Interaction of Toughening Mechanisms in a Hybrid Epoxy System

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ABSTRACT: Interaction between different toughening mechanisms is studied using a heat treated hybrid system, consisting of carboxyl-terminated butadiene acrylonitrile (CTBN) rubber and EXPANCEL (expandable hollow microspheres) as modifiers for an epoxy resin. It was found that the fracture toughness of the hybrid system is higher than that of either individually EXPANCEL- or CTBN-modified system for a given content of modifier, although the maximum toughness was not substantially high compared with maxima of single modifier systems. Microscopic examination revealed that damage zone due to CTBN particles ahead of the crack reduces due to the presence of EXPANCEL particles and nevertheless its fracture toughness increased. A possibility was deduced that the cavitation due to CTBN assists with promoting compressive stresses around EXPANCEL particles ahead of the crack tip, resulting in increase in fracture toughness. J Appl Polym Sci 100: 4470–4475, 2006

Key words: toughening; interaction of toughening mechanisms; hybrid; epoxy; rubber

INTRODUCTION

Toughness, which is the capability of resistance to cracking, is often the deciding factor in materials selection. Conventional plastics, particularly thermosets such as epoxies, vinyl esters, etc., are brittle and hence possess low toughness because of their inherent crosslinked molecular chain structure. In an attempt to overcome such weakness, the research on toughening of thermosets has been conducted since 1970s.[1] The toughening method involves adding second phase particles to the resin matrix.[2–7] In rubber toughening, rubber cavitation and shear yielding have been identified as dominant toughening mechanisms.[6,8]

Another development in toughening is some attempts to toughen thermosets by reducing effective stress intensity using a method similar to the one used for ceramics, in which toughness increase was achieved by a volume dilation in the vicinity of the crack tip resulted from tetragonal to monoclinic phase transformation.[9,10] Kim and Robertson[11–13] have made efforts in toughening with semicrystalline thermoplastic polymers as modifiers, and substantial toughening has been achieved. They thought phase transformation was the major toughening mechanism, but it was inconclusive.[5,11] Recently, Kim's[14–16] employed expandable hollow microspheres (EHM) to produce compressive residual stresses around dispersed microspheres by means of heat treatment, resulting in similar effect to that resulting from volume dilation in ceramics.

In this article, interaction between rubber and EHM toughening mechanisms is studied. Cavitation in the presence of compressive stresses and *vice versa* will be brought into focus.

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EXPERIMENTAL

Materials used

An epoxy system was adopted as a model material for this study. The system consisted of West System Epoxy 105 (a blend of Bisphenol A and Bisphenol F) and West System Slow Hardener 206 (a blend of aliphatic amines and aliphatic amine adducts based on diethylene triamine and triethylenetetramine) as curing agents. An average density of five measurements was found to be 1.1 for the epoxy system.

Two different modifiers were used carboxyl-terminated butadiene acrylonitrile (CTBN) copolymer (Hycar® 1300 × 8, Noveon) and expandable EHM (EXPANCEL, 551 DU40, Akzo Nobel), which consist of copolymer shell and gas. The microspheres were analyzed for chemical structure using a Perkin–Elmer Fourier Transform Infra Red Spectrometer (Paragon 1000) and found to be $(C_5H_8O_2—C_3H_3N—C_2H_2Cl_2)x$. An average density of microspheres from three mea-

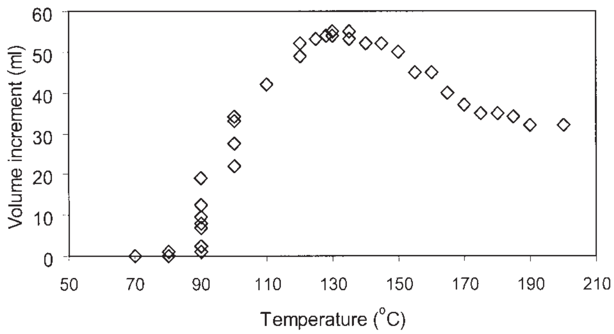

Figure 1 Volume expansion measurement of 551 DU40 as a function of temperature.

surements at room temperature was found, using an air comparison pycnometer (Beckman 930), to be 1.2.

The microspheres expand when heated. As part of characterization for volume expansion of 551 DU40, a 10 mL of microspheres was put in a measuring cylinder of 100 mL and tapped for 5 min, and then placed in an oven preheated at 70°C. Further heating was conducted every 5–6 min for an increment of 10°C until it reached 200°C. The volume expansion as a function of temperature is shown in Figure 1. It is seen that the volume reaches its maximum and then decreases because some EHM explode when the temperature is high.

Preparation of test specimens

Three different types of modified epoxy specimens were prepared using CTBN and EXPANCEL individually and both CTBN and EXPANCEL together for a hybrid system.

A predetermined amount of epoxy was first placed in a container, and modifier was added while stirring at room temperature. The mixture was placed in an oven at 120°C in the case of CTBN, and at 70°C in the case of EXPANCEL, for 30 min to reduce the viscosity for further mixing for a couple of minutes.

In the case of hybrid, CTBN was first mixed with epoxy as described earlier, and after cooling, EXPANCEL was added and then reheated at 70°C for 30 min to reduce the viscosity for further mixing for a couple of minutes.

The mixture was allowed to cool gradually in a water bath at room temperature for about half hour before curing.

Finally, a 17 phr (by weight) of hardener was added to the mixture and then slowly stirred for at least 5 min. It was poured into an aluminum mold with a 6-mm thick cavity and left for curing at room temperature at least for 1 day. Pure epoxy was cured at room temperature too.

All the molded specimens were placed in a preheated oven at 135°C for 2 h. Specimens containing

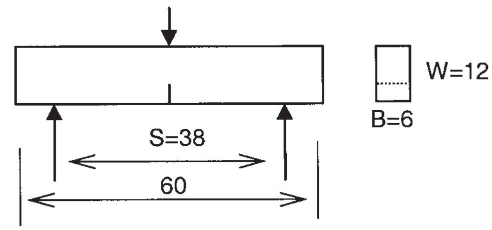

Figure 2 Three-point loading for both flexural and fracture tests but without the notch for flexural tests.

EXPANCEL are expected to have compressive residual stresses around EHM, as already demonstrated elsewhere.[14–16]

Mechanical testing

All the specimens for mechanical testing were machined into dimensions of 12 × 60 × 6 mm^3 for edgewise placement, as shown in Figure 2. Three-point bending tests on a universal testing machine (Shimadzu 5000) were conducted for elastic modulus, strength, and fracture toughness. A crosshead speed of 10 mm/min was adopted for tests of flexural properties, and 0.5 mm/min for the fracture toughness measurements at a room temperature of 21°C.

Elastic moduli (E) and flexural strengths (σ_y) were calculated using the following equations given in ASTM D970M–93:

$$E = \frac{S^3 m}{4BW^3} \tag{1}$$

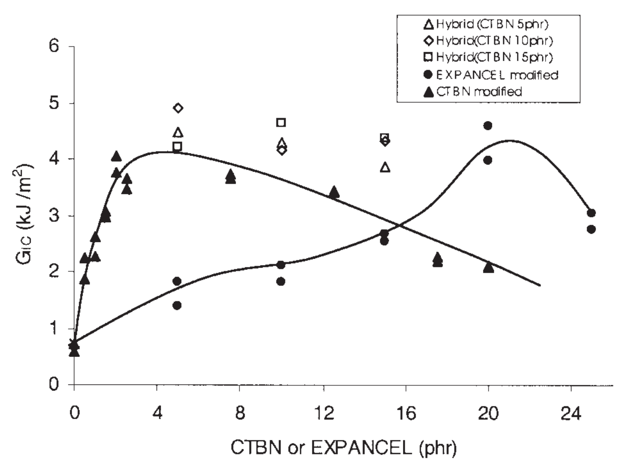

Figure 3 Specific fracture energy versus CTBN or EXPANCEL content. CTBN-modified epoxy system is denoted by (▲), EXPANCEL modified system by (●), hybrid system with a 5 phr of CTBN for various EXPANCEL contents by (Δ), hybrid system with a 10 phr of CTBN for various EXPANCEL contents by (224), and hybrid system with a 15 phr of CTBN for various EXPANCEL contents by (□).

TABLE I
Mechanical Properties of CTBN-Modified Epoxy System

CTBN (phr)	Specific fracture energy (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)
0	0.64	131.04	1.5
0.5	1.94	115.4	1.2
1.0	2.44	115.18	1.31
1.5	2.96	113.41	1.18
2.0	3.93	114.79	1.17
2.5	3.57	109.67	1.13
7.5	3.72	98.39	1.07
12.5	3.4	84.01	0.87
17.5	2.23	74.64	0.76
20.0	2.08	73.81	0.72

and

$$\sigma_y = \frac{3PS}{2BW^2} \tag{2}$$

where S is the support span, B is the thickness, W is the width, m is the slope of the tangent to the initial straight-line portion of the load–deflection curve, and P is the load.

The critical stress intensity factor (K_{IC}) expression[17] used was

$$K_{IC} = \frac{3PS\sqrt{\pi a}}{2BW^2}Y \tag{3}$$

where a is the crack length and Y is a geometry factor given by

$$Y = \frac{1}{\sqrt{\pi}} \frac{1.99 - \frac{a}{W}\left(1 - \frac{a}{W}\right)\left(2.15 - 3.93\frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right)}{\left(1 + 2\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)^{3/2}} \tag{4}$$

A precrack, 4–5 mm long, was produced by tapping a razor blade into the tip of a saw-cut notch, 2 mm long, of each fracture test specimen, and its length was measured with a pair of Vernier calipers.

Specific fracture energy values for mode I were approximated using

$$G_{IC} = \frac{K_{IC}^2}{E} \tag{5}$$

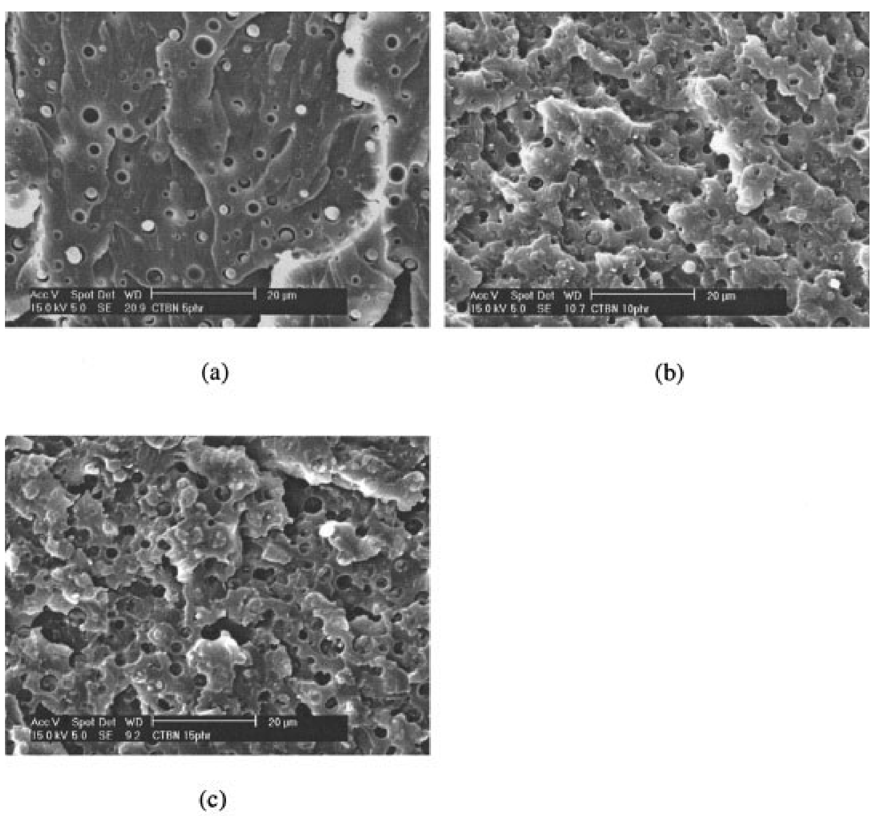

Figure 4 SEM images for fracture surfaces of slow cracking for CTBN-modified epoxy system. (a) 5 phr, (b) 10 phr, and (c) 15 phr.

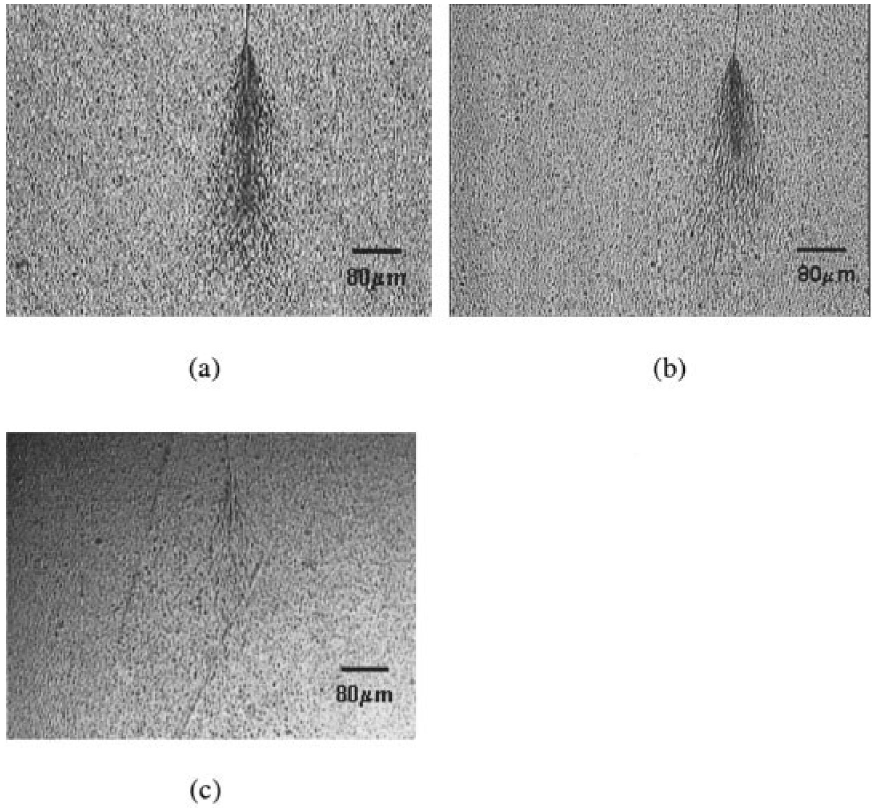

Figure 5 Damage zones ahead of the crack tip for CTBN-modified epoxy system. (a) 5 phr, (b) 10 phr, and (c) 15 phr.

Microscopy

Scanning electron microscopic (SEM) work (Oxford-XL30, Philips) was conducted for specimens coated with gold. The specimens were cleaned with water using a Bran Sonic 52 and dried in an oven at 30°C for 30 min before coating for SEM. Fracture surfaces for SEM photos were taken from mid sections in the vicinity of precracks unless otherwise stated. Also, thin sections of mid-plane from broken specimens were prepared for transmission microscopy (Axioplan 2, Carl Zeiss). The thicknesses of thin sections were obtained to be about 19 μm.

RESULTS AND DISCUSSION

Specific fracture energy for CTBN-modified system is given in Figure 3 and also given in Table I, with flexural strength and flexural modulus. The maximum fracture specific fracture energy is found at 2 phr for this particular epoxy system. SEM fracture surfaces of slow cracking region for 5, 10, and 15 phr are shown in Figure 4. Some particles are seen to be debonded from the matrix. It was observed that the damage size correlates well with the specific fracture energy. Some selected TOM photographs for damage zone are shown in Figure 5—the higher the specific fracture energy the larger the damage size. The damage zone consists of largely shear banding as a result of cavitation.[6]

Specific fracture energy for EXPANCEL-modified system is given in Figure 3 and also given in Table II. As already discussed elsewhere[16] for the same system, the maximum is found at 20 phr. Further features associated with the toughening mechanism based on the compressive residual stress are provided in Figure 6. The thin section (Fig. 6) shows two different images for the same section, which is perpendicular to fracture surface. The first image [Fig. 6(a)] was obtained under polarized light, where the fringe patterns indicate the compressive residual stresses around EXPANCEL particles, and the second image [Fig. 6(b)]

TABLE II
Mechanical Properties of EXPANCEL-Modified Epoxy System

EXPANCEL (phr)	Specific fracture energy (kJ/m^2)	Flexural strength (MPa)	Elasticity modulus (GPa)
0	0.64	131.04	1.50
5	1.61	116.08	1.25
10	1.96	102.52	1.11
15	2.61	90.27	1.10
20	4.29	34.78	0.85
25	2.89	43.36	0.95

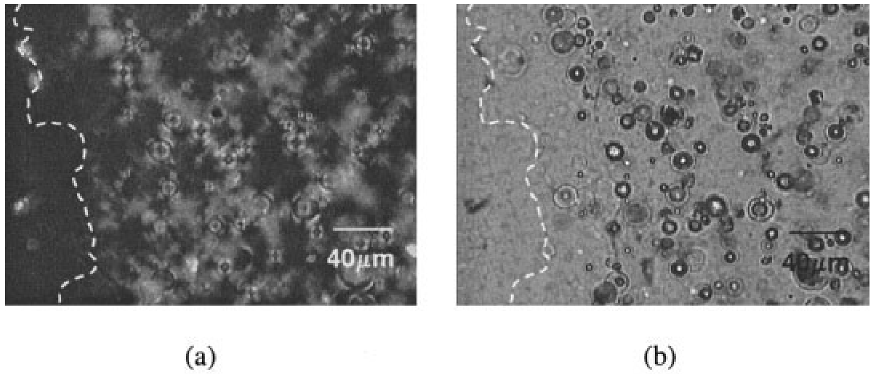

Figure 6 TOM images of mid-plane thin section perpendicular to fracture surface for EXPANCEL-modified epoxy system (20 phr) with heat treatment. The dashed line indicates the crack path propagated from bottom to top: (a) polarized and (b) unpolarized. It is seen that fringe pattern is weakened along the crack path, indicating that residual compressive stresses are relieved after cracking.

without polarized light where particles are more visible. The dashed line represents the crack path propagated from bottom to top. It is noted that fringe patterns are weakened along the crack path, indicating that residual compressive stresses are relieved after cracking. It was observed that, in contrast with the CTBN-modified system, there were no measurable damage zones (cf. Fig. 5) and hence no cavitation. As this was already discussed elsewhere in relation to a necessary condition for cavitation, the residual compressive stresses act in opposite direction to that of cavitation, and thus reduce or prevent the cavitation.[16]

Specific fracture energies for hybrid epoxy system denoted by open symbols are given in Figure 3 and also given in Table III. The hybrid system consists of CTBN contents, 5 phr, 10 phr, and 15 phr combined with EXPANCEL contents, 5 phr, 10 phr, and 15 phr, giving nine different combinations. The specific fracture energy of the hybrid system appears to be higher than that of either individually EXPANCEL or CTBN-modified system for a given content of modifier, although the maximum toughness is not substantially high compared with maxima of single modifier systems. In regard to this improvement, it is possible that CTBN assists EXPANCEL with toughening in the hybrid system. This possibility can be explained as follows. When the crack is loaded, the residual compressive stresses around EXPANCEL particles ahead of the crack would be decreased (relieve), but the cavitation due to CTBN obviously does not demote the compressive stresses. It is further possible that the cavitation would promote the existing compressive stresses, because the cavitation is in the opposite direction to the compression. This reasoning is supported by the fact that (a) the damage size (which is due to CTBN) ahead of the crack tip is influenced by the presence of EXPANCEL particles as shown in Figure 7—the damage size is substantially reduced due to the presence of EXPANCEL particles (cf Fig. 5) and (b) specific fracture energy is nevertheless improved substantially for some hybrids (Fig. 3). However, it is obviously not possible that the cavitation is promoted by the residual compressive stresses.

Figure 8 shows typical SEM images of fracture surfaces for slow and fast cracking regions of a hybrid (10 phr of CTBN and 15 phr of EXPANCEL). Large and

TABLE III
Mechanical Properties of Hybrid Modified Epoxy System

CTBN/EXPANCEL (phr)	Specific fracture energy (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)
Control	0.64	131.04	1.50
5/5	4.47	94.42	1.13
5/10	4.29	82.25	0.98
5/15	3.88	54.45	0.91
10/5	4.00	90.61	0.97
10/10	4.15	77.55	0.92
10/15	4.37	65.06	0.77
15/5	4.21	82.61	0.90
15/10	4.65	78.16	0.83
15/15	4.38	61.95	0.70

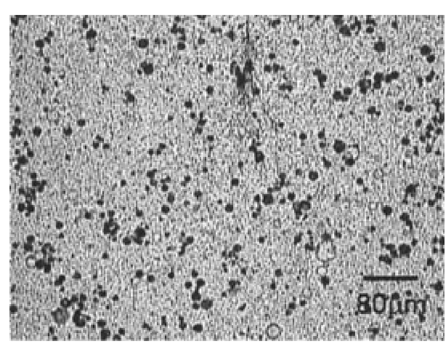

Figure 7 TOM image of hybrid system with a 10 phr of CTBN and a 5 phr of EXPANCEL.

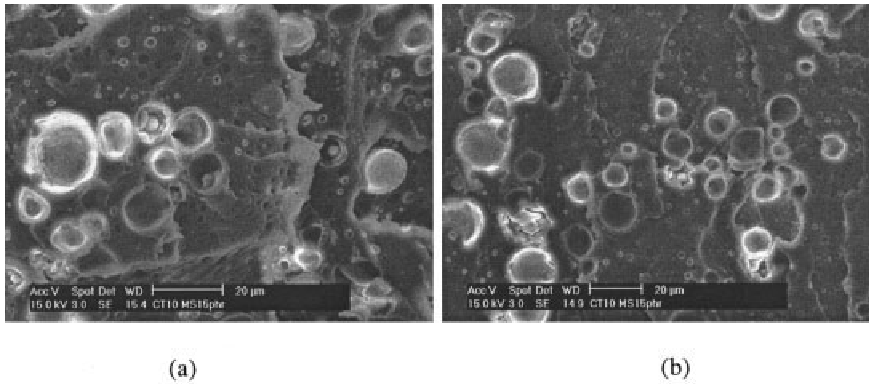

Figure 8 SEM images of fracture surfaces for (a) slow and (b) fast cracking regions of hybrid system with a 10 phr of CTBN and a 15 phr of EXPANCEL. Large and small particles are EXPANCEL and CTBN, respectively. Some CTBN particles around EXPANCEL particles are in elliptical shape because of the heat treatment. The crack propagation direction is from bottom to top.

small particles are EXPANCEL and CTBN, respectively. The major difference between slow and fast regions is in EXPANCEL deformation. The EXPANCEL particles in slow region [Fig. 8(a)] are seen to be once stretched, whereas particles in fast region [Fig. 8(b)] are relatively clear-cut. This indicates that crack faces were bridged, giving some additional toughness. Some CTBN particles around EXPANCEL particles are seen to be elliptical, which was possibly taken place when EXPANCEL particles expanded and produced the residual compressive stresses during the heat treatment.

CONCLUSIONS

Interaction between different toughening mechanisms has been studied using a heat treated hybrid system, consisting of CTBN and EXPANCEL as modifiers.

It was found that the specific fracture energy of the hybrid system is higher than that of either individually EXPANCEL- or CTBN-modified system for a given content of modifier, although the maximum toughness is not substantially high compared with maxima of single modifier systems.

A possibility was deduced that the cavitation due to CTBN assists with promoting compressive stresses around EXPANCEL particles ahead of the crack tip in increasing fracture toughness.

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