

Influence of External Environments on Fracture Toughness of Epoxy Resin

K. MIZUTANI and T. IWATSU, *Osaka Prefectural Industrial Research Institute, Takaida-naka, Higashi-Osaka, 577, Japan*

Synopsis

Crack propagation in an epoxy resin in the presence of organic solvents was investigated. Fracture toughness (K_{IC} , a critical stress intensity factor) of the epoxy resin in various external environments was measured using a double cantilever beam specimen. Fracture toughness for initiation (K_{ICi}) of the resin in the presence of organic solvents was larger than that in the absence of solvents, and the epoxy resin showed a minimum value of K_{ICi} in the presence of the organic solvent whose solubility parameter was about $11 \text{ (cal/cm}^3)^{1/2}$. This was due to large plastic deformation at a crack tip and the yield strength was lowered by exposure to organic solvents. The former increases K_{IC} , while the latter decreases K_{IC} . Fracture surfaces of the resin fractured in solvents suggest that a crack grew slightly when accompanied by a large plastic deformation, and then propagated at high speed.

INTRODUCTION

Crack propagation in amorphous thermoplastic resins, such as polystyrene, poly(methyl methacrylate), and polycarbonate, is accompanied by craze formation ahead of the crack tip. Except for thermosetting resins, a craze has never been observed directly. However, Yamini et al. reported that a localized plastic deformation occurred at the crack tip prior to crack extension in the case of an epoxy resin.¹⁻⁵ Also, Mijović and Koutsky observed a correlation between the fracture morphology and the ultimate mechanical properties of epoxy resins.^{6,7} For these investigations linear elastic fracture mechanics could be used effectively. In fracture mechanics, fracture toughness, i.e., critical stress intensity factor (K_{IC}) or critical strain energy release rate (G_{IC}), is regarded as a measure of the ability of materials to resist extension of a preexisting crack.

Mostovoy and Ripling investigated resistance to crack extension in an aggressive environment, i.e., fracture toughness in the presence of water vapor (G_{ISCC}), which can be considered as G_{IC} below which stress corrosion cracking cannot occur. G_{ISCC} was approximately $1/10$ to $1/2 \times G_{IC}$, depending on the composition of the epoxy resins.^{8,9} Also theoretically, Thomson investigated the effect of external environments (diatomic gases) on crack propagation in brittle materials, and discussed how the gas molecules define crack extension as a chemical reagent.^{10,11} Results indicated that fracture toughness of epoxy resins in the presence of the reagent was smaller than in vacuum. On the other hand, Ripling et al. reported that fracture toughness in the presence of water was larger than in vacuum.⁹

As thermosetting resins are widely used as chemical resistant materials, it is

very significant to investigate the fracture mechanisms affected by external environments. In this paper, fracture toughness of an epoxy resin in the presence of organic solvents will be reported, and the effect of solvents on crack propagation in the epoxy resin will be discussed.

EXPERIMENTAL

Epikote 828 (Shell's liquid diglycidylether of bisphenol A) was used with 10 phr (parts per hundred parts of resin) of triethylenetetramine. The resin and curing agent were thoroughly mixed and degassed, and then cast between glass plates 6 mm apart. After curing for 24 h at room temperature, the molding plate (thickness of 6 mm) was postcured for 30 min at 115°C. Then, this epoxy plate was allowed to cool gradually to room temperature.

To calculate the fracture toughness, K_{IC} or G_{IC} , of the epoxy resin, a double cantilever beam (DCB) specimen was utilized. This DCB specimen was prepared (Fig. 1). The DCB specimens were machined from a molded plate. A precrack, which had a very small crack tip radius, was formed by applying an overload on the specimen. For the DCB specimen, a stress intensity factor (K_I) is given by¹²

$$K_I = \frac{Pa}{w^{1/2}b^{1/2}d^{3/2}} \left(3.467 + 2.315 \frac{d}{a} \right) \quad (1)$$

where P , a , w , b , and d are the applied load, the crack length, the plate thickness in the plane of the crack, the beam width, and the beam height, respectively.

Cleavage tests were conducted at $23 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ humidity, using an Instron testing machine at a crosshead rate of 0.5 mm/min. Also, cleavage tests in organic solvents were conducted at the same rate and temperature in a special container which could contain various organic solvents. These tests were conducted under the following condition: a crack was extended within 1 min from the immersion of the DCB specimen in the solvent. Organic solvents used in this experiment are shown in Table I. In this table, the solubility parameter and viscosity at 20°C are shown. Three solvent groups were used: the upper group is nonpolar and poorly H-bonded, the middle group is moderately H-bonded, and the lower group is strongly H-bonded. All organic solvents were reagent grade.

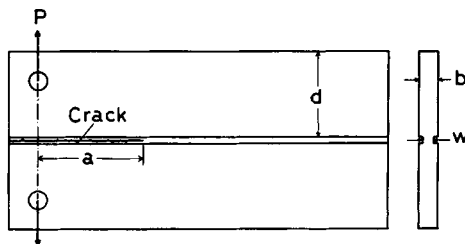


Fig. 1. Schematic diagram of double cantilever beam (DCB) specimen, where $d = 30$ mm, $b = 6.0$ mm, $w = 3.5$ mm, and $a = 20 \sim 80$ mm

TABLE I
Organic Solvents Used in This Experiment

Solvent	SP, ^a (cal/cm ³) ^{1/2}	Viscosity, ^a c.p. (20°C)
<i>n</i> -Hexane	7.3	0.326
Cyclohexane	8.2	0.979
Benzene	9.2	0.52
Diethyl ether	7.4	0.233
Ethyl acetate	9.1	0.455
Methyl acetate	9.6	0.385
Acetone	9.9	0.316
<i>n</i> -Butanol	11.4	2.498
<i>n</i> -Propanol	11.9	2.256
Benzyl alcohol	12.1	5.8
Ethanol	12.7	0.789
Methanol	14.5	0.597
Water	23.4	1.005

^a From *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975.

RESULTS AND DISCUSSION

Fracture Toughness of Epoxy Resin

A typical load-displacement curve observed in this cleavage test is shown in Figure 2. The load increased linearly with opening displacement until a crack was initiated. The crack propagated some distance and then arrested. In this case, the crack propagated in a stick/slip manner, which was investigated by Kinloch et al.^{2,13,14} The load (P_i) that caused a stationary crack to propagate rapidly was associated with the fracture toughness for initiation (K_{ICi}), which was determined by eq. (1), where $P = P_i$. The load (P_a) that caused a running crack to stop was associated with the arrest toughness (K_{ICa}), which was also determined by eq. (1), where $P = P_a$. From this experiment, the following K_{IC} values were determined: K_{ICi} and K_{ICa} of the epoxy resin were 0.53 and 0.48 MN/m^{3/2}, respectively.

In fracture mechanics, the critical strain energy release rate (G_{IC}) is related to K_{IC} by Young's modulus (E) and Poisson's ratio (ν) as follows:

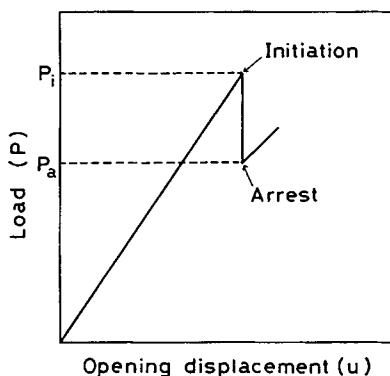


Fig. 2. Typical curve of load (P) vs. opening displacement (u) for epoxy DCB specimens.

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

The values of G_{ICi} and G_{ICa} calculated by eq. (2) were 71 and 57 J/m², respectively, where $E = 360$ kgf/mm² and $\nu = 0.35$ were used for this epoxy resin.

Crack Propagation in the Presence of Organic Solvents

Fracture toughness (K_{IC} , G_{IC}) obtained from the cleavage test in various external environments are presented in Table II. In calculating the G_{IC} value, it was assumed that the Young's modulus of this epoxy resin was constant in the presence of organic solvents, because the immersion period was too short to give appreciable absorption of the solvent on the epoxy resin. That is, we considered that the absorption of the solvent was located only in the crack tip.

Thomson investigated the effect of the external environment on crack propagation in brittle materials. When a stressed solid is subjected to an external chemically embrittling atmosphere, the surface energy of the solid is lowered by the adsorption of the atmosphere on its cleavage face and the Griffith's critical crack length is shorter.¹¹ In this case, the presence of the organic solvent increased the fracture toughness or apparent surface energy. The critical stress intensity factor for initiation of the epoxy resin in the presence of the solvent was 1.2 to 1.5 times that in the absence of the solvent. Solvent molecules which penetrated into the resin in the region surrounding the crack tip weakened the yield strength of the resin at the crack tip; local plastic deformation occurred more widely than in the absence of the solvent. Blunting of the crack tip took place when solvent molecules reached the crack tip.

Correlation of the viscosity of the solvent with fracture toughness was not obtained. But a correlation of the solubility parameter of the solvent with fracture toughness was observed (Fig. 3). In this SP- K_{ICi} curve, a minimum value was observed about 11 of SP, the solubility parameter of the epoxy resin. Because K_{ICi} was affected by the degree of plastic deformation and yield strength

TABLE II
Fracture Toughness of Epoxy Resin in Various Environments

Environment	K_{ICi} , MN/m ^{3/2}	G_{ICi} , J/m ²	K_{ICa} , MN/m ^{3/2}	G_{ICa} , J/m ²
Air	0.53	71	0.48	57
<i>Solvent</i>				
<i>n</i> -Hexane	0.73	133	0.52	69
Cyclohexane	0.70	123	0.53	69
Benzene	0.71	127	0.53	69
Diethyl ether	0.80	157	0.57	81
Ethyl acetate	0.74	137	0.54	72
Methyl acetate	0.70	123	0.53	69
Acetone	0.69	119	0.52	67
<i>n</i> -Butanol	0.69	120	0.52	66
<i>n</i> -Propanol	0.72	128	0.57	79
Benzyl alcohol	0.63	101	0.56	79
Ethanol	0.72	128	0.51	64
Methanol	0.77	147	0.48	58
Water	0.80	158	0.50	61

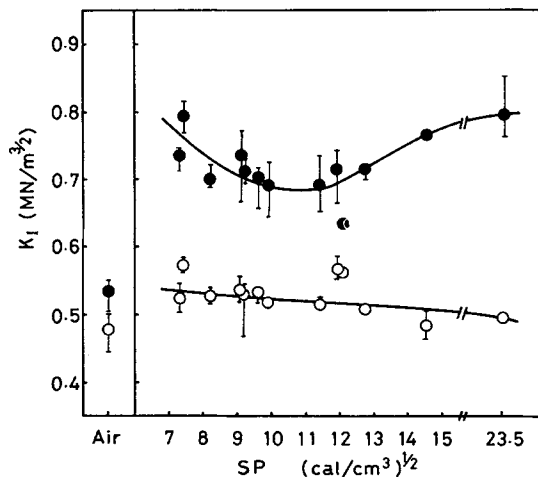


Fig. 3. Relationship between fracture toughness [(●) K_{ICi} and (○) K_{ICa}] and solubility parameter of organic solvent.

of the resin, the resin had a minimum value of K_{ICi} . That is, plastic deformation which became large in the presence of organic solvent increased the fracture toughness, while the yield strength which was lowered in the presence of the solvent decreased the fracture toughness.

On the other hand, the K_{ICa} value did not vary with SP, namely, the effect of the solvent on K_{ICa} was very slight. Solvent molecules could not penetrate into the area around the crack tip, which was running very fast. Therefore, the solvent could not affect K_{ICa} .

In conclusion, the improved toughness by organic solvent was localized to the vicinity of the crack tip. After the crack grew to some short distance, K_{IC} reverted to its original value.

Fractography

Crack propagation in the presence of various organic solvents was investigated by fractography. Fracture surfaces of the epoxy resin fractured in air, *n*-hexane, butanol, acetone, and methanol are shown in Figure 4. These photographs were taken using a differential interference microscope. The magnification was the same in all cases. The arrow in the photographs indicates the direction of crack growth. A crack arrest line and crack initiation area in which the crack grew slowly are shown in these photographs. In the case of air, a crack arrest line was clear, but a large plastic deformation area was never observed. A feature of the fracture surface of the epoxy resin fractured in the presence of organic solvent was different from that in the absence of the solvent, in that a large plastic deformation or a crack slow-growth region was observed.

The critical stress intensity factor for initiation in the presence of butanol was the same as that in acetone, but a feature of the fracture surface in the former case was quite different from that in the latter case, in the degree of plastic deformation. Also, K_{ICi} in the presence of acetone differed from that in methanol, but the morphology of the fracture surfaces were very similar. It is significant to investigate the correlation of morphology with fracture toughness. Further investigations are necessary.

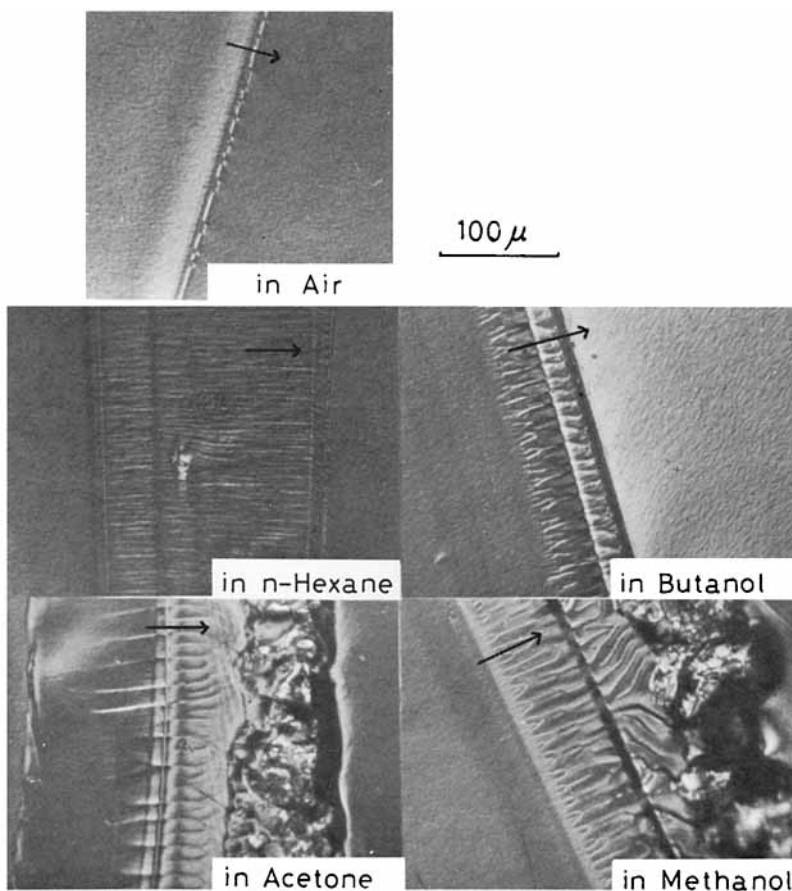


Fig. 4. Crack arrest and initiation region on fracture surface of epoxy resin which was fractured in various environments (arrow indicates crack growth direction.)

The degree of swelling, i.e., the weight of the absorbed solvent divided by the original weight of the resin was investigated. The swelling degree in acetone and methanol was very large (about 20%), while that in *n*-hexane and butanol was small (about 0.5%). There is a correlation of the degree of swelling with the morphology of the fracture surface. For example, in the presence of the organic solvent in which the epoxy resin swelled easily, plastic deformation occurred more widely.

References

1. S. Yamini and R. J. Young, *Polymer*, **18**, 1075 (1977).
2. R. A. Gledhill, A. J. Kinloch, S. Yamini, and R. J. Young, *Polymer*, **19**, 574 (1978).
3. S. Yamini and R. J. Young, *J. Mater. Sci.*, **14**, 1609 (1979).
4. S. Yamini and R. J. Young, *J. Mater. Sci.*, **15**, 1814 (1980).
5. S. Yamini and R. J. Young, *J. Mater. Sci.*, **15**, 1823 (1980).
6. J. Mijović and J. A. Koutsky, *Polymer*, **20**, 1095 (1979).
7. J. Mijović and J. A. Koutsky, *J. Appl. Polym. Sci.*, **23**, 1037 (1979).
8. S. Mostovoy and E. J. Ripling, *J. Appl. Polym. Sci.*, **15**, 641 (1971).
9. E. J. Ripling, S. Mostovoy, and C. Bersch, *J. Adhesion*, **3**, 145 (1971).
10. R. Thomson, *J. Mater. Sci.*, **15**, 1014 (1980).
11. E. R. Fuller, Jr. and R. Thomson, *J. Mater. Sci.*, **15**, 1027 (1980).

12. S. M. Wiederhorn, A. M. Short, and R. L. Moses, *J. Appl. Phys.*, **39**, 1569 (1968).
13. R. A. Gledhill and A. J. Kinloch, *Polym. Eng. Sci.*, **19**, 82 (1979).
14. A. J. Kinloch and J. G. Williams, *J. Mater. Sci.*, **15**, 987 (1980).

Received December 22, 1980

Accepted April 27, 1981