# Mechanical Behavior and Structure of Rubber Modified Vinyl Ester Resins

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Received 1 July 1998; accepted 6 August 1998

ABSTRACT: Vinvl esters are used widely as thermoset matrix materials for reinforced composites; however, they suffer from low-impact resistance. Substantial enhancement of the toughness of brittle polymers may be achieved by dispersing elastomeric inclusions or rubber particles in the polymer matrix, inducing multiple crazing and shear yielding of the matrix. The main objectives of this work are morphological characterization of vinyl ester/reactive rubber systems and investigation of the mechanical and fracture behavior of these systems. Additional studies focused on rubber endcapped vinyl ester in the absence and presence of added reactive rubber. The initial compatibility of the liquid rubber with the liquid resin was studied. This is a key factor, along with cure conditions, in determination of the possible morphologies, namely, the degree of phase separation and particle size. The initial rubber/resin compatibility was found poor and all attempts to improve it by means of surfactants or ultrasonic treatment have not been successful. The flexure mechanical and fracture behavior of the cured resin/rubber systems was investigated. Three basic types of crack propagation behavior, stable, unstable, and stick-slip, were observed. Fracture toughness of various resin/rubber systems was evaluated and was found to increase with increased content of rubbery second-phase material. However, there is some payoff in stiffness and flexural strength of the cured resins. The addition of rubber does not affect the resin toughness at impact conditions. Analysis and interpretation of fractures morphology show that both multiple crazing and external cavitation play an important role in the fracture mechanism of the rubber modified specimens. No shear yielding is evident. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 647-657, 1999

**Key words:** vinyl ester; rubber toughening; fracture toughness; toughened thermosetting composites

## **INTRODUCTION**

Epoxide resins, unsaturated polyesters, and vinyl esters are used widely as base materials for ad-

hesives and thermosetting matrix materials for composites reinforced with glass, polyamide, or carbon fibers. However, these resins exhibit lowimpact resistance in comparison with most engineering plastics. There are a number of ways for improving the fracture toughness of thermosetting resins. One method of toughening, which achieved significant results with epoxy resins, is

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Contract grant sponsor: Israeli Ministry of Defense. Journal of Applied Polymer Science, Vol. 72, 647–657 (1999)

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the modification of the resin with reactive liquid rubbers, especially with butadiene–acrylonitrile rubbers.<sup>1–8</sup> These rubbers are added to the liquid resin, and during curing, precipitate out from the solution in the form of dispersed particles.

The experiments with epoxide resins have shown the important advantage of this approach, namely, significant enhancement of the resin fracture toughness obtained at relatively low rubber contents. Thus, the deterioration in mechanical properties (such as stiffness, strength, and heat distortion temperature) of the resin upon toughening is minimal. The mechanisms ascribed to this toughening mode<sup>2,9–13</sup> include shear yielding and shear band formation in the matrix, crazing, triaxial dilation of particles at the crack tip, and particle elongation and tearing.

The initial compatibility of the liquid rubber with the liquid resin is a key factor, along with cure conditions, in determination of the toughened resin morphology, namely, the degree of phase separation, particle size, and its distribution. The morphology of the toughened resin may determine the toughening mechanism and its effectiveness. The initial compatibility can be improved by use of rubber with reactive functional terminal groups to enable the rubber molecules to react with the resin to produce a graft copolymer. This approach can cause a dispersion of relatively small rubber particles in the matrix. According to the literature,<sup>14–15</sup> the initial compatibility of unsaturated polyesters and vinyl esters with most liquid rubbers is poor, making it rather impossible to obtain a rubber solution in a resin.

The objectives of the present work are to investigate the mechanical and fracture behavior of vinyl ester/reactive rubber systems and to characterize their morphology and the acting toughening mechanisms.

# **EXPERIMENTAL**

## Materials

The following two vinyl ester (VE) resins, manufactured by Dow Chemical Co., (Midland, MI) were used in this investigation:

- 1. Derakane 411-45 (VE), based on methacrylated diglycidyl ether of bisphenol A, containing 45 wt % styrene.
- 2. Derakane 8084 (MVE), based on Derakane 411-45 resin modified by carboxyl terminated butadiene–acrylonitrile (CTBN) rub-

ber. The endcapped rubber does not precipitate as a dispersed phase during curing and actually serves as a flexibilizing agent. The modified vinyl ester contains about 40 wt % styrene.

All liquid rubbers used in this investigation were obtained from BF Goodrich Co. and are based on butadiene-acrylonitrile copolymers, containing functional terminal groups. The following three liquid rubbers were used:

- 1. Hycar 1300  $\times$  33 (VTBN-33). Vinyl terminated rubber with acrylonitrile content of 17% and Brookfield viscosity of 250,000 cP (at ambient temperature).
- 2. Hycar  $1300 \times 43$  (VTBN-43). Vinyl terminated rubber with acrylonitrile content of 16% and Brookfield viscosity of 425,000 cP (at ambient temperature).
- 3. Hycar  $1300 \times 44$  (ETBN). Epoxy terminated rubber, containing 50 wt % styrene because of extremely high molecular weight (Brookfield viscosity of 1,500,000 cP).

The catalyst for room temperature curing was methyl ethyl ketone peroxide (MEKP, Fluka), accelerated by cobalt naphthenate solution (8 wt %, Fluka).

## **Compatibility Studies**

The investigation of initial compatibility of liquid resin and liquid rubber was carried out using an Olympus BH-2 (Japan) optical microscope equipped with a Mettler FP5 hot stage device. This enabled visual observation of the rubber dispersion in the resin as a function of time at different temperatures and rubber contents. The morphology of the resin/rubber mixtures was observed in a phase contrast regime to enhance the contrast at phase boundaries.

## **Sample Preparation**

The liquid rubber was first dissolved in styrene (50 wt %) to facilitate compatibility with the liquid resin. Mixtures of vinyl ester and liquid rubber with 0.3 phr cobalt naphthenate were stirred at 70°C for 1 h and then 2 phr MEKP was added to the mixtures. Curing was performed in a flat glass mold, with an aluminum U-shaped spacer. The curing duration was 48 h at ambient temperature followed by postcuring at 100°C for 3 h. The

latter was carried out for completion of the chemical reaction and release of residual stresses that may affect the mechanical and fracture behavior of specimens. The ASTM D 790 samples for flexure testing, ASTM D 5045 samples for fracture toughness testing, and DIN 53453 samples for impact strength testing were machined.

#### **Fracture and Mechanical Properties Evaluation**

Three-point single-edge notch bend (SENB) specimens were chosen for the fracture toughness measurements. According to ASTM D 5045 requirements, the rectangular specimens were 44  $\times$  10  $\times$  5 mm<sup>3</sup> in size to assure plane strain conditions. An initial crack was machined in a specimen and a *natural* crack was generated by tapping on a fresh razor blade placed in the notch. The samples were tested using an Instron machine in the flexure mode at a crosshead rate of 2 mm/min. All tests were made at ambient temperature.

The following relationship was used to determine fracture toughness in terms of plane strain critical-stress-intensity factor  $K_{Ic}$ :

$$K_{Ic} = \frac{P_Q}{BW^{1/2}} f(x)$$
 (1)

where  $P_Q$  is the critical load for crack propagation (kN); *B* is the specimen thickness (cm); *W* is the specimen width (cm); and f(x) is a nondimensional shape factor given by

$$f(x) = 6\sqrt{x} \frac{\begin{bmatrix} 1.99 - x(1-x) \\ \times (2.15 - 3.93x + 2.7x^2) \\ (1+2x)(1-x)^{3/2} \end{bmatrix}}{(2)}$$

where x = a/W and *a* is the crack length (cm).

Fracture toughness at impact conditions was evaluated using a Charpy-type impact machine. The sample preparation was the same as for the SENB specimens, with dimensions of  $50 \times 6 \times 4$  mm<sup>3</sup>, according to DIN 53453 requirements. The tests were performed at two temperatures: ambient and  $-60^{\circ}$ C (below  $T_g$  of the rubber). The total fracture energy measured (w) depends, according to Plati and Williams,<sup>16</sup> on the strain energy release rate  $G_{Ic}$  as follows:

$$w = G_{Ic} B W \phi \tag{3}$$

where  $\phi$  is a calibration factor, which can be calculated either theoretically or by experiment.<sup>16</sup>

The strain energy release rate under impact conditions can be obtained from eq. (3). The stress-intensity factor  $K_{Ic}$  can be calculated from the following relationship:

$$K_{Ic} = \sqrt{\frac{E}{1 - \nu^2} G_{Ic}} \tag{4}$$

where *E* is the elasticity modulus (MPa) and  $\nu$  is the Poisson's ratio.

Mechanical properties testing was performed using an Instron machine at a crosshead rate of 2 mm/min for a three-point bending mode. All tests were conducted at ambient temperature.

### Morphology

Investigation of the morphology of the toughened vinyl ester samples was performed using a Jeol JSM-5400 scanning electron microscope (SEM) at an acceleration voltage of 10 kV. Fracture surfaces were produced at three different temperatures: ambient, 80, and  $-185^{\circ}$ C (liquid nitrogen) to investigate the influence of fracture conditions on the resulting interphase contrast. Fracture surfaces were gold sputtered prior to their observation.

## **RESULTS AND DISCUSSION**

#### **Compatibility Studies**

For all studied rubbers the initial resin/rubber compatibility was found to be poor, based on the observation of a large number of  $10-12 \mu m$  spherical rubber droplets dispersed in the resin. Heating of the mixture to  $100^{\circ}$ C with prolonged stirring (3–4 h) caused partial dissolution of the droplets, but a homogeneous solution was not obtained. Moreover, the temperature rise brought about a decrease of the resin viscosity, resulting in an enhanced coalescence tending to form larger droplets (>30  $\mu$ m). A similar effect was reported by Ullett<sup>14</sup> for a mixture of CTBN with unsaturated polyester.

Ultrasonic treatment of the rubber/resin mixture at an elevated temperature (80°C) resulted in better dispersion of the large droplets and reduction of their mean diameter to 10  $\mu$ m, but it did not actually change the rubber/resin compatibility.

A number of surfactants (lecithin, castor oil, acetyl acetone, and others) were added to the resin/rubber mixtures in an attempt to reduce the





**Figure 1** Vinyl ester/VTBN-33 mixture at 100°C: (a) original and (b) with lecithin.

interfacial tension and to facilitate better dispersion. Figure 1 shows the effect of the presence of lecithin. It is seen clearly that with lecithin two droplet populations are produced, i.e., very large  $(30-50 \ \mu\text{m})$  and much smaller droplets (~ 5  $\ \mu\text{m}$ ). Overall the addition of lecithin did not improve compatibility, but it did change the mode of rubber dispersion compared with the mixture without lecithin.

#### **Crack Propagation and Fracture Behavior**

Ullett and Chartoff<sup>15</sup> described four basic types of crack propagation behavior, which were observed in samples of toughened thermosetting resins: unstable, stable, stick-slip, and ductile. Neat resins generally are characterized by unstable crack propagation, i.e., when the load reaches a critical value required for crack propagation, the initial crack propagates at an extremely high rate and specimen failure occurs almost abruptly. The stress–strain diagram of such a behavior for a neat vinyl ester specimen is represented in Figure 2(a).

The presence of rubber particles dispersed in the resin matrix, caused a change of the crack propagation behavior [Fig. 2(b)]. The mode shown can be defined as *stick-slip*, or according to Ullett and Chartoff<sup>15</sup> a *dual stick-slip*, where crack propagation is arrested and reinitiated one or several times during loading. Thus, the specimen failure does not occur immediately and unloading can prevent fracture.

Rubber content, within the range studied, did not affect the crack propagation behavior. When VTBN-43 (having molecular weight higher than VTBN-33) was used as a toughening agent, the crack propagation mode was the same as in the case of VTBN-33. Vinyl ester samples toughened by ETBN exhibited stick-slip behavior too, but, unlike vinyl terminated rubbers, the arrest and reinitiation of crack propagation occurred multi-



**Figure 2** Flexural stress-strain curves of notched vinyl ester specimens: (a) neat and (b) with 4-phr VTBN-33.



**Figure 3** Schematic illustration of a fracture surface: (a) unstable crack propagation and (b) stick-slip crack propagation.

ple times, and more than one *knee* was seen on the stress-strain diagram. The crack propagation mode in ETBN-toughened samples was not affected by rubber content, similar to the VTBNtoughened specimens. The difference between unstable and stick-slip propagation can be seen visually on the fracture surface, as schematically illustrated in Figure 3.

Investigation of the crack propagation mode in the endcapped vinyl ester samples was performed to examine the effect of the unprecipitated rubber presence. The endcapped samples exhibited an unstable crack propagation behavior, like the neat vinyl ester, and immediate failure occurred when the load reached its critical value. Thus, addition of the liquid rubber to the endcapped resin did not affect the crack propagation behavior.

Endcapped vinyl ester samples containing phase separated rubber were characterized by a stable mode of crack propagation with slight yielding before failure. The type of added rubber or its content did not have an effect on the crack propagation behavior in most specimens. The stable propagation observed is characterized by a relatively slow propagation rate, where unloading may prevent failure.

The stress intensity factor  $(K_{Ic})$  evaluation, according to ASTM D 5045, can be performed if the load displacement curve is linear (unstable or stable crack propagation behavior). For the stick-slip mode the initial value of  $K_{Ic}$  (for the first crack *jump*) was evaluated. All the  $K_{Ic}$  values are averages of six to seven measurements. Note that repeatability of the experiments was good and the absolute deviation of the measured values was less than 0.04 MPa m<sup>-2</sup>.

Figure 4 shows the effect of rubber addition on the fracture toughness of the vinyl ester specimens. For all the regular vinyl ester samples toughened by the different reactive rubbers, fracture toughness increases with rubber addition. The ETBN was found as the most effective toughening agent: 6 phr of ETBN caused about 70% increase of the fracture toughness, whereas the addition of the same content of VTBN-33 or VTBN-43 resulted in a 30 and 50% increase, respectively. Most of the fracture toughness improvement has occurred already by addition of about 2 phr rubber. The general trend of the effect of rubber addition to the endcapped vinyl ester is the same as in the case of regular vinyl ester: fracture toughness increases with rubber content; however, a gradual increase is found in this case. The ETBN again is the most effective toughening agent, but its effectiveness is less than for the



**Figure 4** Stress-intensity factor  $K_{Ic}$  as function of rubber content: (a) regular vinyl ester and (b) end-capped vinyl ester.

Resin	Rubber (phr)	Flexural Modulus			Stress at Yield			Strain at Break		
		Neat (GPa)	Modified (GPa)	Change (%)	Neat (MPa)	Modified (MPa)	Change (%)	Neat (%)	Modified (%)	Change (%)
VE	VTBN-33 (6)	3.84	3.20	-17	138	92	-33	5.9	3.6	-39
	VTBN-43 (6)	3.84	3.27	-15	138	100	-28	5.9	5.0	-15
	ETBN (6)	3.84	3.07	-20	138	71	-49	5.9	3.0	-49
MVE	VTBN-33 (10)	4.12	2.82	-31	111	77	-31	4.9	12.4	153
	VTBN-43 (10)	4.12	2.95	-28	111	70	-37	4.9	12.7	159
	ETBN (10)	4.12	2.60	-37	111	59	-47	4.9	14.0	186

Table I Summary of Mechanical Properties

regular vinyl ester: an addition of 10 phr causes just a 50% increase in the fracture toughness.

Fracture toughness evaluation at impact conditions was performed to examine the effect of loading rate on the toughening process. Stressintensity factors of all the vinyl ester specimens at all the studied rubber contents were found equal to about 1 MPa  $m^{-2}$ ; i.e., the reactive rubber addition did not actually change the fracture toughness at the impact conditions. The same behavior was observed at  $-60^{\circ}{\rm C}$  (below  $T_g$  of the rubber). These results agree with the conclusions of Crosbie and Phillips,<sup>17</sup> namely, that the rubber presence does not have a significant effect on notched impact energy. The expected effect of a rubber particle is to enlarge the plastic zone around the crack tip. However, if the loading rate is extremely high, a plastic zone around the crack tip does not develop and the toughening effect is thus negligible. Therefore, the influence of loading rate on toughening effectiveness must be taken into account in designing the structure of thermosetting resin composites.

#### **Mechanical Properties**

The mechanical properties of the various studied neat and toughened resins are given in Table I. Figure 5 shows the effect of rubber presence on the flexural modulus. Rubber addition results in a decreased stiffness, with little dependence on the rubber's type. An addition of 6 phr rubber results in a 15–20% decrease in modulus for the regular and 30-35% for the endcapped vinyl ester samples. Figure 6 represents the effect of rubber presence on yield stress of the resin samples. Rubber addition significantly lowers the stress at yield for both vinyl ester resins. In the case of ETBN a decrease of about 50% is observed. The results of



**Figure 5** Flexural modulus as function of rubber content: (a) regular vinyl ester and (b) endcapped vinyl ester.



**Figure 6** Stress at yield as function of rubber content: (a) regular vinyl ester and (b) endcapped vinyl ester.

the strain at break as function of rubber content are shown in Figure 7. The endcapped samples exhibit the expected behavior; i.e., the strain at break increases significantly with rubber content. An opposite effect was found for the regular vinyl esters with rubber, where a decrease ranging from 15% (VTBN-43) to 50% (ETBN) is shown. Such a behavior can be explained by the detailed course the propagating cracks experience through the different materials (to be shown later).

#### Morphology and Toughening Mechanisms

Specimens for SEM observation were prepared at three different conditions: *hot* fracture (at 80°C), fracture at ambient temperature, and *freeze* fracture (at liquid nitrogen temperature). Fracture surfaces were observed without any staining. The SEM observations showed that for the freeze fractured and ambient temperature fractured surfaces the interphase (resin-rubber) contrast was very weak. On the other hand, the hot fractured surfaces have shown clearly the toughened resins morphology. Therefore, all the SEM micrographs shown in this work represent hot fractured surfaces.

Figure 8 shows SEM micrographs of fracture surfaces of regular vinyl ester samples with VTBN-33. The fracture surface of the neat vinyl ester is relatively smooth, typical of brittle materials. The rubber particle-size distribution is quite wide. The number of particles and their mean diameter increase with rubber content. The white thin strips connecting the rubber particles represent one of the rubber energy absorbing toughening mechanisms, i.e., crazing. Rubber particles are shown to serve both as crack initiators and crack arrestors. No difference was observed in the morphology of VTBN-33 and VTBN-43 containing resins, except for the larger mean diameter of VTBN-43 particles.

Figure 9 shows SEM micrographs of fracture surface of regular vinyl ester samples with ETBN. The particles exhibit some internal structure, not seen in the VTBN particles, which may indicate dual-phase structure. Cavities around the rubber particles are observed clearly, unlike in the case of VTBN. This phenomenon results from a weak



**Figure 7** Strain at break as function of rubber content: (a) regular vinyl ester and (b) endcapped vinyl ester.



**Figure 8** Fracture surfaces of regular vinyl ester with VTBN-33 at two magnifications: (a and b) neat, (c and d) 1 phr, (e and f) 2 phr, and (g and h) 4 phr rubber.



**Figure 9** Fracture surfaces of regular vinyl ester with ETBN at two magnifications: (a and b) 2 phr and (c and d) 6 phr rubber. The bar size in the pictures in (a) and (c) is 11  $\mu$ m and in the pictures in (b) and (d) is 50  $\mu$ m.

interfacial adhesion and represents another possible rubber toughening mechanism, namely, cavitation. This mechanism actually is expected for ETBN (epoxy terminated)-toughened samples where chemical reactions with the vinyl ester chains are unlikely. The occurrence of both crazing and cavitation in the ETBN samples certainly explains the difference in fracture toughness compared with the VTBN samples, as shown in Figure 4.

Figure 10 shows SEM micrographs of fracture surfaces of rubber modified endcapped vinyl ester samples. The fracture surface of the neat endcapped samples is different from the previous case; a cracked network is seen throughout the cross section. This can result from the very tiny endcapped rubber inclusions unobservable under the magnification level used. This network formation process absorbs fracture energy, resulting in fracture toughness of the endcapped vinyl ester higher than that of the regular resin. The structure shown in the micrographs of the endcapped vinyl ester samples with phase separated rubber is different from that of the regular vinyl ester samples. The strong interfacial adhesion, caused by rubber/resin grafting, eliminates the possibility of cavitation on loading.

## **CONCLUSIONS**

• The initial compatibility of vinyl ester resins with rubbers is poor. Attempts to improve the compatibility (temperature, ultrasonic, and surfactants) have not been successful.



**Figure 10** Fracture surfaces of endcapped vinyl ester with added rubber at two magnifications: (a and b) neat, (c and d) 6 phr VTBN-33, and (e and f) 6 phr ETBN.

- The neat resins are characterized by an unstable crack propagation behavior, which causes failure when the load reaches its critical value. The crack propagation behavior changes to a stick-slip or a stable one as a result of rubber addition.
- The fracture toughness at a low loading rate of

vinyl ester resins increases with reactive rubber content. The fracture toughness improvement ranged from 30 to 70%. The ETBN is the most effective toughening agent because of an external cavitation mechanism action.

• The fracture toughness at impact conditions is not improved as a result of rubber addition.

- There is a 15–35% reduction of flexure modulus and a 30–50% reduction of yield stress upon rubber addition. In the case of endcapped vinyl ester the strain at break increases by 150–200%, whereas for the regular vinyl ester it decreases as a result of the cracks passing through the matrix and interface but not through the rubber inclusions.
- Crazing and external cavitation are toughening mechanisms active in the investigated thermosetting resins. Cavitation was observed in ETBN-toughened samples, where a weak rubber/matrix adhesion was observed.
- Fracture surfaces produced at 100°C, rather than at the common low temperatures, yield outstanding SEM micrographs.

The partial financial support of the Israeli Ministry of Defence is gratefully appreciated. The authors acknowledge the careful Charpy tests performed by Jian-Wei Xu (Institute of Materials Science of the University of Connecticut).

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