

Fracture of an Epoxy Polymer Containing Recycled Elastomeric Particles

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ABSTRACT: The fracture behavior of elastomer-modified epoxy was investigated using compact-tension geometry. The elastomeric modifiers included a liquid carboxyl-terminated butadiene acrylonitrile and solid rubber particles of different sizes which were obtained from recycled automobile tires. When used with solid rubber alone, no significant improvement in the fracture toughness was observed. However, when used in combination with the liquid rubber modifier, it was observed that the fracture toughness of these hybrid epoxies was higher than that of those toughened with liquid rubber alone. This synergistic effect is explained in terms of crack deflection and localized shear yielding. Furthermore, we observed a slight improvement in the fracture toughness as the size of the solid rubber particles increased. Although using a combination of both reactive rubber liquids and solid rubber particles as toughening agents had been investigated previously, in this study, the solid rubber particles used were from recycled rubber tires. Therefore, we have clearly demonstrated an application of producing high-quality engineering epoxy systems using toughening modifiers that are relatively low in cost and created higher-value products for recycled solid rubber. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 271–277, 1997

Key words: toughened epoxy; fracture; recycled solid rubber; liquid elastomers; hybrid composites

INTRODUCTION

Structural thermoset polymers such as epoxies and polyimides are amorphous and highly cross-linked. The high degree of crosslinking has resulted in many useful engineering properties such as good mechanical performance and dimensional stability at elevated temperatures and good solvent resistance. However, this crosslinking structure leads to an undesirable property. They are relatively brittle materials with poor resistance to crack initiation and propagation. To overcome this, one may incorporate a second phase of dispersed particles into the polymer network. The

degree to which the second phase enhancing the fracture toughness depends on many factors such as particle, size, size distribution, shape, rigidity, and interfacial adhesion to the matrix. Hence, many toughening mechanisms have been proposed and investigated. Today, it is possible to greatly increase the fracture toughness of structural epoxies without significantly reducing the desired engineering properties.

The most often used toughness modifiers are elastomers. The fracture behavior of elastomeric-modified epoxy was reported extensively.^{1,2} Specifically, reactive liquid rubbers such as carboxyl-terminated or amine-terminated butadiene acrylonitrile (CTBN or ATBN) copolymer are most commonly used. At first, the liquid rubber is miscible with the epoxy resin. The phase separation occurs during curing where the CTBN or ATBN forms a dispersed phase of particles having diameters of a few microns or less.

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There have also been investigations of hybrid composites with combinations of soft rubbery particles and hard ceramic particles into thermosetting polymers. The hard particles can improve fracture toughness in three ways: (1) crack pinning,^{3,4} (2) deflection of the crack front due to the generation of a larger crack-tip opening displacement,⁵ and (3) particle fracture.⁶ As hybrid epoxies contain both soft and hard fillers, it is natural to assume that the resulting fracture mechanisms in hybrids will at least equal the sum of the individual contributions observed in the rubber-toughened epoxies and the glass-filled resins. However, there may be synergistic effects. This variety had been reported in the epoxy-rubber-zirconia⁷⁻¹⁰ system.

In this study, we were interested in hybrid epoxy composites with a combination of reactive rubber liquid and solid rubber as collected from the recycling of tires. A similar study using the combination of liquid rubber and virgin solid rubber particles was found in the work of Bascom et al.¹¹ The fracture energy of this hybrid system was higher than that of resins toughened by either kind of rubber alone. The same effect is expected in our study. In Bascom et al.'s work, the total content of added rubber was not held constant, and since the rubber volume fraction plays a major role in determining the fracture toughness of a modified epoxy composite, the net effect of their work might be complicated. In this investigation, we maintained the matrix property and total rubber content was held constant, while the ratios of liquid rubber and solid rubber particles were varied. In addition, the effects of solid rubber particle size on the fracture toughness were reported.

EXPERIMENTAL

Materials

The material used was a liquid diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin (DER332, Dow Chemical) cured with a diamine-terminated poly(propylene oxide) (Jeffamine D230, Texaco Chemical). Two types of additives were used as toughening agents: a reactive carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) reactive rubber liquid (B.F. Goodrich, HYCAR 1300 × 8) and a series of surface-modified tire rubber recyclates with different mean particle sizes (Composite Particles Inc., Vis-

Table I Dimensions of Solid Rubber Particles Used

Name	Average Diameter (μm)
VISTAMER™ R4200	75
VISTAMER™ R4100	150
VISTAMER™ R4060	250
VISTAMER™ R4040	425

tamer™ R-series). Table I shows the average particle size of the Vistamer used in this study.

The weight ratio of the DGEBA epoxy resin to the D230 diamine curing agent was that of a stoichiometric ratio. The total weight of the toughening agent added was 6% of the entire mixture's weight. The DGEBA epoxy and rubber additives were mixed by hand until homogeneous at a temperature of about 60°C. The amine curing agent was then added and mixed at room temperature. The mixture was degassed in a vacuum for 20 min at room temperature, then cast into a flat sheet with dimensions of 10 × 20 × 0.635 cm. The resin plaques were cured in an oven at a temperature of 100°C for 24 h, then allowed to cool slowly down to room temperature overnight. The fracture tests were conducted using compact tension specimens which were machined from the molded plaques. Since the specific density of the individual components is known, the specific density of the test specimens was determined using Archimedes's principle to verify the weight ratios of all the rubber-toughened compact tension specimens. Within experimental error, the rubber particles in all specimens were homogeneously mixed.

Thermal Properties

Heat flow and glass transition measurements were performed with a TA Instrument 2920 differential scanning calorimeter (DSC). The sample was first heated to 160°C and held for 10 min. The sample was then cooled to -60°C at a rate of 10°C per min; it was then heated to 120°C at a rate of 5°C per min with a modulation amplitude of $\pm 1^\circ\text{C}$. The glass transition temperature was determined by the inflection point of the glass transition region on the DSC thermograms. The heat capacity was directly measured by using the modulated DSC technique.

Fracture Test

The geometry of the compact tension specimens is as specified by the American Standards Testing

Table II Glass Transition Temperature of Rubber-toughened Epoxies

Sample	T_g (°C)
A	85.1
B	86.0
C	81.1
D	85.5
E	83.9

Sample A is neat epoxy resin. Sample B is filled with 6 wt % of Vistamer R4200. Sample C is toughened with 6 wt % CTBN liquid rubber only. Sample D is toughened with 2 wt % CTBN liquid rubber and filled with 4 wt % Vistamer R4200. Sample E is toughened with 4 wt % CTBN liquid rubber and filled with 2 wt % Vistamer R4200.

Methods (ASTM) D5045.¹² The equation used to calculate the fracture toughness, K_Q , can also be found in the annual books of ASTM standards. The precracks were made in the elastomer–epoxy composite specimens by notching the end of the saw cut with a liquid N₂-cooled razor blade. The exact precrack length was measured using a traveling optical microscope after fracture. Prior to making the precrack, all specimens were annealed for 30 min at a temperature 20°C above their glass transition to erase any physical aging effects. All specimens were tested at room temperature within 30 min after the annealing process. The fracture test results reported in this study were obtained using a computer-controlled screw-driven Instron mechanical tester (Model 4302) with a crosshead speed set at 10 and 15 mm/min, respectively.

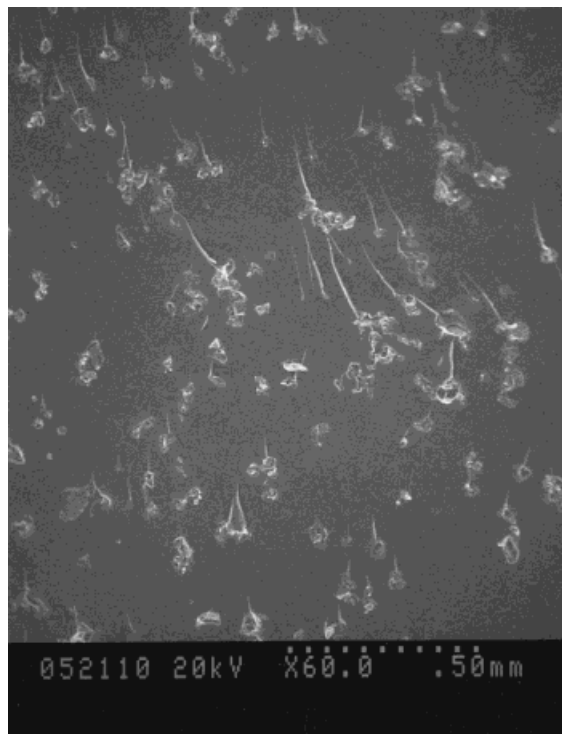


Figure 1 Low magnification scanning electron microscopy of epoxy toughened with 6 wt % of Vistamer R4200.

Fractography

The fracture surfaces were examined using a Hitachi-2500 scanning electron microscope (SEM) operated with an accelerating voltage of 20 kV. Prior to examination, the fracture surfaces were coated with a thin evaporated layer of gold to im-

Table III Fracture Toughness of Various Rubber-filled Epoxy Networks

Sample	Fracture Toughness, K_c (MPa·m ^{1/2}) at 10 mm/min	Fracture Toughness, K_c (MPa·m ^{1/2}) at 15 mm/min
A	1.10 (±0.10)	0.76 (±0.04)
B	1.16 (±0.15)	0.84 (±0.08)
C	2.06 (±0.02)	1.78 (±0.01)
D	2.36 (±0.05)	1.90 (±0.09)
E	2.47 (±0.08)	2.11 (±0.09)
F	2.64 (±0.09)	N/A
G	2.71 (±0.12)	N/A
H	2.55 (±0.07)	N/A

Above values of K_c are the average of at least five test samples. Sample A is neat epoxy resin. Sample B is fill with 6 wt % of Vistamer R4200. Sample C is toughened with 6 wt % CTBN liquid rubber only. Sample D is toughened with 2 wt % CTBN liquid rubber and filled with 4 wt % Vistamer R4200. Sample E is toughened with 4 wt % CTBN liquid rubber and filled with 2 wt % Vistamer R4200. Sample F is toughened with 4 wt % CTBN liquid rubber and filled with 2 wt % Vistamer R4100. Sample G is toughened with 4 wt % CTBN liquid rubber and filled with 2 wt % Vistamer R4060. Sample H is toughened with 4 wt % CTBN liquid rubber and filled with 2 wt % Vistamer R4040.

prove the conductivity and prevent surface electron-charging. With an ultrathin evaporated gold layer, we were able to observe the imprint of the CTBN particles or the CTBN themselves on the fracture surfaces. Hence, transmission electron microscopy (TEM) was not needed.

RESULTS

Thermal Analysis

The glass transition temperatures, T_g , obtained using differential scanning calorimetry are shown in Table II. It was observed that the presence of solid rubber particles had little effect on the glass transition temperature of the epoxy matrix phase. With the addition of reactive liquid rubber, the glass transition temperature decreases as the concentration of liquid rubber increases. The reduction in the glass transition temperature due to the addition of reactive liquid CTBN rubber can be attributed to the reaction between the amine hardener and the carboxyl end-group. Although the rate of this reaction is much slower than is the primary epoxy-amine reaction, it will still occur for the curing cycle used. Since the molar ratio

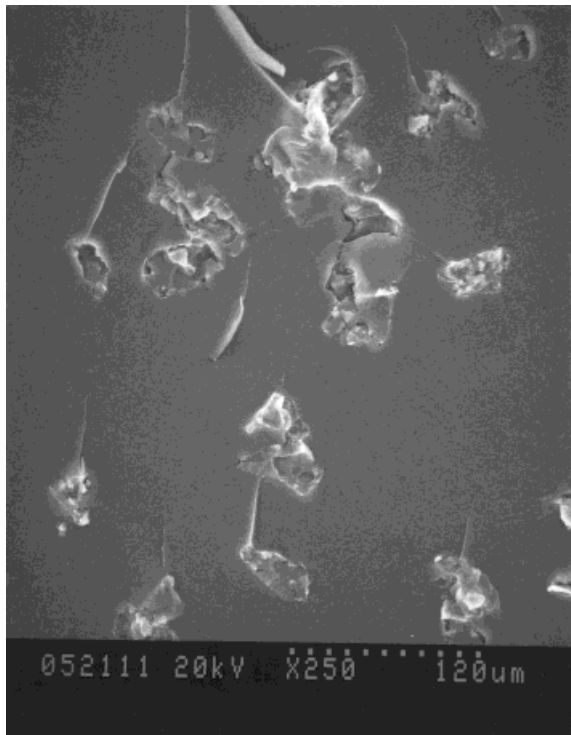


Figure 2 High magnification scanning electron microscopy of epoxy toughened with 6 wt % of Vistamer R4200.

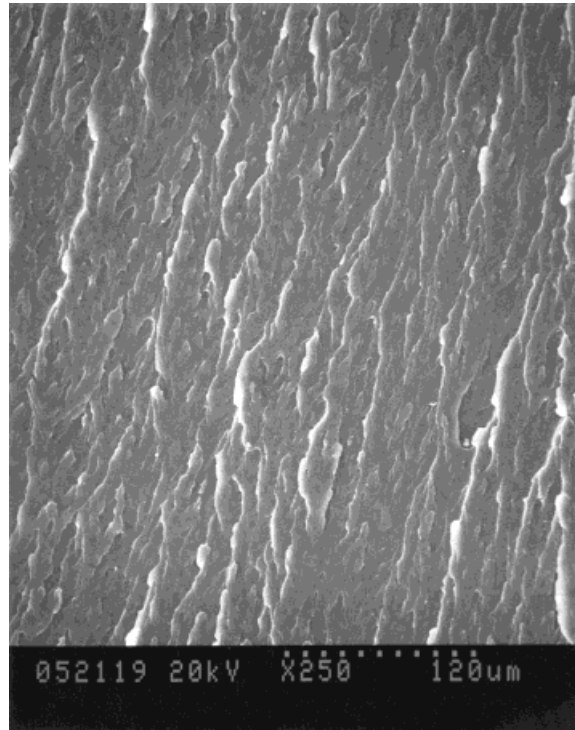


Figure 3 Low magnification scanning electron microscopy of epoxy toughened with 6 wt % of CTBN.

of epoxy and amine used in this study is 1, we expect that some epoxy groups remain unreacted, thus reducing the overall T_g of the rubber-toughened epoxy composites.

It is important to note here that the solid rubber particles do not reduce the glass transition of polymeric networks. This strongly suggests that no chemical reactions take place between the solid rubber particles and the epoxy matrix. Therefore, poor adhesion may be expected. Consequently, we expect that the system reinforced with solid rubber particles will show no increase in toughness as compared to the neat resin system.

Fracture Study

The fracture toughness values as measured using compact tension sample geometry for various rubber-filled epoxy networks are listed in Table III. In general, with an increase in crosshead speed, the apparent fracture toughness decreases somewhat. This result has been observed in many other similar studies. Due to poor adhesion between the solid rubber particles and the epoxy matrix, the sample toughened with only solid rubber particles showed no improvement in fracture toughness. For the system toughened with only 6 wt % of CTBN rubber, a factor of two increase

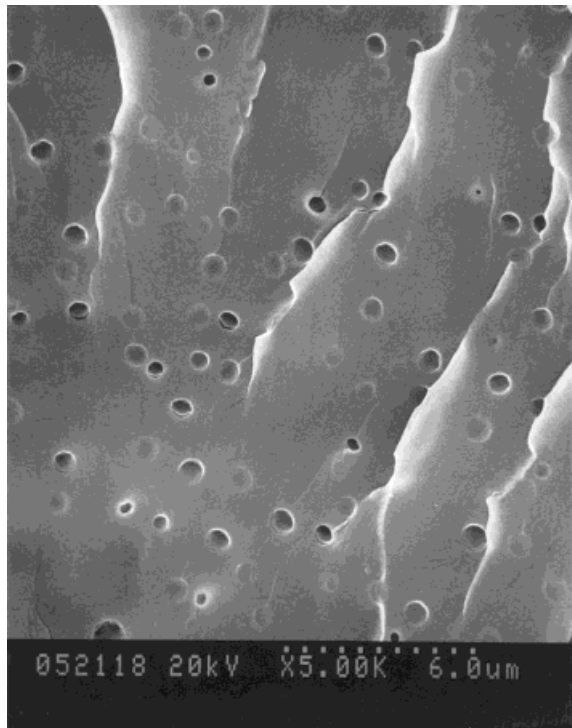


Figure 4 High magnification scanning electron microscopy of epoxy toughened with 6 wt % of CTBN.

in the fracture toughness was observed. It was interesting to observe that samples toughened with a combination of solid rubber particles and CTBN rubber showed higher fracture toughness values when compared with samples toughened with CTBN rubber alone. This synergistic effect can be explained by the observations from scanning electron micrographs.

With the total rubber content held constant, the increase in the size of solid rubber particles shows a slight enhancement in the fracture toughness. It is difficult to explain this observation. However, it is possible that with increases in particle diameter the total number of particles decreases, and then the average distance between particles increases. Hence, it requires more energy to generate the fracture path in between, which then gives higher fracture toughness.

Microstructures

Scanning electron micrographs of the fracture surfaces of compact tension specimens toughened with Vistamer R4200 and CTBN rubber are shown in Figures 1–7. Figures 1 and 2 depict the fracture surfaces of epoxy reinforced with solid Vistamer rubber particles only. The featureless fracture surface and the imprints of solid rubber

particles support the claim of poor adhesion between the epoxy matrix and the Vistamer. At high magnification, Figure 2 shows “tailing” of the particle, thus indicating crack pinning by the particles.

Figures 3 and 4 show the fracture surfaces of CTBN-toughened epoxy networks. At low magnification, Figure 3 shows considerable deformability. The high magnification of Figure 4 shows that the CTBN droplets are relatively uniform in size. The average diameter of the CTBN particles is approximately $0.6 \mu\text{m}$. However, the final size of CTBN particles was controlled by the curing conditions. In this study, all epoxy samples were cured under similar conditions; therefore, we did not expect the size of the CTBN particles to vary much.

Figures 5–7 show the fracture surfaces of epoxy matrix samples toughened with a combination of CTBN liquid rubber and Vistamer solid rubber particles. Similarly to the sample toughened with only CTBN, i.e., reference to Figure 3, the low magnification of Figure 5 shows considerable deformability. However, the presence of Vistamer solid rubber particles provided crack propagation pinning. Furthermore, if one treats the CTBN-toughened epoxy as the “matrix,” there seems to be an improvement in the adhesion of the

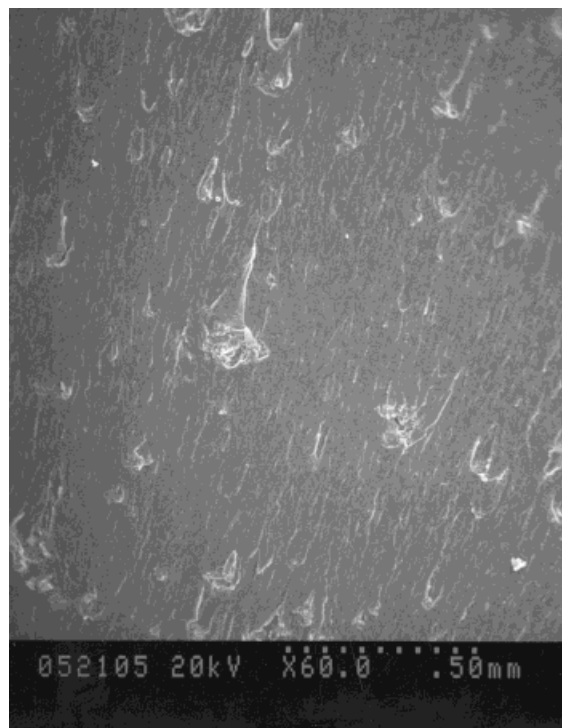


Figure 5 Low magnification scanning electron microscopy of epoxy toughened with 2 wt % of Vistamer R4200 and 4 wt % of CTBN.

Vistamer particles with the CTBN. As the crack encounters the Vistamer particles, we observe deformation perpendicular to the direction of crack propagation on the CTBN-toughened epoxy matrix as shown on the high magnification micrograph of Figure 7. Therefore, it is possible to conclude that the synergistic effect on the improvement of the fracture toughness of the hybrid epoxies is due to the combination of crack pinning of the solid Vistamer particles, deflection of the crack front due to the Vistamer particles, and the plastic deformation of CTBN/epoxy matrix surrounding the Vistamer particles.

CONCLUSIONS

It has been shown that the modification of neat epoxy resins using a combination of solid rubber particles and reactive liquid rubber improves the fracture toughness of the base epoxy to a greater extent than when either modifier is used alone. The enhanced toughness was observed over a wide range of particle sizes. The modified epoxy systems showed a decrease in fracture toughness with increasing strain rate. The use of recycled solid rubber particles is of economic and environ-

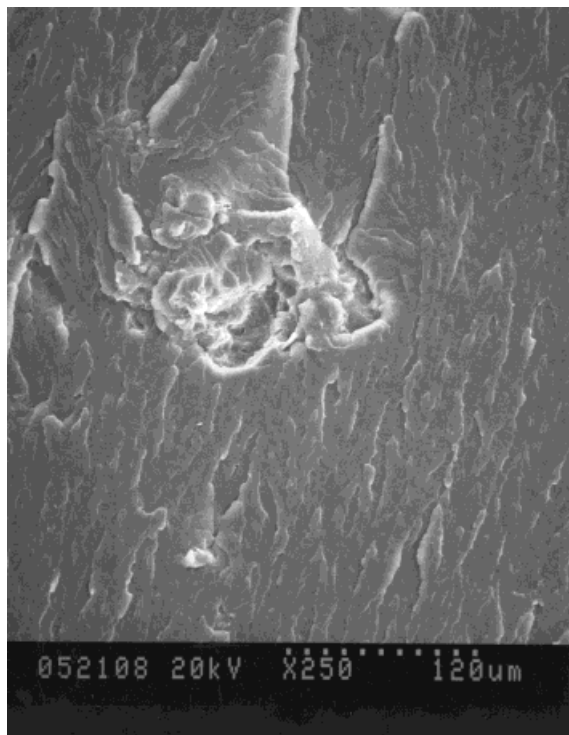


Figure 6 High magnification scanning electron microscopy of epoxy toughened with 2 wt % of Vistamer R4200 and 4 wt % of CTBN.

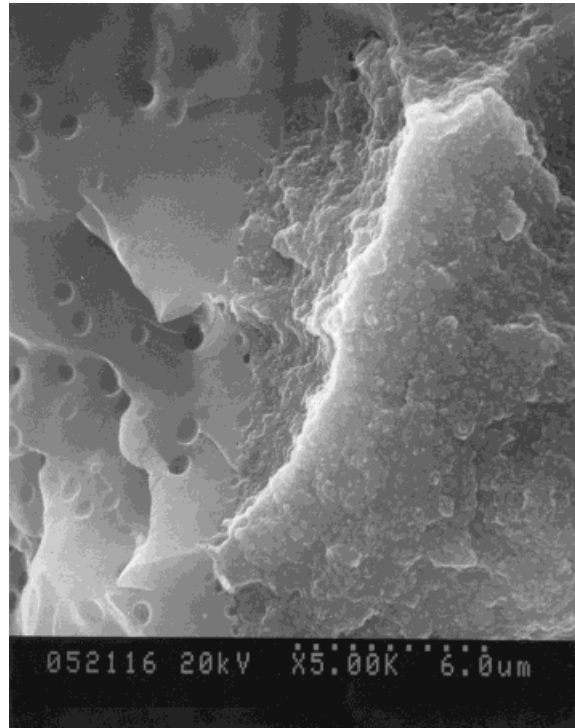


Figure 7 High magnification scanning electron microscopy around the solid particles for epoxy toughened with 2 wt % of Vistamer R4200 and 4 wt % of CTBN.

mental interest. These hybrid-toughened epoxies not only have better fracture properties but should exhibit higher mechanical performance as well.

It has also been shown that there are no chemical reactions between the solid particles and the epoxy matrix. Therefore, it is expected that the thermal and physical properties of the hybrid system are better than those of an epoxy toughened with liquid rubber alone. The enhanced thermal properties can be an improvement in the dimensional stability, which is most critical to many applications involving epoxy matrix composites.

Postfailure examination of the fracture surfaces using SEM indicated that the liquid rubber additive formed droplets which averaged $0.6 \mu\text{m}$ in diameter and the size of solid Vistamer particles does correspond with the values given by the supplier. Similarly to many previous studies involving epoxies toughened with solid particles, we observed the pinning mechanism due to the presence of solid particles. However, in this study, poor adhesion between the epoxy matrix and the particles resulted in no change in the fracture toughness. For the system reinforced with both CTBN liquid rubber and Vistamer rubber recyclates, significant improvement in the fracture

toughness was observed. For these hybrid epoxies, in the crack-tip deformation zone, we observed the combination of crack pinning and dilatational deformation and induced shear yielding of the surrounding CTBN/epoxy matrix. The synergistic effect to improve fracture toughness can be translated to the fiber-reinforced composite materials and the use of recycled rubber is an obvious interest to the effort of recycling polymeric materials.

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