunt starter notch; (b) after soaking 10 min in water with wetting agent; (c) after soaking 2 hr in water with wetting agent; (d) after soaking 20 hr in water with wetting agent.

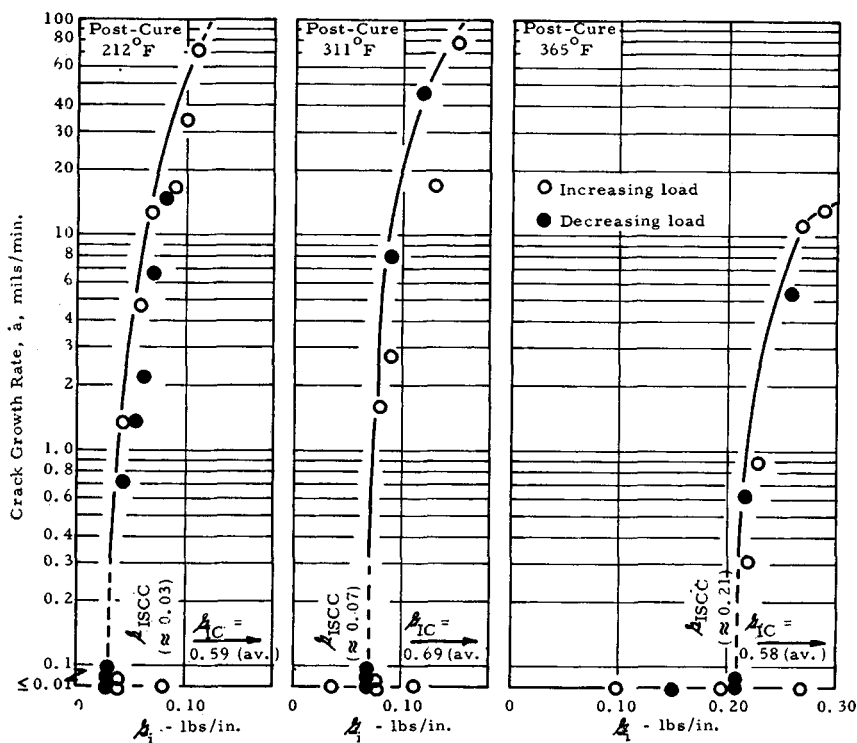


Fig. 14. Stress corrosion cracking of 5 mil, 50 phr HHPA adhesive bond in liquid water with wetting agent. Postcured at 212°, 311°, and 365°F for 5 hr: (O) increasing load; (●) decreasing load.

The dry toughness, after the crack progressed beyond the blunt starter notch, had a value of G_{T_0} of 0.63 to 0.68 lb/in. After a 10-min soaking, it increased to more than 0.70 lb/in. and 2 hr of soaking raised the toughness to approximately 1.00 lb/in. After a 20 hr soaking, however, the toughness was only moderately increased over its initial value of approximately 0.65 lb/in. Examination of the fracture surface after testing indicated that the long-time soak weakened the interface. Whereas all the cracking, excepting for a short section immediately after the long-time soak, was CoB, the long-time soaking weakened the interface sufficiently to cause IF cracking. In all cases, the toughening produced by water existed only over a short length of crack extension. Other than the interface weakening, this behavior is identical to that previously reported for the amine-hardened adhesive.⁴

Weakening of the joint after long-time soaking suggests that $G_{T_{ISCC}}$ for the anhydride system is far lower in relationship to G_{T_0} than is the case for the amine-hardened joints.

The cracking rate in water for the joints, having the same combinations of composition and postcure temperature used for toughness testing, as a

function of applied \mathcal{G} , i.e., \mathcal{G}_i , is shown in Figures 14, 15, and 16. It is seen that this material is far more sensitive to water than the amine-hardened one. Whereas for 10T/180, \mathcal{G}_{ISCC} was approximately $\mathcal{G}_{Ic}/4$ and for the 12.5T/270, it was approximately $\mathcal{G}_{Ic}/2$, for many of the HHPA-hardened adhesives, \mathcal{G}_{ISCC} was as low as $\mathcal{G}_{Ic}/10$. This severe sensitivity to water of the anhydride-hardened joints is apparent from the comparison of the \mathcal{G}_{ISCC} with \mathcal{G}_{Ic} for the three compositions and postcure temperatures in Figure 17.

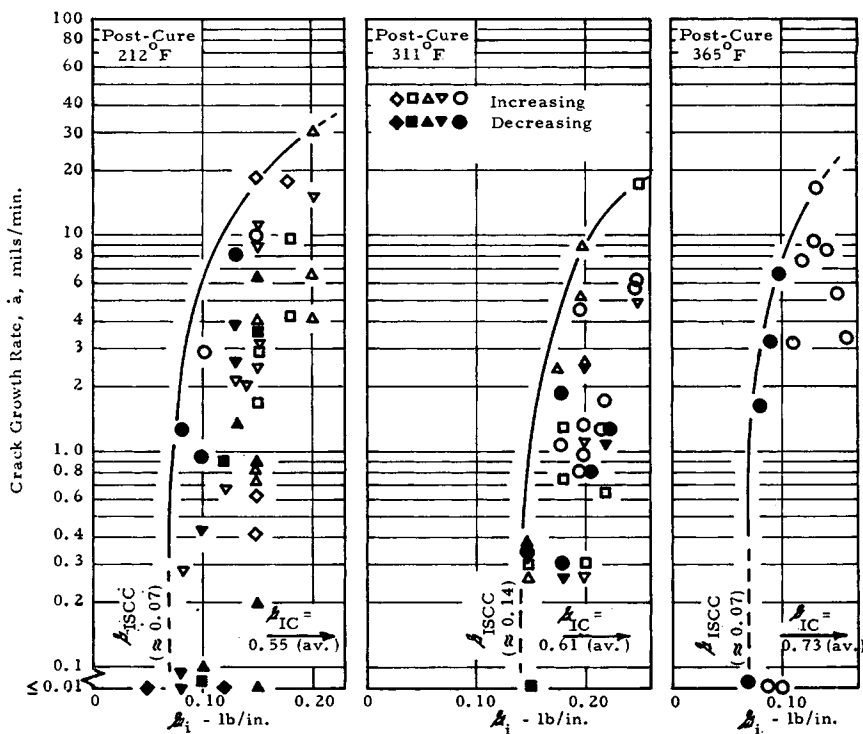


Fig. 15. Stress corrosion cracking of 5 mil, 70 phr HHPA adhesive bond in liquid water with wetting agent. Postcured at 212°, 311°, and 365°F for 5 hr: ($\diamond \square \triangle \circ$) increasing; ($\blacklozenge \blacktriangle \blacktriangledown \bullet$) decreasing.

The cracking morphologies for the TEPA- and HHPA-hardened systems were identical. In short-time loading, cracking occurred CoB, while all subcritical cracking (i.e., at less than \mathcal{G}_{Ic}) was at the interface between the adhesive and adherend.

CONCLUSIONS

1. The crack toughness of amine- and anhydride-hardened epoxy joints are similar although the range of toughnesses that can be obtained with the former is far broader than for the latter.

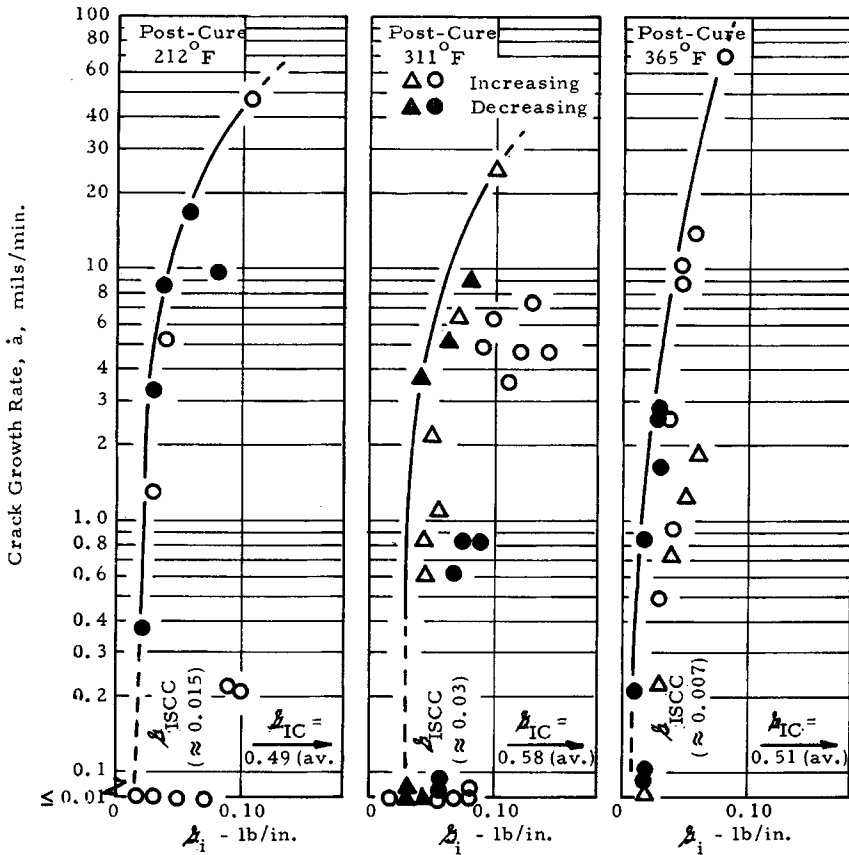


Fig. 16. Stress corrosion cracking of 5 mil, 120 phr HHPA adhesive bond in liquid water with wetting agent. Postcured at 212°, 311°, and 365°F for 5 hr: (Δ O) increasing; (\blacktriangle) decreasing.

2. Like the amine-hardened epoxies, the toughness of anhydride-hardened joints could not be correlated with the toughness of the bulk material. Further, the bulk toughness could not be correlated with any properties measured on uncracked specimens, while the joint toughness for both hardener systems was dependent on tensile modulus and/or yield strength.

3. Both systems are toughened in the vicinity of the crack tip by the addition of water if cracking is fast enough for the crack to remain CoB.

4. Under sustained loads, the anhydride system is far more sensitive to water than the amine one. The ratio of G_{ISCC} to G_{IC} for the former is of the order of $1/4$ to $1/2$, while for the latter it can be as low as $1/10$.

5. The fracture morphologies for the amine and anhydride systems are the same, i.e., fast cracking occurs CoB, and slow cracking occurs at the interface.

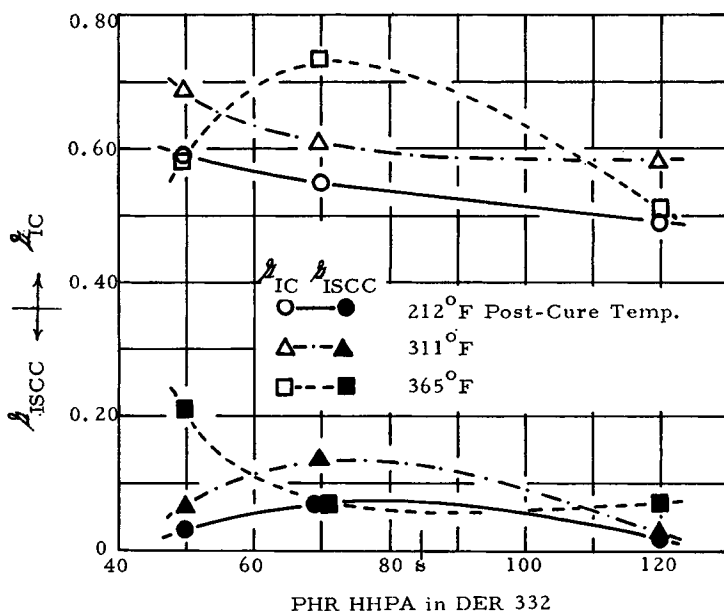


Fig. 17. Comparison of G_{IC} and G_{ISCC} of HHPA-hardened epoxy joints.

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