

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

## The Fracture Behavior of CTBN Modified Epoxy

Paul Peyser<sup>a</sup>; Yitchak Steg<sup>a,b</sup>

<sup>a</sup> Code 6126, Naval Research Laboratory, Washington, D. C., U.S.A. <sup>b</sup> Israel Ministry of Defence, Israel

**To cite this Article** Peyser, Paul and Steg, Yitchak(1988) 'The Fracture Behavior of CTBN Modified Epoxy', The Journal of Adhesion, 25: 2, 133 – 144

**To link to this Article:** DOI: 10.1080/00218468808071255

**URL:** <http://dx.doi.org/10.1080/00218468808071255>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# The Fracture Behavior of CTBN Modified Epoxy†

PAUL PEYSER and YITCHAK STEG‡

*Code 6126, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.*

*(Received March 16, 1987; in final form October 21, 1987)*

Rubber toughened epoxy resins are widely used as adhesives, as a matrix for glass and carbon fiber composites for rocket cases and sporting goods, and as a potting agent in the electronics industry. A common rubber added is CTBN, a carboxyl terminated copolymer of butadiene and acrylonitrile.

In this study we have measured toughness ( $K_{IC}$  and  $G_{IC}$ ) using the E399 ASTM standard for a compact tension (CT) specimen, with special attention to the variability of the measured  $K_{IC}$  and  $G_{IC}$  with the method of starter crack formation and the time delay between starter crack formation and toughness measurement. We also investigated the toughness of the toughened epoxy after initiation, for a growing crack, by using the short rod (SR) method and when possible in a CT specimen by using a simple marking technique.

The CT toughness of unmodified epoxy measured using a liquid nitrogen initiator crack technique is the same as that of earlier work, but we found that the  $K_{IC}$  and  $G_{IC}$  toughness increases when there is a delay between initiator crack formation and toughness measurement. Moreover, an initiator crack produced at room temperature gave higher toughness values. For the rubber toughened samples, we obtained low toughness for a liquid nitrogen initiated crack and a higher toughness measured either in a CT or SR test after the crack grew. The low values differ from earlier works, but is the same as that previously obtained at lower temperatures and for 5% and 20% rubber modified epoxy. Moreover, we found no  $K_{IC}$  and  $G_{IC}$  dependence with rubber content or rate (0.002–0.2 in/min crosshead speed). The higher toughness of the growing crack was the same as that for the 15% material of previous work. Presumably the apparent toughness of these systems is very dependent on the method of producing the initiator crack, and we possibly produced a sharper crack. This sharper crack shows no dependence on rubber content or rate.

Our results suggest that the advantage of adding rubber to epoxy is not in the load that the material will normally be able to sustain. A crack in bulk epoxy may not be

† Presented as a Poster Paper at the Tenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 22–27, 1987.

‡ Present address: Israel Ministry of Defence, Israel.

sharp and even if it is, will spontaneously blunt with time. There is, however, a greater tendency for a blunter crack to be produced in the rubberized epoxy and for an initiated crack to grow stably. Moreover, a stable, slowly-growing crack will increase the toughness of the modified epoxy.

**KEY WORDS** Fracture toughness;  $K_{IC}$ ;  $G_{IC}$ ; epoxy; rubber modified epoxy; CTBN.

## INTRODUCTION

The expression "fracture toughness" is often used to qualitatively describe the ability of a material to withstand the presence of cracks. Typical quantitative measures of this toughness (in mode I) are the fracture mechanics quantities, the stress intensity factor,  $K_{IC}$ , and the energy release rate,  $G_{IC}$ . If linear fracture mechanics is applicable, as is assumed in this paper, then both these quantities are material properties, interrelated by the modulus and the Poisson ratio.

Rubber toughened epoxy resins are widely used as adhesives, as a matrix for glass and carbon fiber composites for rocket cases and sporting goods, and as potting agents in the electronics industry. The highly crosslinked epoxy of the diglycidyl ether of bisphenol A has excellent mechanical properties but poor fracture toughness. Rubber-type additives are often used to overcome this deficiency. A common rubber added is CTBN, a carboxyl-terminated copolymer of butadiene and acrylonitrile. This rubber is incompatible with the epoxy resin and appears predominately as a second phase, but some mixing of the rubber and epoxy in each of the phases occurs.

It is reported<sup>1</sup> that the mechanical properties of the epoxy resins are not greatly impaired by the CTBN addition while  $G_{IC}$  can increase by as much as 3000%. These systems have been studied for more than 15 years, but no comprehensive theory has been found to explain fully the ongoing processes contributing to the toughening of epoxy resins. The model suggested by Kinloch *et al.*<sup>2</sup> stresses a crack-tip-blunting mechanism due to rubber particle cavitation, void formation at the epoxy rubber interface, dilatation and shear band formation. However, these processes occur not only during the toughness measurement while the sample is being loaded before crack initiation, but also when the starter crack is

being made. Hence elucidation of the toughening mechanism may be obscured by the toughness measurement itself.

In this study we have measured not only  $K_{IC}$  and  $G_{IC}$  in a normal manner using the E399 ASTM standard for a compact tension (CT) specimen, but have paid attention to the variability of the measured toughness with the method of starter crack formation, and even the time delay between starter crack formation and toughness measurement. We also investigated the  $K_{IC}$  and  $G_{IC}$  of the toughened epoxy by using the short rod (SR)<sup>3</sup> method for a growing crack, and when possible in a CT specimen after initiation, by using a simple marking technique to be described.

## EXPERIMENTAL

The polymer samples were prepared and supplied by Dr. Alan Siebert of the B. F. Goodrich Company. The resin system consisted of Epon 828 epoxy resin (Shell Chemical Co.) and 0, 5, 10 and 15 percent of CTBN rubber toughener cured with piperidine for 16 hours at 120°C. Dr. Siebert also measured the Young's modulus of these materials using ASTM method D638. The moduli are 2619, 2463, 2059, and 1887 MPa for the 0–15% rubber epoxies, respectively.

The glass transitions of these materials were measured on a Perkin Elmer model DSC7 differential scanning calorimeter (DSC). They were first given a specified thermal history (which eliminated an endotherm normally found in the glass transition region) by heating the samples to 185°C, holding at this temperature for ten minutes and then quickly cooling to 30°C. After a few minutes, the samples were heated at 10°/minute to 150°C and the glass transitions were determined by the mid-point (inflection point) method. The glass transition was 91°C for the unmodified epoxy and two degrees lower for the modified epoxies. These results indicate that the epoxy was slightly plasticized by the addition of the rubber. However, they also indicate that proper phase separation of the rubber particles had occurred since otherwise the lowering of the glass transition by the rubber would have been much greater.

Except as noted, the ASTM E-399 metals standard for a 1/2-inch CT specimen was followed. In particular, the samples were

machined to the necessary close tolerances, the plastic zone thickness criterion was exceeded, and the length-to-thickness ratio ( $W/B$ ) was two. The 95% secant line was used to determine the load. Five points were measured for each crack front to determine the proper crack length average and to check if the edge points of the crack front exceeded specified criteria. Except for marginal situations, unacceptable measurements not meeting E399 criteria were discarded. The starter crack was not a fatigue crack as will be described below. Also, we did not limit the crack length ( $a$ ) to  $0.45W-0.55W$  as is first required by the standard. We relied on an alternative E399 statement that notes that the equation provided to calculate the toughness is accurate within  $\pm 0.5\%$  over the range of  $a/W$  of 0.2 to 1.

The CT specimens contained either a chevron notch or a V-slot at the end of the crack-starter slot. The specimens were tested in a 5000 Kg capacity Instron machine under 3 crosshead speeds: 0.002, 0.02 and 0.2 in/min. Starter cracks were produced by a variety of methods. Some experience and skill was necessary to stop the starter crack before splitting the sample. In a few experiments a crack was initiated by the point of the chevron at the end of the starter slot as one does in a SR measurement. Another method involved compressing the sample in a vise perpendicular to the crack front and using a razor blade to initiate a crack. In both these methods no sharp crack front was discernible and the toughness presented is only a rough approximation. For most CT specimens, the V-slot or chevron notch portion was first immersed in liquid nitrogen for 30 seconds and then a crack was initiated at its cold end by striking with a razor blade. This method of initiator crack preparation has been previously used by most researchers in this field.<sup>1,4,5,6</sup> For the toughened epoxy, the crack fronts were easy to distinguish as whitening occurred along the crack path. For the untoughened epoxy, less visible markings were found which at times were hard to distinguish from ripples, and sometimes two very close markings were seen. In general the measurement of the crack length in the pure epoxy specimens involved some deduction to relate the measured load to the proper marking.

For the toughened epoxy under conditions where the crack grew and did not almost immediately pop and split the sample, it was possible to mark the crack front by suddenly increasing the strain

rate, at which time the sample split with no further whitening. Such a toughness measurement is not a measurement of an initiation toughness as is required by the E399 standard.

We also measured the  $K_{IC}$  and  $G_{IC}$  of the growing crack using a 1/2-inch diameter SR specimen. The method has been described previously.<sup>3</sup> Briefly, a 1.25-in long cylinder with a chevron slot in the center is pulled apart on an Instron at a rate of 0.05 to 0.2 in/min while the loads and displacements are measured. The crack is self-initiating at the point of the chevron and grows stably in the chevron. The compliance calibration of this specimen is known in terms of the ratio of the initial slope to a download slope measured after the crack has grown. Two downloads are performed during a run, one before and one after the maximum in the load displacement curve. Three toughness values were thus determined for each specimen, one at each of the downloads and one at the so called "critical  $r$ "<sup>3</sup> in the vicinity of the maximum. We did not apply a p-correction for reasons previously discussed.<sup>3</sup>

In a previous work<sup>3</sup> there was good agreement between the SR method for a 3/4-inch diameter specimen and the CT and tapered double cantilever beam methods for polysulfone. We therefore compared the SR 1/2-inch specimen for polysulfone taken from the same stock with the previous results and found a 20% increase in the measured  $K_{IC}$ . The most probable reason for this discrepancy is that the crack in the smaller polysulfone and the epoxy SR specimens grew somewhat out of the plane of the chevron slot or, at best, in the plane of the slot but at one edge. We therefore corrected all the epoxy SR  $K_{IC}$  values by decreasing them 20%.

## RESULTS AND DISCUSSION

The results are summarized in Table I. With regard to the compact tension results, it is important to note that we followed E399 criteria (except as noted). We therefore base our discussion upon the assumption that linear fracture mechanics apply. The same assumption, but with occasional less assurance, will apply to cited earlier works.

There are two parallel approaches to fracture toughness determination, the stress intensity factor  $K_{IC}$  and the energy release rate

TABLE I

(A) Compact Tension					
(a) Liquid Nitrogen-Razor blade initiated cracks. 0.002–0.2 in/min loading rate.					
% Rubber	$K_{IC}$ (MN/m <sup>3/2</sup> )	$G_{IC}$ (J/m <sup>2</sup> )	Valid samples	Samples discarded <sup>3</sup>	Type of crack growth
0	0.64 ± 0.08	140 ± 36	7	12	stick-slip, unstable
5	1.90 ± 0.14	1302 ± 185	3	7	stable-unstable
10	1.95 ± 0.23	1656 ± 368	12	12	stable-unstable
15	1.92 ± 0.26	1763 ± 427	11	5	stable-unstable
5 & 10 & 15	1.93 ± 0.24		26	24	stable-unstable
(b) After crack growth					
10	2.85 ± 0.13	3489 ± 334	5		stable to unstable mixed (occasionally)
15	2.81 ± 0.19	3720 ± 514	8		stable to unstable
10 & 15	2.82 ± 0.17		13		stable to unstable
(c) Chevron-Notch and compression-initiated cracks $K_{IC} = 1.07-5.00$ MN/m <sup>3/2</sup> . Bulk of measurements 2–3 MN/m <sup>3/2</sup> . No variation with rubber content.					
(d) Bulk Epoxy Liquid Nitrogen initiated crack after sample held 48 hours in desiccator.					
0	2.3		1	6	stick-slip
Other runs which were discarded showed same effect.					
(B) Short Rod. Average of three measurements from each sample. Loading rate comparable to slow compact tension rates.					
% Rubber	$K_{IC}$ (MN/m <sup>3/2</sup> )	Samples	Popped	Type of crack growth	
5	3.20 ± 0.15	3	5	Crack growth varied from slightly out of plane to in plane of chevron slot.	
10	3.13 ± 0.16	3	4		
15	3.02 ± 0.20	6	0	in plane of chevron slot.	
10	2.91	1		in plane of chevron slot.	
15	2.81	1		in plane of chevron slot.	

<sup>3</sup> Did not meet E399 criteria.

$G_{IC}$ . They are related by:

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

where  $E$  is Young's modulus and  $\nu$  is the Poisson ratio, equal to approximately 0.34 for these epoxies. In this work and in the others which we will be comparing,  $K_{IC}$  is first measured and then  $G_{IC}$  is calculated from  $E$  and  $\nu$ . For earlier works,<sup>1,4,6</sup> where the data were presented using  $G_{IC}$ , we were able to determine  $K_{IC}$  by referring to the original notebooks. Although we will now refer to

$K_{IC}$  measurements, it is understood that if  $E$  and  $\nu$  are known, then  $G_{IC}$  was also determined.

The CT  $K_{IC}$  of bulk (0% CTBN) epoxy we measured by the liquid-nitrogen-initiator crack technique is the same as that of earlier work,<sup>1,2,4</sup> but we found that  $K_{IC}$  increases when there is a time delay between initiator crack formation and the toughness measurement. However, the second measurement made after fast arrest of the first crack was low, similar to the low values for initial liquid nitrogen cracks which were not allowed to relax. An initiator crack produced at room temperature gave higher  $K_{IC}$  values. All of the bulk epoxy SR specimens popped after the crack grew a minute amount. Only a rough approximation of  $K_{IC}$  could be obtained. It was in the same range as that found *via* the SR method for the modified epoxies.

For the rubber-toughened samples, we obtained low  $K_{IC}$  values with a liquid-nitrogen-initiated crack and a higher  $K_{IC}$  measured either in a CT or SR test after the crack grew. Moreover, we found no  $K_{IC}$  dependence on rubber content or loading rate (0.002–0.2 in/min crosshead speed). These results differ from those of earlier work where a broad maximum at 15–20% rubber was found in a plot of  $G_{IC}$  vs. % rubber.<sup>1</sup> Also, a significant rate dependence was previously demonstrated.<sup>2,5</sup>

The necessity to use liquid nitrogen to produce a sharp crack is not a method which we preferred. One can easily visualize how such drastic treatment may affect the toughening capabilities of the imbedded rubber. For this reason, we were most interested in the short rod method where the crack is self-initiating. We also tried other methods to initiate a crack in a compact tension specimen. However, the bulk of past experimental data make use of liquid nitrogen to initiate a crack for these modified epoxies and like others, we were unable to initiate a sharp crack in these systems by any other means without splitting the sample. An exception is the work reported in Ref. 2. Despite our reservations, our experiments tended to show that the toughening capability of the modified epoxy was not greatly affected by the liquid nitrogen treatment. Namely, no systematic difference was found in the measured toughness between an initiator crack which arrested close to the area treated with liquid nitrogen or far away. Moreover, again irrespective of



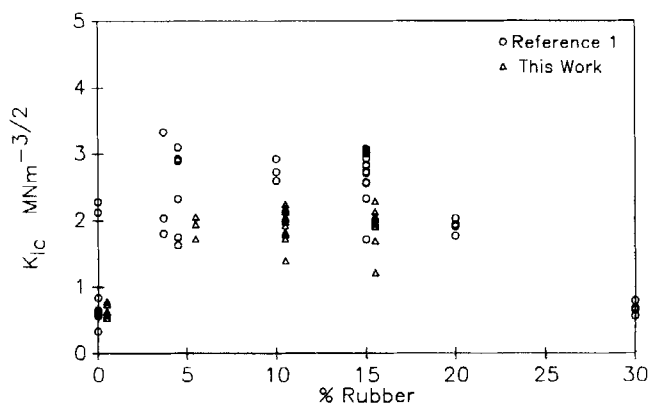


FIGURE 1  $K_{IC}$  Toughness vs. % Rubber.  $\circ$ —replot of the data of Ref. 1 using  $K_{IC}$  instead of  $G_{IC}$ .  $\triangle$ —CT initiation toughness of liquid nitrogen produced starter crack, (this work shifted 1/2% to right).

crack length, upon growing a slight amount,  $K_{IC}$  reached the higher values normally reported in the literature.

In Figure 1 we have replotted the data of Ref. 1 using  $K_{IC}$  instead of  $G_{IC}$  and have also included the low  $K_{IC}$  values of our work. Notice that now the sample with 20% rubber is no longer as tough as the sample with 15% rubber. Also, while 30% added rubber produced a significant improvement in  $G_{IC}$  toughness, it is no better than bulk epoxy if  $K_{IC}$  is used.

The different picture seen by the two toughness parameters,  $K_{IC}$  and  $G_{IC}$ , is due to the change in modulus of the system which occurs when rubber is added. One may ask which toughness measurement is important,  $K_{IC}$  or  $G_{IC}$ ? Of course both are important, being interrelated by the equation given. One tells us the stress that a crack can sustain and the other the energy, which is a combination of the stress and the strain. One can show, using a classical "fixed grip experiment", what happens to  $G_{IC}$  if  $K_{IC}$  stays the same but the modulus changes. Namely, if we lower the modulus of a material, the material will sustain the same load at crack initiation (a measure of  $K$ ) but must be strained to a larger extent in direct proportion to the change in modulus. This increase in strain is directly proportional to an increase in  $G$ . Normally, a lowering of the modulus, such as adding a plasticizer or raising the temperature above the glass transition, is not considered to be a toughening mechanism. If

the modulus changes,  $G_{IC}$  alone presents a distorted picture of the toughness of a system. It should be noted that our discussion of the importance of  $K_{IC}$  relative to  $G_{IC}$  relates to the toughness of bulk modified or unmodified epoxy, the scope of this paper. For an adhesive situation where the strain of the adhesive is negligible relative to the adherend, the change in modulus affecting  $G_{IC}$  becomes unimportant. Now  $G_{IC}$  is the proper measure of the toughness of the bond.

Referring again back to Figure 1 and Table I, we see that the earlier data<sup>1</sup> can be represented by two sets of points, a low  $K_{IC}$  of about 1.9 and a high  $K_{IC}$  of about 2.8, similar to this work. (The high values at 5% rubber were disregarded in the earlier published work). Note that at 15% rubber a solitary low value was measured. Going back to the original data we also found a solitary low value (15% rubber) in Ref. 6. In Figure 2, data from Ref. 4 are replotted using  $K_{IC}$  instead of  $G_{IC}$ . Notice that our low  $K_{IC}$  measurement at room temperature fits well with a continuation of the toughness determined at lower temperatures. The same high and low  $K_{IC}$  variation can be seen in Ref. 2. Here a high  $K_{IC}$  was found at room temperature and low loading rate, and a low  $K_{IC}$  was found at low temperatures.†

Presumably, the apparent  $K_{IC}$  of these systems is very dependent on the method of producing the initiator crack. We possibly produced a sharper crack. This sharper crack front would show little if any dependence on rubber content or rate as compared to a blunter, more plastic, crack front. A sharper crack is more likely to be produced at lower temperatures, after immersion in liquid nitrogen, with the sharpness increasing with the time of the immersion. A sharper crack is also formed by a fast arrest of a fast-moving initiator crack. A blunter crack is produced by a slowly moving crack.

The increase in toughness with time that we found for bulk epoxy is reminiscent of a little understood phenomenon commonly re-

---

† The dropping of experimental points is quite understandable in view of the information available at the time and statistical arguments. However, experience has shown that almost any conceivable experimental problem in a toughness measurement would tend to give too high a value. Hence, coupled with our findings, the low values previously dropped for valid statistical reasons or averaged should be given more prominence.

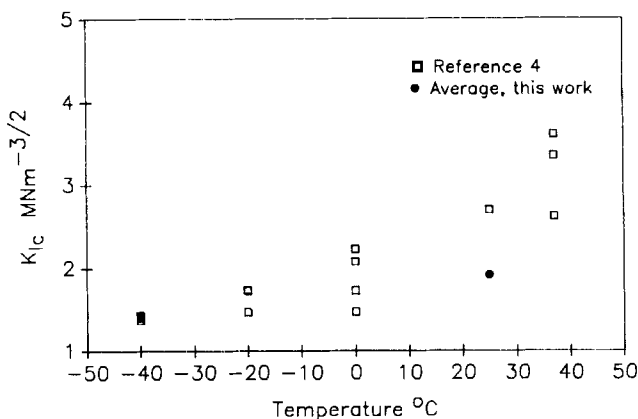


FIGURE 2 Temperature dependence of % Rubber.  $\square$ —replot of the data of Ref. 4 using  $K_{Ic}$  instead of  $G_{Ic}$ .  $\bullet$ —CT initiation toughness of liquid nitrogen produced starter crack, (this work).

ferred to as “crack healing”. However, we found no such effect for the modified epoxy and as such cannot explain differences in measured values of the modified epoxies by this means.

Four types of crack growth characterizing the fracture of untoughened and toughened epoxy resins were found. Unstable crack growth is characteristic of a load-deformation curve represented by a straight line until the maximum, where the sample breaks suddenly. Stick-slip type unstable crack growth is similar to unstable crack growth except that the crack arrests before the sample breaks. Hence, more than one measurement can be made from a single specimen. For stable crack growth the crack grows slowly and the test machine is able to keep up with the crack growth until the sample crack length equals the sample length. This crack growth is accompanied by an extensive whitening that reaches a depth of millimeters, perpendicular to the plane of the crack. The associated load-deflection plot for mixed type stable and unstable crack growth is linear at the beginning (similar to the unstable type of crack growth) followed by a yielding curvature (similar to the stable type of crack growth). After a certain amount of curvature, the extent of which decreases with strain rate, the sample breaks abruptly and the load falls to zero.

The type of crack growth in the CT specimens varied from stick-slip at the low loading rate to unstable at the higher loading rates in the bulk epoxy and from stable to unstable in the rubber-modified epoxies (Table I). The crack growth was of course stable in the SR measurements when a measurement was possible and unstable when the sample popped. Actually, the type of crack growth will vary with the measuring machine and the geometry of the specimen; it is a function of the relative stiffness of the pulling machine and the specimen. This ratio was a constant for this work for each type of specimen. Our results show that there is a greater tendency for the modified rubber to grow stably. This tendency increases with the amount of rubber added. This is important because our results suggest that the major advantage of adding rubber to epoxy is not in the load that the material will normally be able to sustain. A crack in bulk epoxy may not be sharp, and even if it is, it will spontaneously blunt with time. Moreover, no dependence upon rubber content was found. There is however, a greater tendency (increasing with the amount of rubber added) for a blunter crack to be produced in the rubberized epoxy and for an initiated crack to grow stably. A stable, slowly growing crack will be reflected in an increased toughness of the modified epoxy. While we have shown that the laboratory-determined  $K_{IC}$  can be lower than previously reported, in normal use the practical toughening of CTBN-modified epoxies is significant.

## CONCLUSIONS

The type of crack produced in epoxy and rubber-modified epoxy was found to be method- and operator-dependent. We obtained lower  $K_{IC}$  values than previously reported and no toughness dependence on modifier content or loading rate. We attribute this difference to having produced a sharper crack. We showed that our lower  $K_{IC}$  values can also be found in previous works. The initially low  $K_{IC}$  of bulk epoxy having a sharp crack increases with time ("crack healing"). Rubber-modified epoxy  $K_{IC}$  values increase when a slow, stable crack has grown. We conclude that the principal advantage of adding rubber to epoxy is the greater tendency for a crack to be blunt and to grow stably.

**References**

1. W. D. Bascom, R. L. Cottingham, R. L. Jones and P. Peyser, *J. Appl. Polym. Sci.* **19**, 2545 (1975).
2. A. J. Kinloch, S. J. Shaw, D. A. Tod and D. L. Hunston, *Polymer* **24**, 1341 (1983).
3. T. Watson, M. Jolles, P. Peyser, and S. Mostovoy, *J. Materials Sci.* **22**, 1249 (1987).
4. W. D. Bascom and R. L. Cottingham, *J. Adhesion* **7**, 333 (1976).
5. L. Bitner *et al.*, *ibid.* **13**, 3 (1981).
6. R. Y. Ting and R. L. Cottingham, *J. Appl. Polym. Sci.* **25**, 1815 (1980).