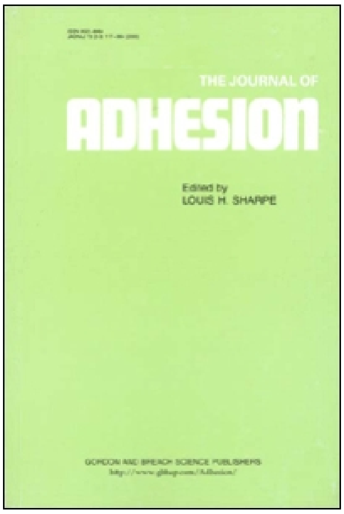

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On the Fracture Energy, Rehealing Velocity and Refracture Energy of Cast Epoxy Resin

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Note

On the Fracture Energy, Rehealing Velocity and Refracture Energy of Cast Epoxy Resin

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The fracture energy of cast epoxy resin was measured by a novel method in the presence of various agents. The crack spontaneously rehealed under heating to above the heat distortion temperature to give a fresh joint of about the same fracture energy as the virgin material.

INTRODUCTION

Cast epoxy resin is a notoriously brittle material, and, even with glass reinforcement, it crazes and a network of cracks is formed at comparatively low stress levels. A useful measure of its strength and resistance to crack propagation is the fracture energy. Another property of cast epoxy resin is its apparent ability to heal its cracks through the application of heat. Little note has been taken of this latter phenomenon though Kulski [1] pointed it out as a property of various viscous materials. A measure of its readiness to reweld or heal its cracks might be the velocity with which the cracks disappear and also the fracture energy to reopen a crack after it has healed. This paper deals with all three aspects of cracks: the fracture energy to form them, the rate at which they reheal and the fracture energy needed to reopen them. A new method of measuring fracture energy is used. The fracture energy under long term loading is also measured. Measurements are made in laboratory air in the presence of various surface treating agents.

GENERAL DISCUSSION

The concept of fracture energy is a recent one and has been largely developed by Irwin and his coworkers [2, 3, 4] in suggesting that the fracture energy or energy required to extend a crack over unit area was a critical factor in crack propagation. The concept of fracture energy differs from the earlier idea of surface energy governing crack propagation which was propounded by Griffith [5]. The concept of fracture energy combines the energy absorbing mechanisms of plastic deformation as well as surface energy itself and the kinetic effects into an overall coefficient of fracture energy $\mathcal{G}$ which is, in turn, dependent on the mode of fracture. The values of $\mathcal{G}$ are different for the open mode of fracture, the forward shear mode and parallel shear mode and are referred to as $\mathcal{G}_{\text{I}}$, $\mathcal{G}_{\text{II}}$, and $\mathcal{G}_{\text{III}}$. We will be concerned with the evaluation of $\mathcal{G}_{\text{I}}$ below. Irwin postulated that, when the strain energy release rate equalled the value of $\mathcal{G}_{\text{I}}$, then the crack would run and fracture occur.

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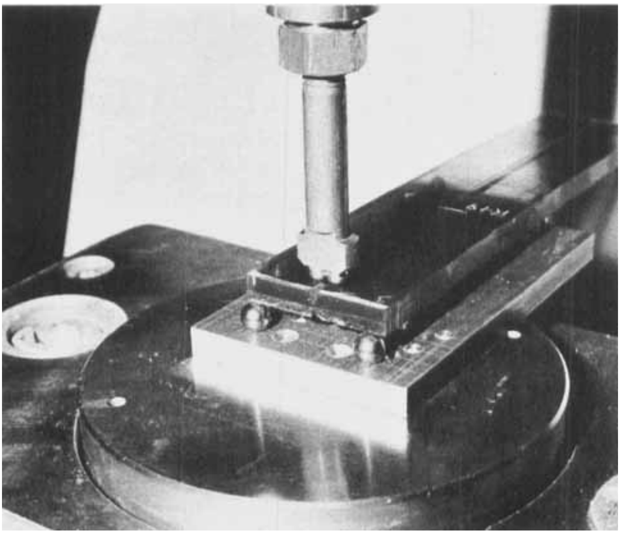

Figure 1. Cast epoxy specimen mounted in Instron testing machine for determination of fracture energy.

There have been several ways of measuring $\mathcal{G}$ [4, 6]. All these methods are such that the loading at the crack tip varies as the depth of the crack increases. This implies that the essential loading changes with the depth and makes the estimation of energies difficult. Attempts to avoid such problems [6] have resulted in awkward specimens that can only be adapted to different media with difficulty. This paper uses a novel method of determining fracture energy [7]. The method uses a simple rectangular cast slab that is machined so that a crack can be propagated down its center by double torsion. In this case the forces at the edge of the crack will be the same regardless of the length of the crack provided a constant load is applied. Mathematical details are given in the appendix.

This simple technique is particularly adapted to obtaining fracture energy under long term loading and also under different environments and such data are also given.

FRACTURE ENERGY

All the specimens consist of 100 parts Epon 826, 90 parts nadic methylanhydride and 1 part benzyl dimethyl amine. They are cast and cured at 250°F for 24 hours prior to being milled with a groove down their center. For short term loading they are loaded in an Instron testing machine as in Fig. 1 where they are subjected to double torsion through the four hemispheres that actually apply the load. Fig. 2 is a diagrammatic sketch detailing the loads and dimensions. This technique is also adapted to long-term loading by using a deadweight as in Fig. 3. In this way it is possible to apply double torsion to the specimen over a period of several weeks to observe any long term crack growth under load.

The fracture energy of such resin was found to be 211, 750 ergs/cm^2 with a standard deviation of 47,775 ergs/cm^2 from testing 20 samples. These specimens were tested in normal air. The nature of the crack formation was different from a similar test with glass in that the crack ran when the torsion reached a certain value and would in no case travel less than at a critical speed. This would not be the case with glass when the crack would merely travel slower if the load were less [7]. This phenomenon was analyzed by loading a series of specimens to loads of 90, 80 and 70% of the load needed for the crack to run and maintaining these loads over a period of 30 days. In no case was the crack observed to lengthen during this period. When the specimens were replaced on the Instron testing machine, then the same or greater load as originally was needed to cause the crack to move was needed to move it again.

This observation indicates a fundamental difference between the nature of the failure of glass and that of cast epoxy resin and one which deserves a closer analysis that is beyond the scope of this paper but which nevertheless indicates the inherent long term stability of epoxy resin under high loads compared to glass under similar conditions.

It was attempted also to determine whether or not various surface treating agents including carboxyethyl silicic acid, chropropyltrimethoxysilane (Dow-Corning XZ-8-0997, XZ-8-0999), the presence of liquid water or kerosene would have any effect on the fracture energy during the long term loading and perhaps cause the crack to run. None of these agents had any effect. The nature of the fracture surface was always the same. It consisted of a glassy smooth surface that was free of any striations and this surface was always perpendicular to the surface of the specimen.

THE REHEALING OF CRACKS

After the specimens had been split along about half their length in the experimental determination of their fracture energy, it was decided to subject them to heat to observe their energy after heating. A curious phenomenon was observed while they were in the oven: the cracks rehealed at a reasonably constant rate starting from their tips.

It was not necessary to apply any clamping pressure, nor was it necessary to deliberately exclude moisture. The specimens had, however, to be raised in temperature.

The velocity of rehealing is shown in Fig. 4 and is shown to be essentially the same during heating at 300°F and at 400°F where the initial cure was for 24 hours at 250°F. There was no rehealing whatsoever if the specimen was heated, after cracking, to 250°F.

It was suspected that the rehealed cracks would be similar to those that are apparent in a partially cracked glass slide: the crack is made and then it becomes invisible until the glass is re-strained when it again becomes visible. This merely indicates that the crack has closed until it is less than a critical width and hence becomes invisible. In order to check for such an occurrence, the specimen was replaced in the device used to test for fracture energy and the energy needed to

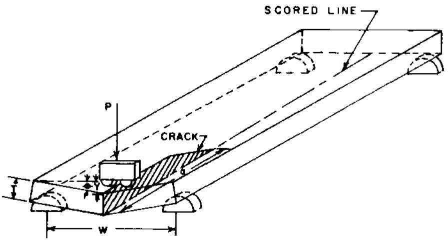

Figure 2. Schematic of test apparatus.

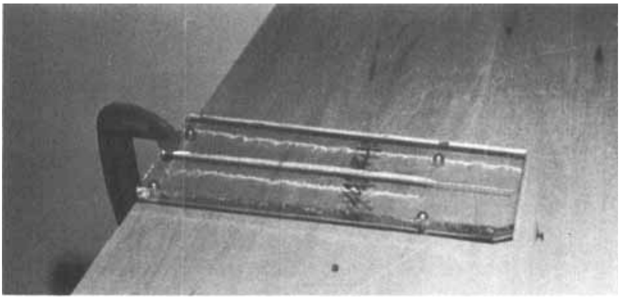

Figure 3. A glass specimen being subjected to a deadweight load for determination of fraction energy at very slow rates of crack propagation.

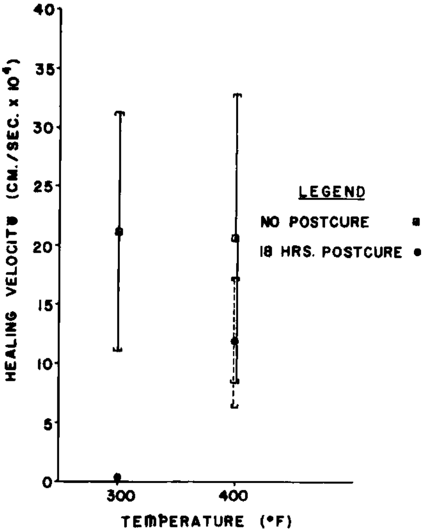

Figure 4. The velocity of rehealing at different temperatures of rehealing.

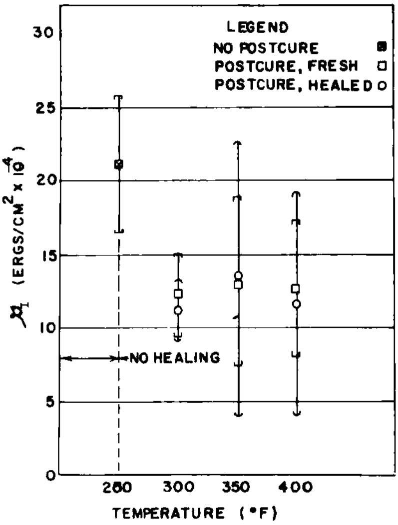

Figure 5. The fracture energy of cast epoxy resin, cured, postcured and after rehealing.

repropagate a crack along the original crack direction was measured. The results are shown in Fig. 5. The crack was made to extend into the material that had not already been cracked and rehealed so that it could be determined whether or not the healing was complete.

The material that had merely been subjected to heating showed a distinctly lower fracture energy than the material that had not been heated, however, the rehealed material showed essentially the same fracture energy upon refracture as that of the virgin heated material. It was also suspected that the postcure that would occur was the important factor in rehealing so a rehealed, rebroken specimen that had been healed at 400°F was subjected to 300°F to observe if it would reheal after it had once been subjected to a high temperature. It did reheal thereby indicating that the rehealing did not depend on concomitant curing.

DISCUSSION

The observation that a crack in an epoxy resin that has been cured at 250°F for 24 hours can be healed by exposure to subsequent heating appears novel. The fact that the fracture energy of rebreaking the crack open is in the same as that for the virgin material is quite surprising and leads to the observation that all bonds broken during the initial fracture are reformed during healing. Also we can postulate that there is not sufficient deformation of the surface resulting from relief of internal energy upon fracture to keep the surfaces separated and hence preclude rehealing.

An examination of the cracked specimen before rehealing shows that there is a distinct stress near the tip of the crack. This is revealed by photographing the specimen in crossed polarized light as in Fig. 6. The lines emanating from the tip of the crack indicate a residual stress and hence some plastic deformation during the cracking process.

A microscopic examination of the fracture surface before and after healing and refracture was made. There was no observable difference or step where the material had refractured. This indicates that the original crack heals and refractures along substantially the same surface that originally was fractured. There is no indication of any smaller pieces of resin being pulled out of the surface.

In order to check on the nature of the fracture, it is illuminating to notice the disparity between the surface energy of the resin which is of the order of 50 ergs/cm^2 and the actual energy of fracture which is of the order of 211,000 ergs/cm^2. It is evident that by far the greater portion of the energy of fracture goes, not into the creation of surface, but into the distortion of the portions of the resin next to the fracture zone. That the resin deforms plastically under stress is shown in Fig. 7 where a scriber is drawn across the surface of cured resin that has been subjected to a postcure of 400°F. The grooves are of two sorts: the smooth groove where the resin has been pushed to one side and has not been cut, and the portion where the resin has been partially fractured. It is apparent that plastic deformation has occurred.

Fig. 8 shows the same scratches after the specimen has been heated to 300°F for 12 hours. The plastically deformed grooves have almost disappeared and the

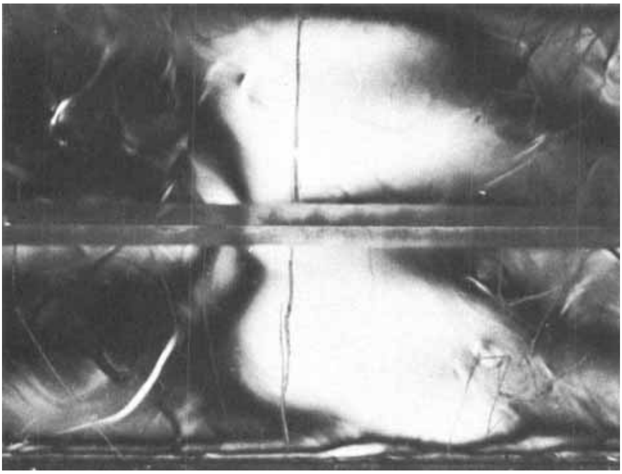

Figure 6. A view of the cracked epoxy resin during the rehealing process under crossed polaroids.

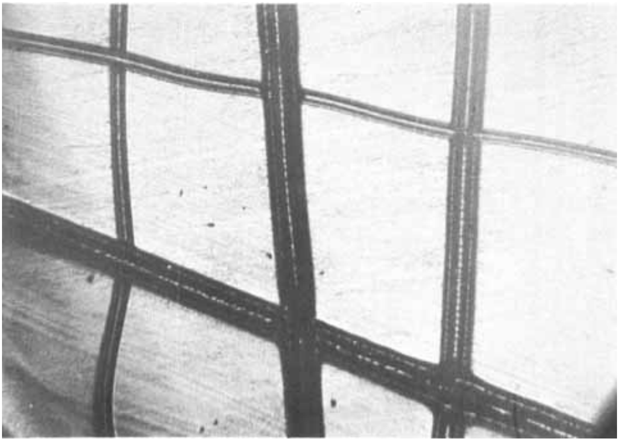

Figure 7. 400°F postcured resin after scriber has been drawn across the surface.

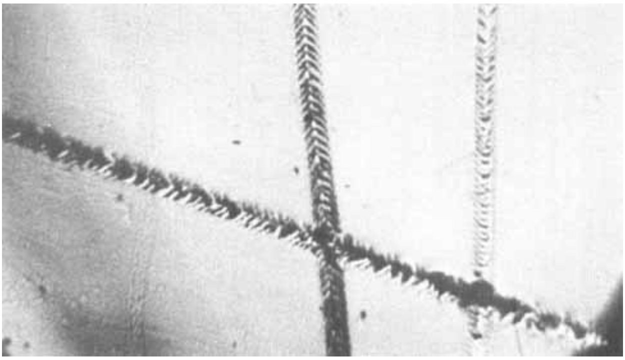

Figure 8. The same surface as Fig. 7 after heating to 300°F for 12 hours.

partially fractured portion has been brought into line so that the original surface is substantially restored though a chevron pattern remains to indicate a surface rupture. Another simple experiment to show that a portion of the energy of fracture has been dissipated in orienting the volume of resin close to the fracture surface is through observing a thin section of the resin cut parallel to the fracture surface through cross-polarized light. Fig. 9 shows the transparency of the section indicating orientation and stress at the fracture surface. Fig. 10 shows the same portion after it has been exposed to 350°F for 1 hour. The transparency is modified indicating that the stress and orientation release through heating. Energy has been absorbed in orienting the resin near the fracture surface and it is the release of this energy by micro-Brownian motion coupled with the pressure engendered between the fracture surfaces that encourages the rehealing of the cracks and the smoothing of the grooves.

It should be noted that the necessary temperature is above the glass transition temperature which, for this resin, is about 250°F [8]. Rehealing has not been observed below this temperature. It is also significant that the fracture energy is about 2000 times the surface energy of the resin as determined by surface tension measurements. The relatively small surface energy of about 50 ergs/cm^2 would be sufficient for cohesive bonding so a very small fraction indeed of the energy of fracture would be needed to promote maximum adhesion.

Micro-Brownian motion has been reported by Sharpe and Schonhorn [9] as being responsible for the adhesion of epoxy resin to chlorotrifluoroethylene copolymer. A similar situation occurs with the two surfaces of cured epoxy resin where the local flow restoring the original surface contour permits the surface energy to ensure a sound bond. Here too it is necessary to heat the epoxy to above the glass transition temperature.

CONCLUSIONS

The fracture energy of cured epoxy resin has been determined by a novel method and shown to be over 2000 times the surface energy. The greater part of the fracture energy results in plastic deformation of the volume of the epoxy resin adjacent to the fracture surface and this plastic deformation is recoverable upon heating to above the glass transition temperature when the fracture surfaces will approach their original configuration and rehealing will take place at a velocity that is substantially independent of the temperature provided it is above a certain value.

The rehealed portion can be refractured at the same fracture energy as the virgin material.

APPENDIX

Theoretical Analysis of the Method of Determining the Energy of Fracture

A central load of P is transmitted symmetrically through two points of loading on a rectangular section of resin of thickness t with a distance between the supporting points of w as in Fig. 2. Let θ be the angle of twist of each half, M_t

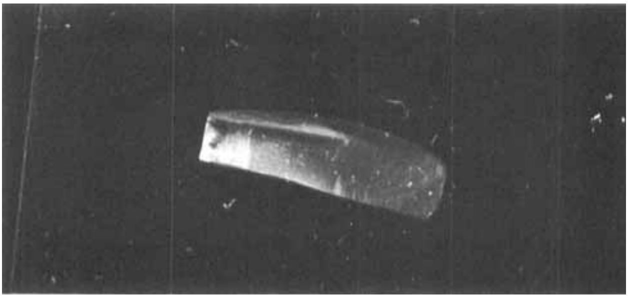

Figure 9. A thin section of resin parallel to the fracture surface viewed under polarized light.

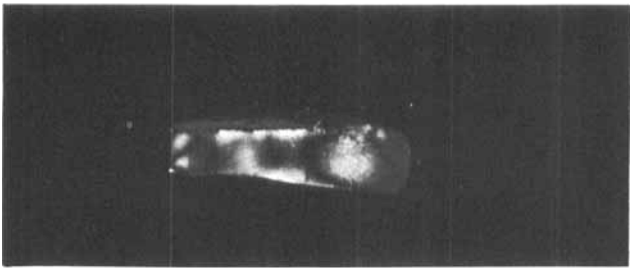

Figure 10. The same section of resin as in Fig. 9 after it has been heated to 350°F for 1 hour.

the applied twisting moment, a the crack length, J the polar moment of inertia of the half and G the shear modulus.

Then $\theta = M(a/Jg) = Pwa/4JG$ as $M_t = Pw/4$
also $\theta = 2y/w$ where y is the displacement of P

So: $C = w^2a/8JG$

and $dC/da = w^2/8JG$ which is a constant for the specimen and it should particularly be noted that it is independent of a.

Thus as the surface energy of fracture $\mathcal{G}_I = \dfrac{P^2}{2t}\dfrac{dC}{da}$ according to Irwin [4]

so $\mathcal{G}_I = \dfrac{P^2w^2}{16JGt}$ which is independent of the depth of the crack.

$\dfrac{w^2}{8JG} = \dfrac{y}{Pa}$ is a constant and can readily be determined experimentally so $\mathcal{G}_I = P^2K$ where K is a geometrical function of the original specimen and will not change as the specimen is cracked. The particular advantage of this method of determining $\mathcal{G}_I$ is that the load needed to propagate the crack does not change according to the length of the crack so a stable crack is possible and computation is minimal.

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REFERENCES

1. H. Kulski, Fracture, Proc. International Conference on the Atomic Mechanisms of Fracture. Swampscott, Mass., 1959. Wiley; New York 1959. p. 293.
2. G. R. Irwin and J. A. Kies, Welding Journal Res. Suppl., April 193S-198S (1954).
3. G. R. Irwin, Structural Mechanics. Edited by Goodier and Hoff. Pergamon Press, pp. 557-594 (1960).
4. G. R. Irwin, Appl. Matls. Res., Vol. 3, No. 2, pp. 65-81, 1964.
5. A. A. Griffith, Phil. Trans. London, Series A221, 1920. pp. 163-196.
6. E. J. Ripling and S. Mostovoy, Materials Research Laboratory Inc. Final Report on Contract No. NOw 64-0414-c for Bureau of Naval Weapons. 1965.
7. J. O. Outwater and D. J. Gerry, On the Fracture Energy of Glass, U. S. Naval Research Laboratory Report Contract NONR-(3219) (01) (1) 1966.
8. Shell Chemical Company, SP-27-B. p. 4.
9. H. Schonhorn and L. H. Sharpe, Jour. of Polymer Sci., Part A. Vol. 3, pp. 3078-3097. 1965.