Elastomer-Modified Vinyl Esters as Structural Adhesives

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Vinyl esters (epoxy-methacrylates) are preeminent chemical-and corrosion-resistant materials. Based primarily on addition-esterified epoxy resins with methacrylic acid and diluted with styrene monomer, several products are available based on diepoxide structure, molecular weight, modifier type (nitrile rubber, urethane, glycol, *e.g.*) and blends with styrenated polyester resins. A new class of vinyl ester urethanes has also become commercially available. Elastomer modification of both types has shown that the fracture energy of epoxy vinyl esters can be enhanced to have a four-fold improvement. Despite this, the elastomer-modified vinyl esters have not found use as a basis for free-radical curing structural adhesives. Addition of an epoxy-terminated rubber (ETBN) or a methacrylated-vinyl terminated rubber (VTBNX) to previously elastomer-modified vinyl ester resin significantly improves overlap shear, T-peel, and bulk fracture properties. This suggests potential application in structural adhesive development. The cured specimen morphology of the combined rubber system provides clues for toughness enhancement.

KEY WORDS: vinyl ester resins; elastomer-modified; ETBN; VTBNX; fracture energy; morphology; dynamic mechanical properties.

1. INTRODUCTION

Vinyl ester resins (epoxy-methacrylates), a substantial class of styrenated, free-radically curable corrosion/chemical resistant thermosets recently celebrated a quarter century of use. Largely employed for fiber-reinforced, structural applications, vinyl ester resins have a substantial history with respect to long-term service in numerous environments at elevated temperatures and pressures, usually under load.

Vinyl ester resins are available based on both rigid and flexible epoxy resins (glycol-based, usually). These flexible epoxy resins generally have depressed T_gs and chemical resistances. Nitrile-rubber modified vinyl esters[1] appeared on the market in

the mid-to-late '70s. Later on, the appearance of both urethane prepolymer modified vinyl esters and vinyl ester urethanes occurred.[2] Structural and non-structural uses proliferated. Recently, vinyl ester resins made advances in markets other than classic glass fiber reinforced composite uses. Vinyl ester resins with a high percentage of bound rubber segments have found uses in circuitry and civil engineering/construction markets, *i.e.*, flooring.

Few, if any, of these vinyl ester resins, whether epoxy or urethane types, have produced a thermoset resin with potential utility in designing structural or semi-structural adhesives with a respectable balance of peel resistance, shear strength and durability in metal bonded assemblies.

Recent work, the subject of this paper, examines the modification by both reactive and non-reactive elastomeric liquid polymers of vinyl ester resins already synthesized with rubber segments. These materials appear to be a new class of adhesive raw materials which have inherent chemical and corrosion resistance.

2. MATERIALS AND PROCEDURES

The elastomer-modified vinyl ester resin used in this work is Derakane® 8084, herein referred to as the elastomer-modified vinyl ester resin. The unmodified vinyl ester resin used was Derakane 411, herein referred to as the unmodified vinyl ester resin and the unmodified epoxy novolac vinyl ester resin was Derakane 470, herein referred to as the unmodified novolac vinyl ester resin. All of the Derakane vinyl ester resins are products of Dow Chemical Co. Derakanes 8084 and 411 are based on the diglycidyl ether of bisphenol A (DGEBA) epoxy resin. Derakane 8084 has about 7.5 phr of a carboxyl-terminated butadiene-acrylonitrile (CTBN) liquid polymer reacted into the base resin.

The Hycar® reactive liquid rubbers, used as additives, are epoxy and vinyl terminated. These are designated as ETBN 1300 × 40 and VTBNX 1300 × 33, respectively. ETBN 1300 × 40 is made by reacting CTBN 1300 × 8, 17% bound acrylonitrile, with a liquid DGEBA epoxy resin (EEW = 190) at a molar ratio of 1:2. The reaction is carried out in bulk at 130°C for 5 hours to an acid number of 1.7. Since CTBN is very close to a difunctional polymer the resulting ETBN can be considered a triblock polymer, with CTBN as the center rubbery block and end blocks of the DGEBA epoxy resin. Due to the high viscosity of ETBN it is dissolved in styrene to give 50% solids, ETBN × 40. ETBN × 40 is listed on all tables as ETBN and styrene so that the amounts of ETBN combined with various vinyl ester resins can be compared with VTBNX combinations with the same resins. VTBNX 1300 × 33 is made by reacting CTBNX 1300 × 9, 17% bound acrylonitrile, with glycidyl methacrylate. This is also a bulk reaction run at 95°C for about 6 hours to an acid number of 4.0. The CTBNX 1300X9 contains some random acid groups in addition to the two terminal carboxyl groups.

A combination of cobalt naphthenate and MEK peroxide were used to cure the samples. Cured plaques having a sample thickness of about 6.35 mm were made in 20 × 25 cm Teflon-coated aluminum molds. The molds are mounted vertically, the mixed resins are poured into the molds and cured under ambient atmosphere. Two different cure schedules were used: (1) one hour at 60°C plus two hours at 120°C (CS1) and (2) 16 hours at room temperature plus 90 minutes at 90°C (CS2).

Tensile specimens were cut and milled from the cured plaques. Tensile strength, elongation and modulus were measured using ASTM procedure D-638M, using a crosshead speed of 0.13 cm/min.

T-peel measurements were made using ASTM procedure D-1876 using a crosshead speed of 25.4 cm/min. Two substrates were used: grit blasted 2024-T3 aluminum and electrogalvanized cold rolled steel with a nominal thickness of 0.76 mm (0.030 in)

Fracture energies were measured using two different procedures. The first was ASTM D-5045 using a compact tension specimen of dimensions of 25.4×31.75 mm machined from the 6 mm plaques. A saw cut is machined into the middle of one end of the specimen and a natural crack was made by using a fresh razor blade and tapping gently. Loading rate was 1.3 mm per minute. The second method used a double torsion (DT) geometry based on the procedures of Kies and Clark.[3] The loading rate was 1 mm per minute. Both methods measure the fracture toughness, K_{1c}, where I refers to mode one, i.e., opening mode, and c refers to the critical value. Equation (1) gives the relationship between K_{1c} and G_{1c}, the energy required to increase the crack by unit length in a specimen of unit width:

$$G_{1c} = K_{1c}^2 (1 - v^2)/E \qquad (1)$$

where E is the tensile modulus and v is Poisson's ratio.

Glass transition temperatures (T_g) were measured using a Mettler TA3000 DSC instrument with a scan rate of 20°C per minute using the second scan to determine the mid-point temperature of the transition (T_m) which is reported as the T_g. T_g was also determined using a Polymer Laboratories dynamic mechanical thermal analyzer at 1 Hz. Using this method, T_g is found using tan delta peaks from a rerun after the sample has been heated above T_g.

The dynamic mechanical analysis (DMA) was done using a DuPont Mechanical Analyzer, Model 983, using a 2/min ramp rate and a resonant frequency of 0.05 mm amplitude between -150°C and 200°C. Samples were cut from the cured plaques and were $38 \times 12.7 \times 6$ mm.

Morphologies of various systems were examined using a JEOL 840 scanning electron microscope (SEM). Transmission electron micrographs were made with a Zeiss CEM 902 and a JEOL 100SX TEM using OsO_4 staining.

3. RESULTS AND DISCUSSION

3.1 Addition of Elastomers to Unmodified and Elastomer-Modified Vinyl Ester Resins

Table I gives the recipes and tensile properties for cured systems with ETBN X40 combined with an unmodified vinyl ester resin (VER) using cure schedule 1 (CS1). From the data in Table I, one can see about a 7–8 fold increase in fracture energy from the unmodified resin using 15 phr of ETBN. Much of the increase in G_{1c} comes from a significant lowering of modulus by elastomer addition.

TABLE I

ETBN combined with Unmodified vinyl ester resin; Recipes & Properties, CS1

RECIPES	1	2	3	4
Unmodified VER	100	100	100	100
ETBN	0	7.5	10	15
Styrene	0	7.5	10	15
Cobalt Naphthenate	0.5	0.5	0.5	0.5
MEK Peroxide	2	2	2	2
Tensile Stg., MPa	42.1	47.4	47.7	33.9
Elongation, %	1.39	3.00	4.67	3.29
Modulus, GPa	3.29	2.22	1.82	1.61
K_{1c}—CT*, $MN/m^{3/2}$	0.63	1.08	1.24	1.20
G_{1c}—CT*, kJ/m^2	0.11	0.46	0.74	0.91
T_g—DSC, °C	119	120	119	121

* Determined from compact tension specimen

Table II gives the recipes and tensile properties for ETBN combined with elastomer-modified vinyl ester resin, again using cure schedule 1 (CS1). Even though less ETBN is used for the recipes in Table II the total rubber levels are comparable with those in Table I. The total rubber levels include the rubber in the elastomer-modified vinyl ester resin and the ETBN that is combined with this resin. Thus, Recipes 2, 3 & 4 in both Tables I & II have about the same total elastomer content, respectively.

There are two significant differences in results listed in Table I and II. The first is that fracture energy, G_{1c} for the dual method, i.e., reaction into and combination with the resin, is 2.08 kJ/m² at 13 phr of total rubber, 7.5 phr from the elastomer-modified vinyl ester resin and 5.5 phr of ETBN combined in the same resin, see Recipe 3, Table II. This value is about 20 times that of the unmodified vinyl ester, about six times that for the elastomer-modified vinyl ester and over two times that for ETBN addition to the unmodified vinyl ester resin. The second is that the dual method shows a much lower loss of modulus than does straight addition of rubber. About a 10°C lowering of the T_g was observed for the elastomer-modified vinyl ester resin over that for the unmodified

TABLE II

ETBN combined with Elastomer-modified vinyl ester resin; Recipes & Properties, CS1

RECIPES	1	2	3	4
E-modified VER	100	100	100	100
ETBN	0	3	5.5	8
Styrene	0	3	5.5	8
Cobalt Naphthenate	0.5	0.5	0.5	0.5
MEK Peroxide	2	2	2	2
Tensile Stg., MPa	64.1	49.7	43.9	37.8
Elongation, %	9.1	11	8.9	9.2
Modulus, GPa	2.94	2.48	2.21	2.22
K_{1c}—CT*, $MN/m^{3/2}$	1.0	2.04	2.23	2.22
G_{1c}—CT*, kJ/m^2	0.33	1.63	2.08	2.31
T_g—DSC, °C	110	109	110	109

* Determined from compact tension specimen

vinyl ester resin. No further lowering of the T_g was observed, by DSC, with ETBN combined with either vinyl ester.

Table III gives the recipes and tensile properties for VTBNX × 33 combined with elastomer-modified vinyl ester using cure schedule 2 (CS2). VTBNX combined with the elastomer-modified vinyl ester did not show as high a G_{1c} as did ETBN combined with the same resin. Modulus values are similar to those in Table II with the exception of Recipe 4, which shows a significant lower value and a corresponding reduction in T_g. T_g values, by DMTA are somewhat higher than those by DSC.

3.2 Dynamic Mechanical Analysis for ETBN Combined with an Elastomer-Modified and Unmodified DGEBA Vinyl Ester Resins

Dynamic mechanical testing is used to characterize viscoelastic properties of a polymer. Two components associated with viscoelasticity are the storage modulus and the loss modulus. Manzione and Gillham[4] used dynamic mechanical testing to show the presence of a second phase in rubber-modified epoxy resins.

Figure 1 is the DMA curve for the unmodified vinyl ester resin. Figures 2 & 3 are DMA curves for ETBN combined with the unmodified vinyl ester resins. Figure 1 shows a beta transition at $-67°C$ due to the epoxy resin portion of the vinyl ester resin and a T_g at 128.7°C for the cured resin. Figures 2 and 3 are for 5 and 10 phr of ETBN combined with the unmodified vinyl ester resin, respectively. The ETBN combined with the unmodified resin is readily detected by DMA as shown by elastomer T_g of $-19°C$ (5 phr) and $-17°C$ (10 phr) in Figures 2 and 3, respectively. These curves also show the rubber T_g of the resin portion and beta transitions at about $-66°C$. The elastomer T_g suggests that the dispersed phase contains a considerable amount of vinyl ester resin (since the T_g for ETBN should be about $-50°C$).

DMA curves for the elastomer-modified vinyl ester resin are quite different from the unmodified vinyl ester resin with and without ETBN. Figure 4 shows the DMA curve for the elastomer-modified vinyl ester resin. Even though this material contains 7.5 phr of elastomer, no rubbery T_g is detected. This is due to the very small particle size, ca. 0.013 μm, of the second phase in this resin, see Section 3.3 on morphology. As ETBN is

TABLE III
VTBNX combined with Elastomer-modified vinyl ester resin; Recipes & Properties, CS2

RECIPES	1	2	3	4
E-modified VER	100	100	100	100
VTBNX X33	0	3	5	7
Cobalt Naphthenate	0.5	0.5	0.5	0.5
MEK Peroxide	2	2	2	2
Tensile Stg., MPa	71.6	56.8	52.5	48.3
Elongation, %	5.8	12	20	14
Modulus, GPa	3.07	2.56	2.20	1.66
K_{1c}—DT*, MN/m$^{3/2}$	1.0	1.51	1.80	1.72
G_{1c}—GT*, kJ/m^2	0.34	0.77	1.16	1.14
T_g—DMTA, °C	124	120	121	117

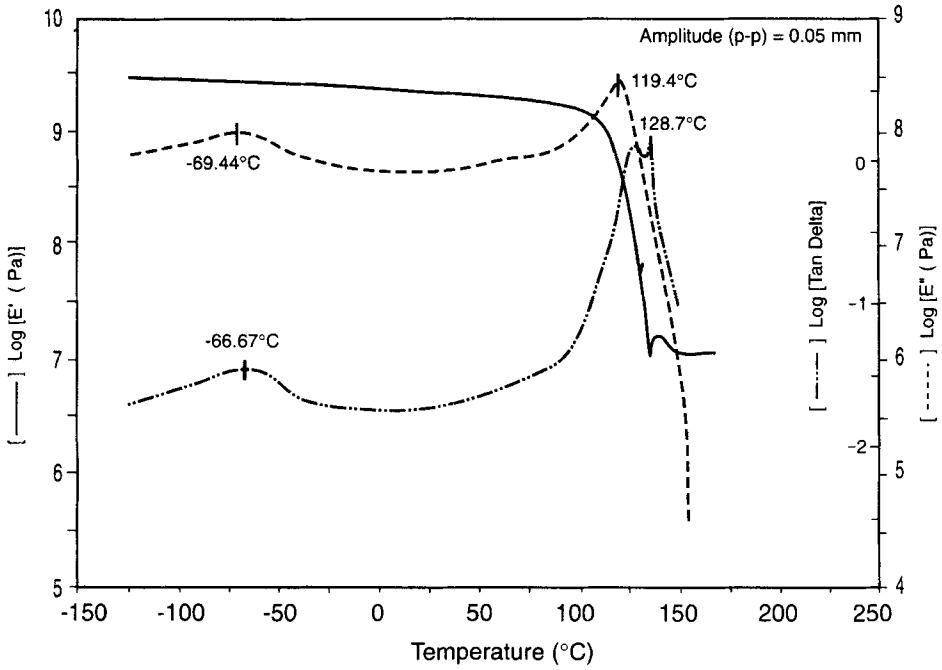* Determined from double tension specimen

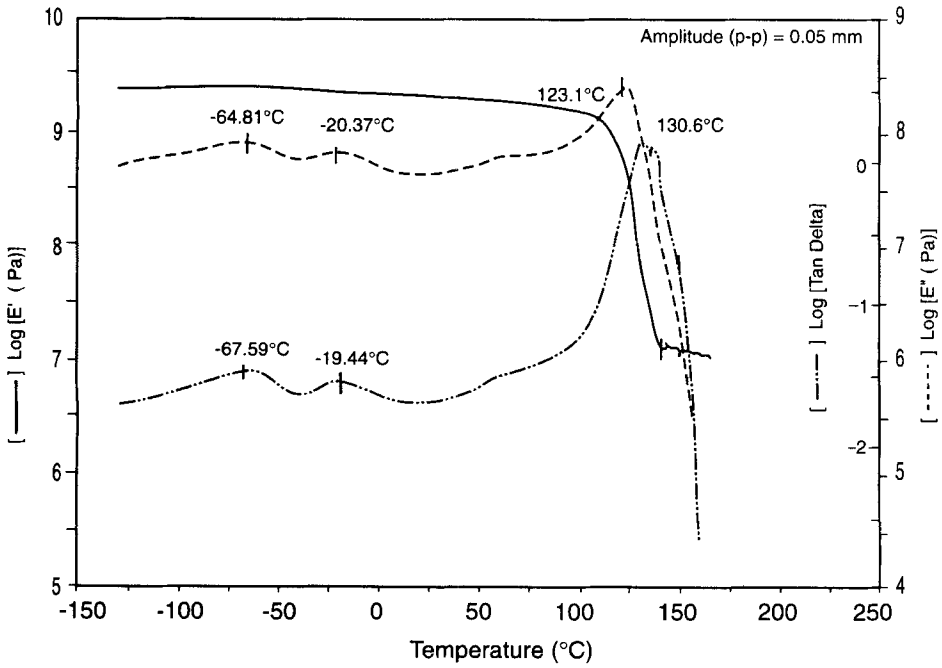FIGURE 1   DMA curves for unmodified vinyl ester resin.

FIGURE 2   DMA curves for ETBN (6.2 phr) combined with an unmodified vinyl ester resin.
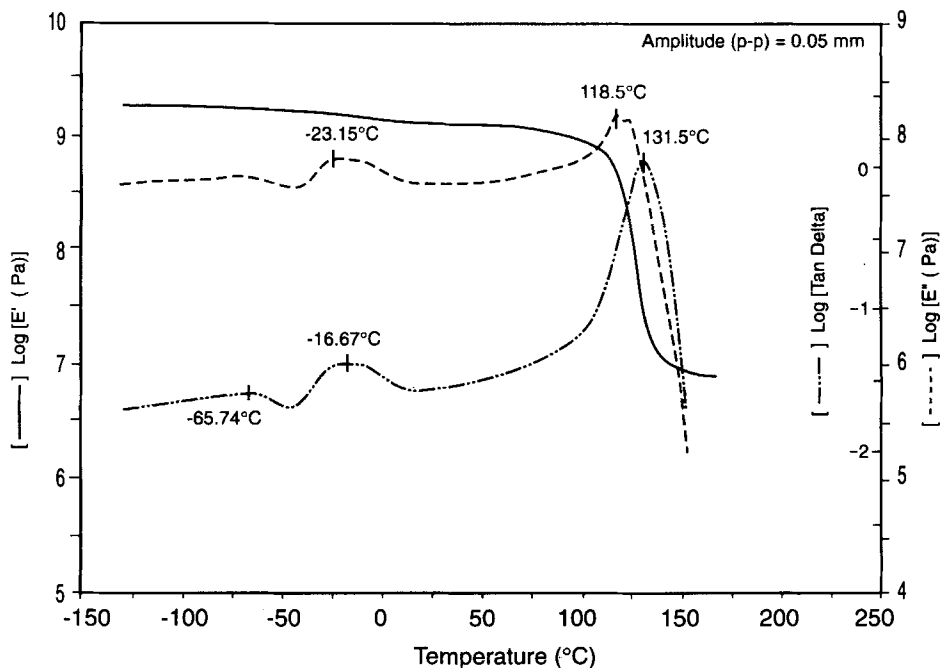
FIGURE 3   DMA curves for ETBN (8.3 phr) combined with an unmodified vinyl ester resin.
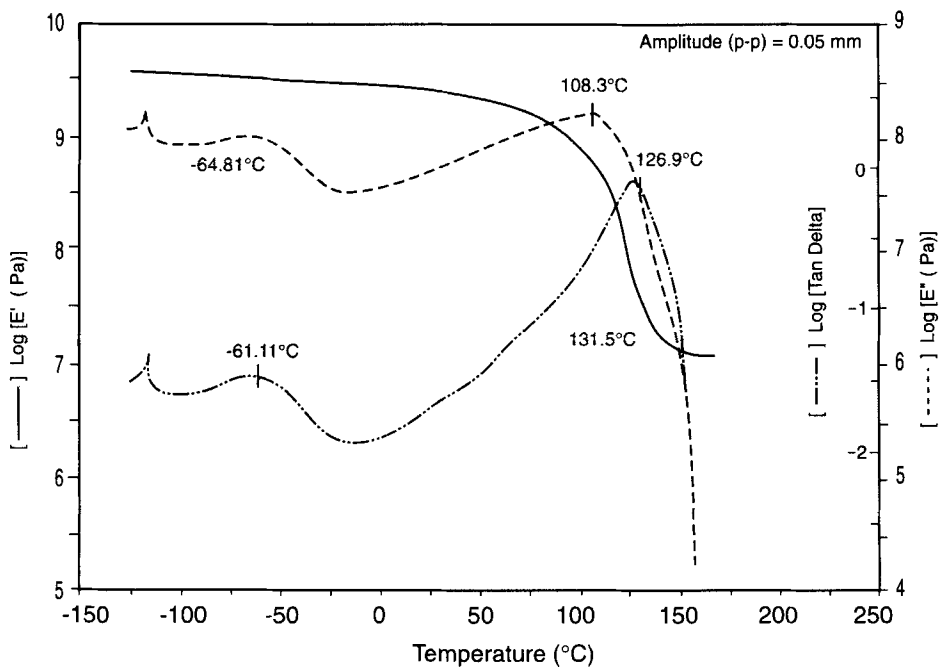
FIGURE 4   DMA curves for elastomer-modified (7.5 phr) vinyl ester resin.

combined with this vinyl ester resin no elastomer T_g is detected at 5 phr ETBN (12.5 phr of total elastomer concentration) as shown in Figure 5. The DMA curve for 6 phr of ETBN (13.5 phr total elastomer concentration) in Figure 6 does show a very small elastomer T_g at $-33°C$. This T_g suggests that it contains more rubber, less vinyl ester resin, than does the ETBN combined with the unmodified vinyl ester resin.

3.3 Morphology

There were notable morphological differences among the various cured vinyl ester compositions. When ETBN was combined with the unmodified vinyl ester, all the cured samples were opaque. As seen with previous elastomer-modified vinyl ester and polyester resins, this shows a dispersed rubber phase where rubber particles are too large for optimum toughness. For ETBN combined with elastomer-modified vinyl ester resin, the cured samples were more translucent, indicating a more ideally dispersed phase of under 1 μm. In addition, we observed a stress-whitened zone in the compact tension specimen. This is only found in systems that have a high degree of toughness, *i.e.*, a G_{1c} higher than about 1.0 kJ/m^2. Stress whitening was never observed in previous elastomer-modified vinyl ester or polyester resin studies.

Scanning electron micrographs of ETBN combined with an unmodified vinyl ester were taken from the fracture surface of the compact tension specimens. Usually, the
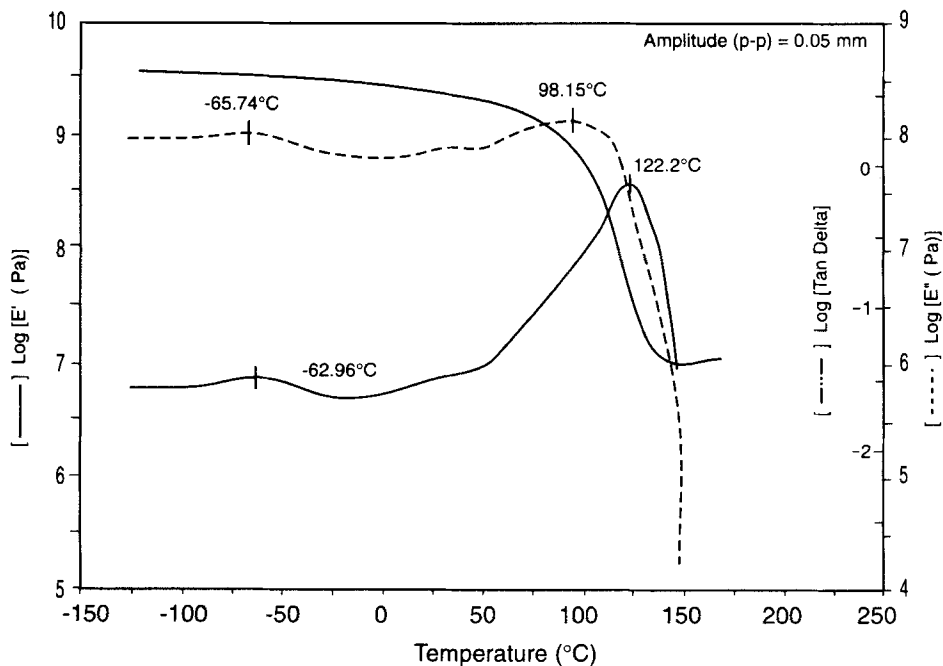
FIGURE 5   DMA curves for ETBN combined with an elastomer-modified (11.7 phr) vinyl ester resin.
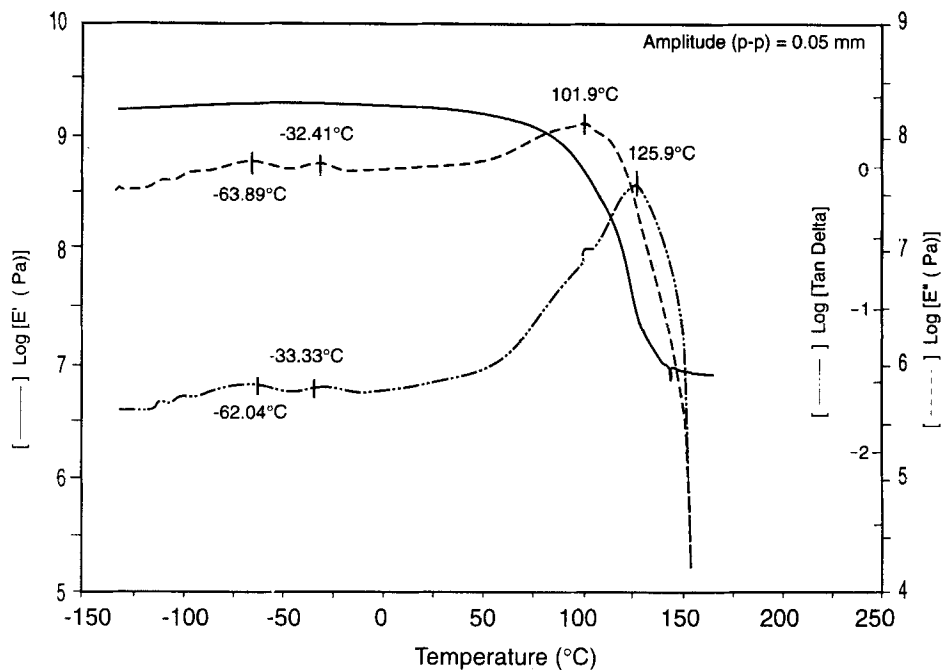
FIGURE 6 DMA curves for ETBN combined with an elastomer-modified (13.7 phr) vinyl ester resin.

micrograph is taken in the slow propagation or initiation areas. This enables one to form some idea of the failure mechanisms occurring in these materials. Figures 7, 8 and 9 show SEM micrographs for Recipes 2, 3 and 4 (Table I). Figure 7 shows particles in the range of 10–33 μm with a nodular interior. Figure 8 shows a particle size range of
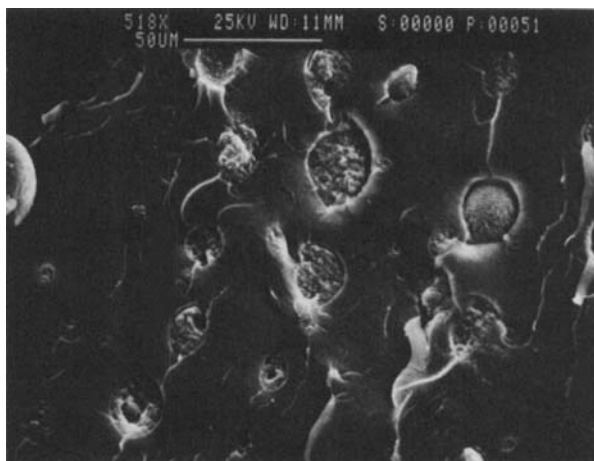

FIGURE 7 SEM micrographs for ETBN (6.2 phr) combined with an unmodified vinyl ester resin.

FIGURE 8   SEM micrographs for ETBN (8.3 phr) combined with an unmodified vinyl ester resin.

10–43μm. There are numerous empty cavities and intact particles, indicating low adhesion between particles and the continuous phase. Where the crack had gone through the particles, there was relatively little deformation of the particles. However, the continuous phase showed more deformation than shown in Figure 7. Figure 9 has a particle size range of 33–64 μm. The particle interior went from nodular to granular.

The SEM micrograph for Recipe 1, Table II, shows no dispersed particles. Figures 10, 11 and 12 are SEM micrographs for Recipes 2, 3 & 4, respectively (Table II for
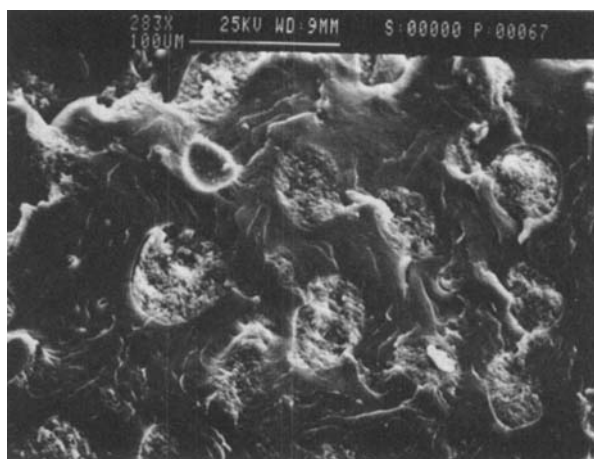

FIGURE 9   SEM micrographs for ETBN (12.5 phr) combined with an unmodified vinyl ester resin.

ETBN combined with an elastomer-modified vinyl ester resin). Figure 10 shows small particles with a granular interior, 1–2 μm. There are also numerous small holes of about 0.5 μm in the continuous phase. Figure 11 shows particles similar to Figure 10 with a larger ranger of particle size 4–25 μm. They also show the small holes. Figure 12 has a particle size range of 20–50 μm with the numerous small holes of about 1 μm diameter. These micrographs all show small holes, presumbly formed by dilation of small particles. They are evident in the continuous phase and they increase in size with increasing ETBN concentration. The large particles increased in size with increasing ETBN concentration but their density decreased. Also evident from these micrographs
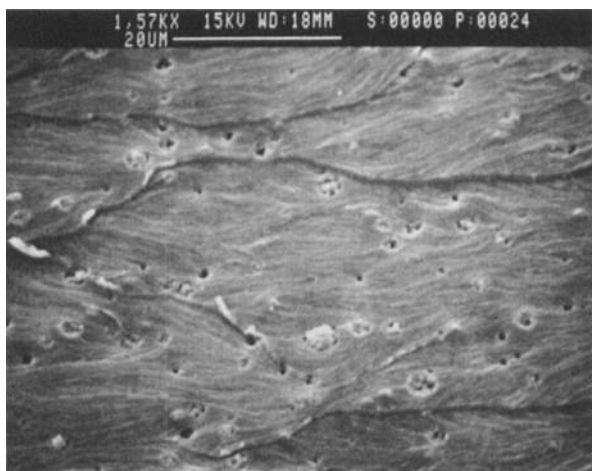

FIGURE 10   SEM micrographs for ETBN combined with an elastomer-modified (10 phr) vinyl ester resin.
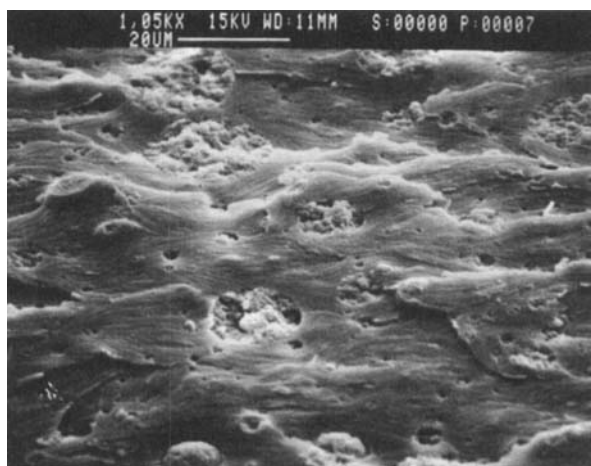

FIGURE 11   SEM micrographs for ETBN combined with an elastomer-modified (12.1 phr) vinyl ester resin.
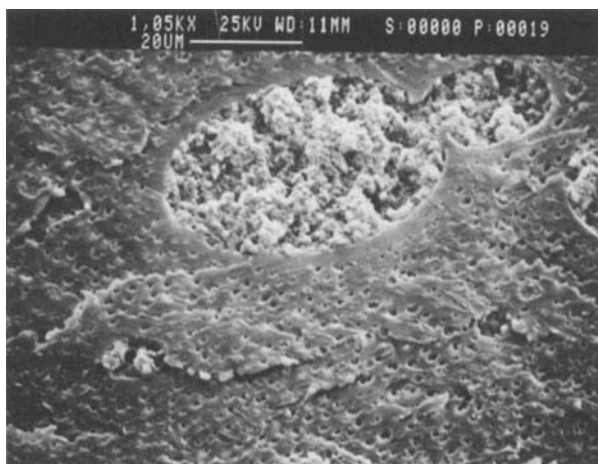
FIGURE 12   SEM micrographs for ETBN combined with an elastomer-modified (14.2 phr) vinyl ester resin.

is the large amount of flow in the matrix due to the presence of small particles. (See *e.g.*, Figure 11).

The SEM micrographs for VTBNX combined with the elastomer-modified vinyl ester resin also show no discernable second phase.

Figure 13 is a TEM micrograph of an OsO_4-stained specimen, at 20,000X, for the elastomer-modified vinyl ester, Recipe 1, Table II. This micrograph shows the presence of very small rubbery particles of about 0.03 μm. This sample is visually clear. Figure 14 is a TEM micrograph of an OsO_4-stained specimen at 20,000X, for Recipe 2, Table II, for ETBN combined with an elastomer-modified vinyl ester resin. This micrograph also shows very small particles, less than 0.10 μm; however, they are larger than those
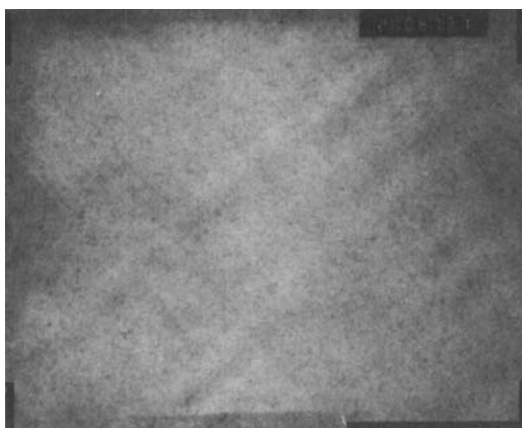

FIGURE 13 OsO_4-stained TEM micrograph (20,000X) of elastomer-modified (7.5 phr) vinyl ester resin.
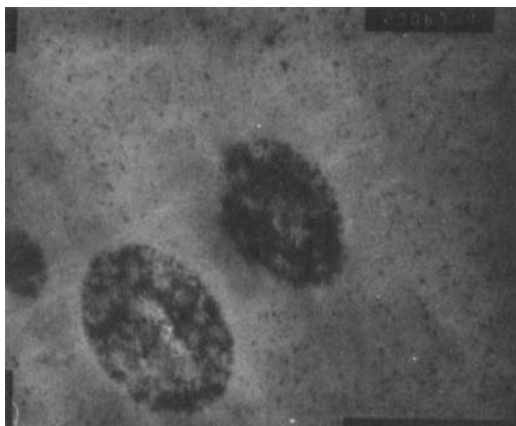
FIGURE 14 OsO_4-stained TEM micrograph (20,000X) for ETBN combined with an elastomer-modified (12.1 phr) vinyl ester resin.

from Figure 13. This TEM micrograph also shows larger elongated particles, of about 1–2 μm. In addition, the larger particles show the presence of both elastomer and resin. Thus, the elastomer is used much more effectively in this system. The dual method gives much smaller particles than does the addition method.

3.4   Effects of Cure Temperature on Addition of ETBN to an Elastomer-Modified Vinyl Ester Resin

Table IV gives the recipes and data for ETBN combined with an elastomer-modified vinyl ester resin with two different cure schedules. Recipe 1 was gelled at room temperature followed by two hours at 120° C. Recipe 2 was gelled and cured at room temperature for seven days. Recipes 1 & 2 in Table IV can be compared with Recipe 3

TABLE IV

Effect of cure temperature for ETBN combined with
an elastomer-modified vinyl ester resin

RECIPES	1	2
E-modified VER	100	100
ETBN	5	5
Styrene	5	5
Cobalt Naphthenate	0.5	0.5
MEK Peroxide	2	2
Tensile Stg., MPà	48.0	42.5
Elongation, %	10.5	19.3
Modulus. GPa	2.30	2.18
K_{1c}—CT*, MN/m$^{3/2}$	2.16	1.88
G_{1c}—CT*, kJ/m^2	1.80	1.44
T_g—DSC, °C	106	102

* Determined from compact tension specimen

in Table II as they all contain about the same amount of elastomer, 5 phr and 5.5 phr of ETBN, respectively. The recipe cured at room temperature gives the lowest G_{1c} value of 1.44 J/m² compared with a value of 2.08 J/m² for the all-heat-cured recipe. However, this is still a very high G_{1c} when compared with the data from Table I for the addition method.

3.5   Addition of ETBN to Blends of Elastomer-Modified and Epoxy Novolac vinyl Ester Resins

Since there is no commercially by-available elastomer-modified epoxy novolac vinyl ester resin, we combined ETBN with blends of the elastomer-modified vinyl ester with an unmodified epoxy novolac vinyl ester. Table V gives recipes and data for an elastomer-modified/novolac vinyl ester blends with 5 phr of ETBN. While the amount of ETBN used in the above recipes was constant, the total elastomer level increases as the amount of the elastomer-modified vinyl ester is increased. However, the same trend is found in these data; that is, the use of rubber reacted into the resin, as well as combined rubber, gives the highest fracture energy and an increase in T_g.

3.6   Adhesive Properties

T-peel values for VTBNX combined with elastomer-modified vinyl ester resin, measured on grit-blasted aluminum and on acetone-washed electrogalvanized steel, are given in Table VI. A significant increase in peel strength over that for the elastomer-modified vinyl ester resin, is found with 5 and 10 phr of VTBNX on both metal substrates.

For 5 phr of VTBNX we found a lap shear value of 35.6 MPa (5170 psi) compared with a lap shear strength for the control elastomer-modified vinyl ester of 27 MPa (3920 psi). Lap shear measurements were not made on electrogalvanized steel.

TABLE V

ETBN combined with Blends of Elastomer-modified and unmodified Novolac vinyl ester resins, CS2

RECIPES	1	2	3	4
E-modified VER	0	40	60	80
Unmod. Novolac VER	100	60	40	20
ETBN	5	5	5	5
Cobalt Naphthenate	0.5	0.5	0.5	0.5
MEK Peroxide	2	2	2	2
K_{1c}—DT*, MN/m³ᐟ²	0.75	1.33	1.44	2.52
G_{1c}—DT*, kJ/m²	0.13	0.36	0.60	2.09
T_g—DMTA, °C	148	142	133	127

* Determined from double tension specimen

TABLE VI
Elastomer-modified vinyl ester resin with VTBNX and ETBN
additions; T-peel Properties

Amount	VTBNX Grit-blasted Aluminum		ETBN Electrogalvanized Steel	
	N/25.4 mm	1bs./in.	N/25.4 mm	1bs./in.
0	23	5	18	4
5	73	16	64	14
10	81	18	78	17
15	67	15	NM	NM

4. CONCLUSIONS

The very small elastomeric particles shown in the TEM micrograph suggest that the combined ETBN is associating with CTBN reacted into the backbone of the vinyl ester resin. This is also suggested from the DMA results, in that no T_g is found when ETBN is combined with the elastomer-modified vinyl ester resin until about 6 phr ETBN. Thus, the dual method appears to provide a way to control the morphology of elastomer-modified-vinyl ester resin systems, *i.e.*, this method eliminates the very large particles associated with the addition of reactive elastomers to the unmodified resins.

Adhesive and bulk fracture properties of elastomer-modified vinyl esters which are further modified with an epoxy-terminated liquid nitrile rubber (ETBN) or a methacrylated-vinyl terminated liquid nitrile rubber (VTBNX) are greatly enhanced, permitting feasibility of structural adhesive development. Large areas of stress whitening are observed on the surface of the tested compact tension specimen. Additive tougheners greatly alter cured specimen morphology providing clues to toughness enhancement.

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