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Toughening of vinyl ester resins with modified polybutadienes

Son Pham and P. J. Burchill*
Aeronautical and Maritime Research Laboratories, PO Box 4331, Melbourne 3001, Australia
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This study is of toughening some vinyl ester resins with low-molecular-weight butadiene-based polymers. Liquid polybutadiene and copolymers with acrylonitrile are immiscible with the commonly used vinyl ester resin, Derakane 411-45. Despite this incompatibility, some toughening is seen in blends with this vinyl ester resin. Modification of hydroxy-terminated polybutadiene through reaction with a diisocyanate and various alcohols renders the polymer more compatible but not miscible with the resin. With increasing length of the end-groups, the ability to provide a tougher cured resin improves such that the energy to propagate a slow crack increases more than 10 times. Addition of 5 wt% of a butadiene polymer resulted in a disperse-phase volume fraction greater than 10%. Blends with Derakane 411-45 showed greater toughness than that of the toughened resin Derakane 8084, which was also improved by addition of butadiene copolymers.

(Keywords: vinyl ester resins; toughening; polybutadienes)

INTRODUCTION

Vinyl ester resins are generally dimethacrylate esters, and are commonly made commercially by reacting methacrylic acid with a bisphenol A-based epoxy resin such as Shell's Epon 828; bisphenol A may be added to the reaction mixture and also maleic anhydride. A commercially toughened vinyl ester resin (Derakane 8084) has a carboxy-terminated low-molecular-weight butadiene–acrylonitrile copolymer (CTBN) included in the manufacture. In addition, the resins contain 40–50% by weight of styrene. These resins are cured at room temperature using a peroxide initiator and a transition-metal salt catalyst, and often post-cured to increase the heat-deflection temperature. The cured resin is quite brittle and there are few reports on toughening[1–6].

Toughening of epoxy resins can be achieved by the addition of a miscible CTBN as a low-molecular-weight elastomer prepolymer[7–15]. During cure the prepolymer reacts with the epoxy end-groups and gives a bimodal distribution of molecular weight between crosslinks. At the same time, before the onset of gelation, phase separation occurs to give a fine dispersion of rubbery domains. Such a physical structure is known to render the glassy matrix tougher because the dispersion facilitates shear yielding of the matrix and hence crack-tip blunting. In the toughest systems it has been shown that, ahead of the crack tip, the rubbery particles cavitate and the matrix ligaments between them yield in shear[16]. Calculations[17,18] have indicated that the Poisson's ratio for the rubber needs to be very close to 0.5 if cavitation is to occur before yielding, which is then enabled due to a local change from plane-strain to plane-stress conditions at the crack tip. An additional requirement is that the ligament thickness is equal to or less than the particle diameter[19], which indicates that a rubber volume fraction of 10% or greater is required; and experimentally particle sizes seem to vary with matrix for optimum toughness, though are generally less than 5 μm.

This work describes the toughening of some commercial vinyl ester resins using modified polybutadienes (liquid rubbers), and some differences to observations on the toughening of epoxy resins have been pointed out.

EXPERIMENTAL

Materials

The vinyl ester resins used were Derakane 411-45 and Derakane 8084 (Dow Chemical Co.) and Hetron 922 (Huntsman Australia Chemical Co. Pty. Ltd), the base chemical composition of which is given in *Figure 1*. Derakane 8084 is a toughened version of Derakane 411-45 in which about 7% of a low-molecular-weight CTBN is chemically bonded through terminal ester groups with 2,2′-bis(4-hydroxyphenyl)propane units during manufacture. The liquid hydroxy-terminated butadiene–acrylonitrile copolymers (HTBN x17, x29, x34) are described in *Table 1*, and have a functionality of almost 2. Vinyl-terminated butadiene–acrylonitrile copolymer (VTBN x33) is a methacrylated polymer with a functionality of 2.4, and acrylonitrile content of 17.5% and a molecular weight of about 3800 (Hycar, BF Goodrich Co.). The liquid hydroxy-terminated low-molecular-weight polybutadiene (HTPB) was obtained from Atochem Inc. (see *Table 1*). Two commercial isocyanates, Suprasec PBA2225 and Daltobond CRM (ICI Ltd, Polyurethane Division), were used as received and are bis(4-isocyanatophenyl)methane (MDI) based products with isocyanate equivalent weights of 135 and

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* To whom correspondence should be addressed

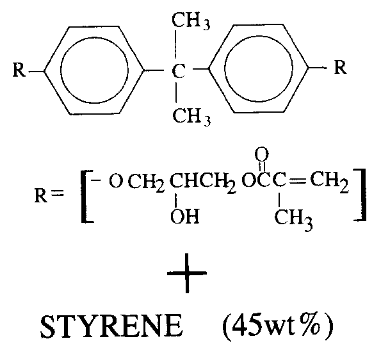

Figure 1 Main components of vinyl ester resins Derakane 411-45, Derakane 8084 and Hetron 922. Resin Derakane 8084 also contains 7% of chemically bound butadiene–acrylonitrile copolymer

Table 1 Chemical data for butadiene polymers

Liquid rubber	Hydroxy No. (mg(KOH)/g)	Carboxyl (ephr)[a]	Acrylonitrile (%)	Viscosity (cPs)
HTBN x17	20.65	0.007	17	112000
HTBN x29	33.13	0.004	10	90000
HTBN x34	37.66	0.007	26	230000
HTPB (R45M)	40.95	n/a	0	n/a

[a] eph = equivalent part per hundred resin

420 respectively. The CRM is also an MDI-terminated polypropylene glycol. Other chemicals were laboratory-grade reagents and used as received.

Modification of the hydroxy-terminated polybutadiene (HTPB) was carried out in two stages. A 500 ml pot equipped with a stirrer, condenser, thermometer and a 250 ml dropping funnel purged with nitrogen gas was charged with a dichloromethane (100 ml) solution of MDI (0.0166 mol, 4.5 g) and dibutyltin dilaurate (0.1 g), and heated to 40°C with continuous stirring on an oil bath. HTPB (0.0066 mol, 18 g), triphenylphosphine (0.1 g) in dichloromethane (50 ml) and dried with molecular sieve (4 Å) for 16 h before use was placed in the funnel and added dropwise over a 2 h period. Stirring was continued for a further 2 h after the final addition[20]. Reaction was monitored using infra-red (i.r.) spectroscopy. Various diols (0.0166 mol) in dichloromethane were added quickly to the pot and stirring at 40°C was continued until all isocyanate had reacted, which was confirmed by i.r. spectroscopy. The solvent was removed under reduced pressure before blending with the resins.

One of the diols used in the second stage was prepared by reacting MDI with a large excess of triethylene glycol (TG) in dichloromethane to give TG-MDI-TG. Unreacted TG was removed by extraction with water, the solution dried and solvent removed, before this product was used in the reaction with the isocyanate ends on the HTPB from above.

Castings of the vinyl ester resins were prepared by first blending the resin, liquid rubber and catalyst using a homogenizer, degassing this mixture, then adding the peroxide and pouring it into a steel mould coated with release agent. This resin mixture was allowed to cure at room temperature for 16 h before post-curing at 90°C for 90 min.

A typical formulation by weight is a follows:

Derakane 411-45	95
liquid rubber	5
6% cobalt naphthenate	0.3
methyl ethyl ketone peroxide	1.5

Test methods

Fracture properties (stress intensity factor K_{Ic} and strain energy release rate G_{Ic}) were determined using the double torsion (DT) test method[21,22] at a crosshead speed of 0.1 mm min^{-1} on plates of thickness t (7 mm), width W (45 mm) and having a central longitudinal groove 2 mm deep.

Stress intensity factor was calculated from:

$$K_{Ic}^2 = \frac{(1+\nu)^2 P^2 l^2}{k_1 W t_n t^3}$$

in which P is load, l is the moment arm, t_n is thickness at the central groove, k_1 is a correction factor for finite width-to-thickness ratio[23], and ν is Poisson's ratio.

Strain energy release rate was calculated from:

$$G_{Ic} = (P^2/2t_n) \quad \mathrm{d}C/\mathrm{d}a$$

in which C is compliance and a is crack length; $\mathrm{d}C/\mathrm{d}a$ was determined experimentally from the compliance of plates with different length cracks.

In the double torsion fracture tests the failure mode was either slow continuous crack growth (stable) or stick–slip crack growth (unstable), from which fracture values at growth initiation (K_{Ici}, G_{Ici}) and arrest (K_{Ica}, G_{Ica}) are obtained, and are given in the tables of results. Where the arrest and initiation values are the same, the crack growth is stable. Coefficients of variation for the values of K_{Ic} and G_{Ic} were less than 5%.

The stress intensity factor was also determined using single edge notch specimens in three-point bending at a span-to-width ratio of 8, and tested at a crosshead speed of 5 mm min^{-1}. Single edge notch specimens had thickness t (10 mm), width W (7 mm) and a notch depth of 2 mm, into which a razor blade was driven to give a sharp initial crack before test.

Stress intensity factor[24] was calculated from:

$$K_{Ic} = y(6M/tW^2)a^{1/2}$$

in which M is bending moment and y is a geometrical factor given by:

$$y = 1.96 - 2.75(a/W) + 13.66(a/W)^2 - 23.98(a/W)^3 + 25.22(a/W)^4$$

Single edge notch toughness is given in tables of results as K_{sen}.

The elastic modulus E was measured by three-point bending, and tensile properties were evaluated according to ASTM 638M-89, M-II geometry.

RESULTS AND DISCUSSION

Toughening with butadiene–acrylonitrile copolymers

None of these elastomer prepolymers, described in *Table 1*, were miscible with Derakane 411-45 and homogenized mixtures separated within 24 h into two phases. In contrast, the hydroxyl-terminated butadiene–acrylonitrile copolymer (HTBN x34) was miscible with the epoxy resin Epon 828 at room temperature and the other copolymers did not separate as quickly. The

Table 2 Mechanical properties of vinyl ester resins modififed with polybutadiene and acrylonitrile copolymers

Rubber (wt%)	K_{Ici}	K_{Ica}	G_{Ici}	G_{Ica}	K_{sen}	E
Derakane 411-45	0.72	0.63	157	122	1.22	3.00
5 (HTPB)	1.20	0.65	560	163	1.02	2.24
5 (HTBN x17)	1.43	0.74	783	207	1.17	2.38
5 (HTBN x29)	1.52	0.82	850	246	1.16	2.28
5 (HTNB x34)	1.13	0.75	479	210	1.09	2.36
5 (VTBN x33)	1.08	0.84	451	269	1.36	2.47
Derakane 8084	1.15	0.73	432	172	1.34	2.82
5 (VTBN x33)	1.71	1.71	1234	1234	1.57	2.36

Table 3 Polybutadiene end-capped with various chain ends

PB1	HTPB end-capped with MDI. Free isocyanate. (MDI-PB-MDI)
PB2	HTPB end-capped with MDI. Excess isocyanate was neutralized with hydroxylpropylmethacrylate (HPM). (HPM-MDI-PB-MDI-HPM)
PB3	HTPB end-capped with MDI. Excess isocyanate was neutralized with triethylene glycol (TG). (TG-MDI-PB-MDI-TG)
PB4	HTPB end-capped with CRM. Excess isocyanate was neutralized with methanol (Me). (Me-CRM-PB-CRM-Me)
PB5	HTPB end-capped with MDI. Excess isocyanate was neutralized with TG-MDI-TG. (TG-MDI-TG-MDI-PB-MDI-TG-MDI-TG)

Table 4 Mechanical test results for vinyl ester resins toughened with modified polybutadiene

Samples	K_{Ici}	K_{Ica}	G_{Ici}	G_{Ica}	K_{sen}	E
Derakane 411-45	0.72	0.63	157	122	1.12	2.82
5 wt% CRM	0.72	0.72	156	156	1.30	2.92
5 wt% HTPB	1.20	0.65	560	163	1.02	2.24
5 wt% PB1	1.86	0.89	1369	314	1.46	2.08
5 wt% PB2	1.67	0.82	1051	253	1.44	2.32
5 wt% PB3	1.91	0.82	1390	258	1.44	2.36
10 wt% PB3	2.36	2.36	2571	2571	1.63	1.95
5 wt% PB4	2.22	2.22	1948	1948	1.56	2.10
5 wt% PB5	2.04	2.04	1751	1751	1.61	2.13
Derakane 8084	1.15	0.73	432	172	1.37	2.82
5 wt% PB3	2.59	2.59	3749	3749	1.75	1.33

solubility parameters of the bisphenol A-based epoxy and of the vinyl ester resin are 20.7 and 20.6 $(\mathrm{J\ cm^{-3}})^{1/2}$ respectively, while the calculated values for the copolymers are 17.4 and 18.9 $(\mathrm{J\ cm^{-3}})^{1/2}$ for acrylonitrile contents of 10 and 26% respectively[25]. This poorer miscibility with vinyl ester resins would seem to occur because of their hydroxyl groups, the effect of which is not adequately accounted for in analysis based on solubility parameters. Similarly the copolymer's acrylonitrile content would be expected to reduce the surface tension between the phases relative to polybutadiene and so give greater droplet stability and compatibility in the homogenized mixtures. These mixtures were used rapidly to minimize gross phase separation before the resin gelled, which was usually within 1 h of homogenizing.

Results of fracture experiments are given in *Table 2* and seem to show some small improvement in toughness due to acrylonitrile content of the copolymers relative to polybutadiene. The fracture values show an opposite trend to that expected. SEM of the fracture surface shows that the particles are large and have a broad size distribution from 2 to 40 μm. The large particle sizes may be overshadowing any beneficial effects due to compatibility improvement. In dispersing immiscible liquids, the size of the dispersed phase is governed by the shearing process[26,27]. Recent work on mixing indicates that in practical mixing devices the final droplet size is not limited by the viscosity ratio of the media being too large. Hence the increasing viscosity of these copolymers with acrylonitrile content would not be a factor in the dispersed phase size. These results are probably a reflection of the time that was available before gelation of the resin for coalescence of the droplets, of which the smallest do so the most rapidly.

In contrast, toughening of epoxy resins with such copolymers results in particles of 0.2–5 μm, which are formed as a separate phase during cure[28–30] and do not result from how the components were originally mixed. Furthermore it was shown by Rowe and coworkers[8] that, as the acrylonitrile content increased, the particle size decreased, whilst others have found that there is a complex relationship between morphology and chemical structure and cure conditions[11,14,29,30].

The reactive copolymer VTBN (x33) when added to Derakane 411 gave toughness improvements no better than an unreactive liquid rubber. In contrast, addition of this copolymer to the modified vinyl ester resin Derakane 8084 produced a large improvement in toughness as seen by the values given in the last two rows of *Table 2*. The copolymer is apparently miscible in this resin up to 5 wt% mainly due to the chemically bound copolymer content, which enables easier dispersion and improved the stability of the mixture (centrifuging for 30 min at 10 000 rpm was required to separate the phases). Derakane 8084 cured alone does not phase separate; its elastomer content only improves ductility but will also stabilize additional liquid rubber as a separate phase during cure. These results indicate that true miscibility followed by phase separation may not be mandatory for achieving large increases in toughness in thermoset resins, but that some compatibility between the matrix and the dispersed elastomeric phase is necessary.

Toughening with modified polybutadiene

In an attempt to achieve either pre-cure miscibility or a more stable dispersion of the liquid rubber before cure, isocyanate chemistry was used to attach various resin-compatible end-groups to the polymer chain; these are listed in *Table 3* in order of increasing molecular weight of the end-group, PB1–PB4. The groups were all attached through 4,4′-bis(isocyanatophenyl)methane (MDI), which had to be used at 25% greater than stoichiometry otherwise gelation occurred during the synthesis. Initially it was considered that using isocyanate-terminated polybutadiene PB1 in a reaction with the hydroxyl groups in the vinyl ester resin would be the best way of dispersing the elastomer. However, such mixtures were found to have a very limited pot-life and had to be cured immediately after mixing. Even though none of the modified HTPBs were miscible in the vinyl ester resins, they showed greater dispersion stability.

From the results given in *Table 4*, it is seen that, as the length and polarity of the end-group are increased, the toughness increases, as shown by the crack growth initiation values for K_{Ici} and G_{Ici} measured in the double torsion experiments. Material PB4 has the longest end-groups, which have increased the molecular weight of the polymer by about 1700. The slow crack growth fracture measurements show that for the largest end-groups the fracture behaviour is changed from unstable stick–slip to stable continuous growth. Increasing the content of PB3 to 10% also promotes a change to stable crack growth. Addition of end-group material on its own to the resin has no beneficial effect as shown by the fracture values for addition of CRM, and so it would appear that the end-groups are not acting as placticizers unless this plasticization is due to the high end-group concentration at the surface of the particles. The improved toughness with end-group size is probably due to the increased volume of the dispersed phase. Blends were mixed on the basis of five parts liquid rubber as polybutadiene to 95 parts of resin.

Fracture toughness measured by a single edge notch three-point bend method, K_{sen} (a catastrophic crack growth test), showed a much smaller improvement in fracture toughness relative to the slow crack growth test. The much shorter time available for deformation processes at the crack tip in the s.e.n. test means that a dispersed phase is more likely to act to initiate cracking than act to promote crack-tip blunting through matrix shear yielding.

A similar study has been made by Achary *et al.*[5] of a methyl methacrylate-based vinyl ester resin toughened with HTPB. By reaction of this liquid rubber first with toluene diisocyanate, they introduced a chemical link between the HTPB and the resin and observed improvements in adhesive and mechanical strength. Likewise, with epoxy resins, changes to the size of the end-groups on the liquid rubber have also been found to be beneficial[31]. Chen and Jan found that attachment of oligomeric propylene glycol units ($MW \sim 600$) to the ends of a carboxy-terminated butadiene–acrylonitrile copolymer (CTBN) increased the toughness G_{Ic} determined by slow crack growth in tapered double cantilever beams by 2.3 times over that in which the CTBN was only reacted with the bisphenol A epoxy.

Toughening of other vinyl ester resins is also given in *Tables 4* and *5*. Values for Derakane 8084 to which has been added 5 wt% PB3 rubber (*Table 4*) indicate that this vinyl ester resin can be toughened by addition of a suitably modified polybutadiene, and greater than through the addition of VTBN (x33) (*Table 2*); however, Young's modulus has now been greatly reduced. Because supposedly similar materials may respond differently to being toughened, PB3 was added to Hetron 922, a similar vinyl ester resin to Derakane 411-45 made by a different manufacturer. This alternative vinyl ester resin displayed similar improvement in toughness (*Table 5*). *Table 6* gives the tensile properties of these latter blends and reveals a reduction in properties because of the increased flaw size. These blends displayed stress whitening at yield in tension, which probably arises from cavitation of the particle or debonding at the interface.

Table 5 Fracture results for Hetron 922 toughened with modified polybutadiene

Samples	K_{Ici}	K_{Ica}	G_{Ici}	G_{Ica}	K_{sen}	E
Hetron 922	0.81	0.75	198	170	1.42	3.00
5 wt% PB3	2.19	0.951	1823	340	1.79	2.31
10 wt% PB3	2.47	2.47	2928	2928	1.71	1.79

Acrylonitrile–butadiene copolymers were expected to be more effective tougheners; however, several attempts to modify the best of the copolymers—HTBN (x29)—were unsuccessful. With a 25% excess of MDI gelation occurred after only 50% of the rubber was added, and when a 150% excess of toluene diisocyanate was used gelation occurred in the second stage upon addition of triethylene glycol. An alternative method[32,33] involves the use of the toluene diisocyanate–acetone oxime adduct in which the *para* isocyanate is blocked. First, reaction occurs between the *ortho* isocyanate and the hydroxyl groups, and then the *para* group is liberated at elevated temperature in the presence of a diol; this reaction was also unsuccessful.

Morphology

Blends of the butadiene–acrylonitrile copolymer with vinyl end-groups (VTBN x33) in Derakane 8084 showed a very fine dispersion of particles about 2 μm in diameter; however, a similar blend with Derakane 411-45 resulted in 20 μm particles. The vast contrast in sizes is due to the chemically bound copolymer present in Derakane 8084, which enables easier dispersion of the liquid rubber, so reducing the overall size and providing greater stability. Both blends showed very good bonding at the rubber–resin interfaces due to the vinyl end-groups of the copolymer permitting formation of chemical bonds across the interface during cure.

Scanning electron micrographs (SEM) of slow crack growth fracture surfaces of materials containing PB2 and PB3 are shown in *Figures 2* and *3*, which display evidence of a strong interface and cavitation of the particles with PB2, but with PB3 interfacial debonding is evident. Blends containing PB1 or PB2 showed similar features to each other, and the end-groups (vinyl ester and methacrylate) have supposedly reacted with the resin to give a strong interface by chemical bonding. SEM micrographs of fractured materials containing PB4 or PB5 were similar to that of PB3, and here also there are only polar attractions available to cross the interface. Hence, a strong interface is only realized when chemical bonding can occur or when the end-group has sufficient length. If void formation is a requirement for improve-

Table 6 Tensile properties of Hetron 922 toughened with modified polybutadiene

Rubber (wt%)	Stress at yield (MPa)	Stress at break (MPa)	Strain at yield (%)	Strain at break (%)	Energy to yield (J)	Energy to break (J)	Tensile modulus (GPa)
Control	88.69	84.2	5.05	6.56	1.94	2.78	3.29
5 PB3	58.11	57.37	4.77	5.71	1.30	1.66	2.52
10 PB3	40.31	39.98	4.55	6.30	0.98	1.48	2.06

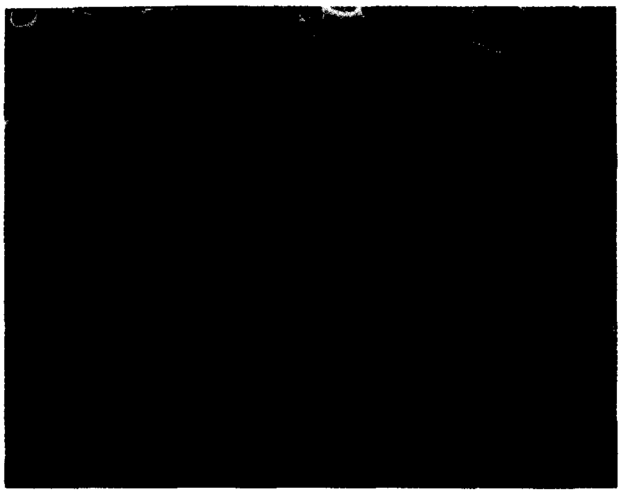

Figure 2 SEM of the slow fracture surface of the blend of Derakane 411-45 with PB2

Figure 3 SEM of the slow fracture surface of the blend of Derakane 411-45 with PB3

ment to fracture toughness, debonding at the interface or cavitation appear to be equally effective in these systems. This observation is in agreement with that of other workers in studies of toughening of an epoxy resin by voids[34,35]. The particle sizes were similar in all modified HTPB systems as seen in the SEM of fracture surfaces, and ranged from about 2 to 10 μm. The micrographs also suggested that the volume fraction of particles is greater than the expected 5%.

Volume fraction V_f can be estimated from the ratio of particle diameter D to the centre-to-centre distance L assuming hexagonal packing and uniform size:

$$D/L = (\pi V_f/4.243)^{1/3}$$

A ratio of 3 would be expected for a volume fraction of 5%, while the micrographs indicated a volume fraction of about 10%.

Measurements from fracture surfaces are known to give poor estimates of particle volume fraction because of a tendency of the crack to pass through the equators of particles, especially the larger ones. This effect contributes to surface roughness and so statistical methods based on sampling by a plane section become biased. Accordingly a blend with PB3 has been investigated by obtaining a highly polished plane surface, which was lightly stained with OsO_4 to improve the contrast in the SEM pictures. These micrographs showed a broad distribution of apparent particle sizes, which is given in *Figure 4*, and a fit to a log-normal distribution as suggested by Wu's work[15]. The estimated volume fraction[29,36] based on these measurements was 11%, confirming what had been suspected from the fracture surfaces, and an average particle size of 5.6 μm. A similar analysis of the blend containing the unmodified polybutadiene (*Figure 5*) gave a volume fraction of 15% and an average particle size of 20.7 μm.

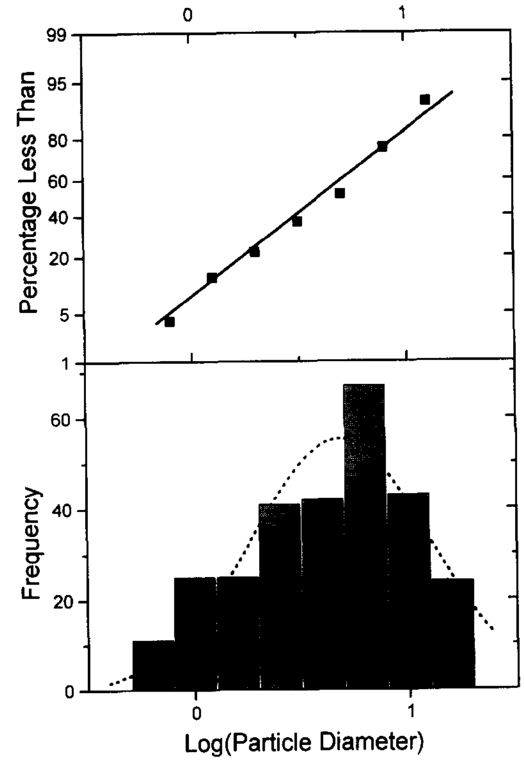

Figure 4 Distribution of particle sizes in the blend of Derakane 411-45 with PB3

In the study by Achary[5] mentioned early, they found a dispersed phase size of 3–8 μm for the unmodified HTPB, which probably reflects that methyl methacrylate is a better solvent for this liquid rubber than is styrene. Their mixture is initially miscible and separation occurs before gelation. When they modified the HTPB, they did not find a separated phase in the cured resin, and their improvements in properties are probably due to internal plasticization. In contrast, the study of toughening an epoxy resin[31] in which the CTBN was compatibilized showed no change in separated-phase particle size.

Dynamic mechanical thermal analysis

Vinyl ester resins (Derakane 411-45 and Derakane 8084) toughened with the acrylonitrile copolymer (VTBN x33) showed very little or no effects on the glass transition temperature (T_g) of the resins taken as the maximum in the temperature vs. $\tan\delta$ curve. This copolymer was apparently completely miscible at 5 wt% in Derakane 8084 before cure, and phase separated during cure to give rubbery domains of $\sim$ 2 μm. D.m.t.a. of this blend showed only a 3°C reduction in T_g of the

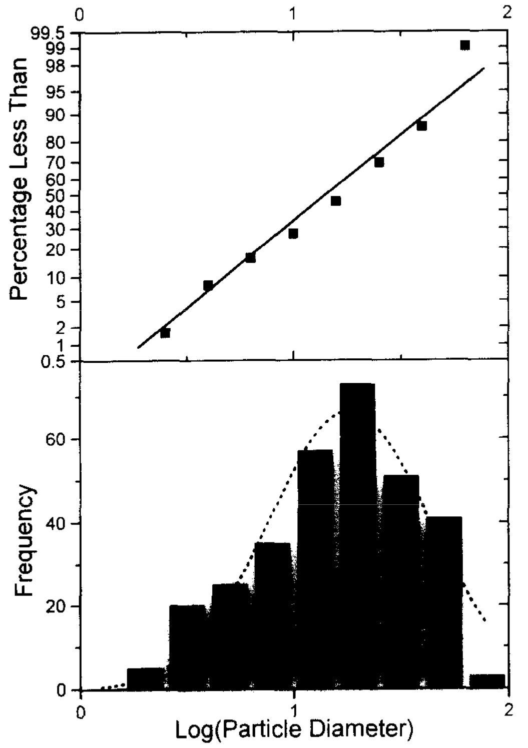

Figure 5 Distribution of particle sizes in the blend of Derakane 411-45 with HTBP

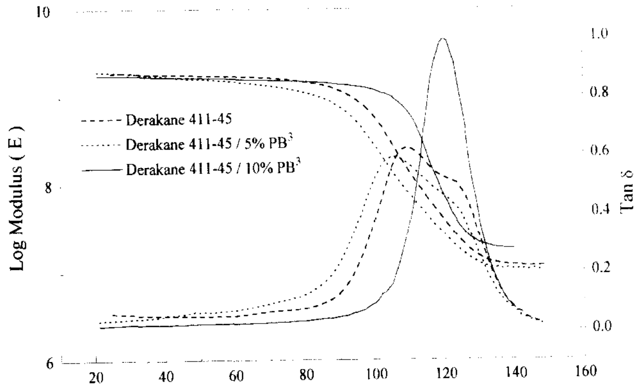

Figure 6 D.m.t.a. of neat resin and mixtures containing 5% and 10% of polybutadiene as PB3

matrix but the tan δ vs. temperature curve was broader. With a similar blend using Derakane 411-45, the rubber was immiscible before cure, and the final product had rubbery domains ~ 20 μm, and a reduction in T_g of about 2°C. Again the tan δ curve showed a greater range of temperatures over which relaxation losses occurred than observed with the neat resin.

D.m.t.a. of vinyl ester resins toughened with PB3 rubber showed a reduction in T_g of about 10°C (*Figure 6*). The broadness and reduced intensities of the tan δ vs. temperature plots would seem to indicate a large amount of the dispersed phase present in the resins; however, SEM studies through staining the blend with osmium tetroxide have shown no polybutadiene in the continuous phase and that this polymer is confined to the dispersed phase. This evidence was supported by spectroscopic analysis discussed below. The cause of this broadening may be due to plasticization of the resin around the particle due to the resin-miscible end-groups, or the particles are so crosslinked and reacted with styrene that their T_g is only 10–20°C less than that of the resin, or both. The estimated volume fraction of the particles (11%) indicates substantial copolymerization with the vinyl ester resin components and most likely styrene due to its partition between the phases. Attempts to find a low-temperature T_g due to polybutadiene by differential scanning calorimetry were unsuccessful even in a blend that contained 10% PB3.

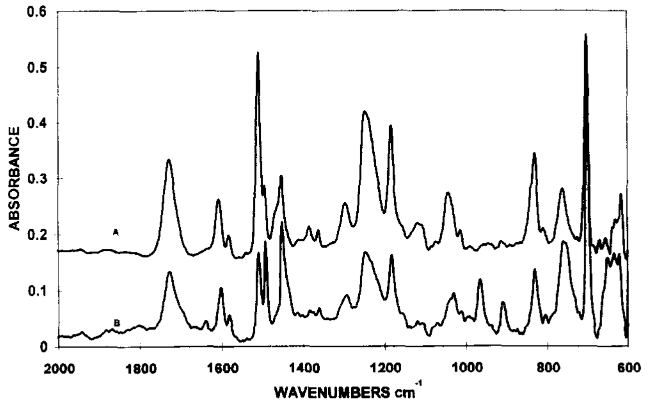

Figure 7 Infra-red spectra from the blend of Derakane 411-45 with HTPB: (a) matrix, (b) dispersed phase

Spectroscopic analysis

The large particles seen in the blend of Derakane 411 with unmodified polybutadiene permitted a direct spectroscopic study of the disperse phase with a Bruker infra-red microscope. *Figure 7* shows the spectra recorded for a particle and matrix from a microtomed slice using a 20 μm aperture. These spectra reveal from the relative intensities of peaks, for example 1720 cm^{-1} ester carbonyl to 690 cm^{-1} monosubstituted benzene, that the particles contain both components of the vinyl ester resin but not in the same ratio as the matrix. Spectral subtraction disclosed that the relative amounts of styrene between particle and matrix ranged from 0.9 : 1 to 1.1 : 1, and that similarly for relative amounts of the methacrylate component from 0.3 : 1 to 0.35 : 1. Spectra of the matrix well removed from the particle did not have any absorptions due to polybutadiene, but adjacent to a particle and outside a low concentration could be discerned. From the composition of the resin, the amount of polybutadiene added and the above analysis, an estimate of the volume fraction of the disperse phase is 14%.

CONCLUSIONS

Improvement in fracture toughness of vinyl ester resins can be achieved with the incorporation of a suitably modified low-molecular-weight polybutadiene. The addition of only 5% modified rubber resulted in 2–3-fold increase in stress intensity factor K_{Ic} and a 10-fold increase in energy required for fracture G_{Ic} in Derakane 411-45 and Derakane 8084. The toughness of the resins increased with increase in length and polarity of the end-groups; however, these blends have reduced modulus and thermal properties. While polar–polar interactions give a more stable dispersion of the rubber in the resin, a strong interfacial bond is only observed when chemical bonding occurs across the rubber–resin interface. Morphology studies and spectroscopic analysis of the cured blend revealed that appreciable amounts of styrene and a lesser amount of the methacrylate component react with the liquid rubber, leading to a volume fraction of dispersed phase 2–3 times greater than the original addition of liquid rubber. Owing to this reaction with the liquid rubber, the disperse phase may no longer be elastomeric at room temperature as suggested by the d.m.t.a. results. Observed toughness improvements are most likely due to a greater than expected volume fraction of the disperse phase, and a reduction in dispersed-phase particle size. Though plasticization of the matrix as a cause of toughening appears to be less likely, adjacent to the disperse phase the matrix may be more ductile, and so contribute to a lower than expected elastic modulus.

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