

The Mechanical Properties of Rubber-Modified Vinyl Esters

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Synopsis

"Vinyl esters" were prepared by reacting an epoxy resin (DGEBA) with acrylic and methacrylic acids, modified with Hycar VTBN, and cured at 90°C for 4 h with *t*-butyl perbenzoate. The resultant materials showed a two-phase structure in electron micrographs and dynamic mechanical spectra. The domain of the dispersed phase was estimated to be on the order of 10 nm in size. Infrared spectroscopy indicated extensive copolymerization of the internal double bonds or pendant vinyl groups in VTBN during the cure of the resin. The mechanical properties of the modified materials were measured, and the differences in mechanical behavior between the acrylic and methacrylic vinyl esters were discussed.

INTRODUCTION

"Vinyl esters" are the reaction products of an epoxy resin, usually a diglycidyl ether of bisphenol A (DGEBA), and an unsaturated carboxylic acid, such as acrylic or methacrylic acid.¹⁻³ The products can be cured thermally with free radical initiators, or by irradiation with ultraviolet (UV), electron beams, and so on. Thus, vinyl esters, while retaining the properties of the epoxies, have a workability and curing characteristics of the unsaturated polyesters. This extends the applicability of the epoxy resins. However, the conversion of an epoxy group into a vinyl group produces a tetra functional vinyl ester from a bifunctional epoxy resin. Therefore, vinyl esters yield highly cross-linked, rigid thermosets.

The use of reactive liquid rubbers, for example, the carboxyl- and amine-terminated polybutadiene and its copolymers, as impact modifiers in epoxy resins have been studied extensively.⁴⁻¹⁸ These reactive rubbers, while miscible with the epoxy resins in the liquid state, are separated into a discrete phase upon cure with the formation of a rubber particle-filled composite which shows a markedly improved toughness. This paper describes the modification of the vinyl esters with a vinyl-terminated poly(butadiene-coacrylonitrile), Hycar VTBN.

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EXPERIMENTAL

Preparation of Vinyl Esters

A 4-L resin kettle equipped with a stirrer, a condenser, and a thermometer was charged with 2000 g of an epoxy resin (DGEMA, epoxy equivalent wt. = 191.5), 900 g of methacrylic acid, 15 g of trimethyl-benzylammonium chloride, and 0.3 g each of quinone and hydroquinone. The reactor was heated to 100°C. After the initiation of the reaction, the heating mantle was removed, and the reactor was cooled with an electric fan to maintain the temperature at approximately 115°C. The reaction was followed by acid number determination in 30-min intervals.

The acrylic ester was similarly prepared with equivalent amounts of acrylic acid and the epoxy resin.

Characterization of the Vinyl Esters and VTBN

In addition to the acid number determination, the prepared vinyl esters were characterized by infrared (Perkin-Elmer Model 567) and near infrared (Beckmann DK-2) spectroscopy. The terminal vinyl group in VTBN (Hycar VTBNX 1300 × 23, B. F. Goodrich Company) was characterized by nuclear magnetic resonance (NMR) spectroscopy, used a C-60 HL spectrometer (JEOL).

Specimen Preparation

A total of 700 g of the vinyl ester and VTBN in varied proportions, 0.07 g each of quinone and hydroquinone were heated to 90°C with stirring. After the resin mix was cooled to 60°C, 7 g of *t*-butyl perbenzoate was added. The well-mixed resin was poured into a mold 23 × 23 × 0.3 cm, degassed at 70°C, then cured at 90°C for 4 h, followed by a postcure at 120°C for 2 h. Testing specimens were prepared to ASTM specifications with a contour cutter.

The curing reaction was studied by infrared spectroscopy with thin films cast on sodium chloride disks and cured under the specified conditions.

Electron Microscopy

Specimens of ca. 70 nm in thickness were stained with a 1% aqueous solution of osmium tetroxide for 15 min. Micrographs were obtained with a JEM-100B (JEOL) transmission electron microscope.

Dynamic Mechanical Spectroscopy

Dynamic mechanical spectra were obtained from a rheometric dynamic spectrometer (Rheometric Inc.) on the torsion-rectangular mode in the temperature range of -160°C to 240°C at a frequency of 0.1 Hz.

Mechanical Testing

The tensile and flexural strength were measured according to ASTM D638 and D790, respectively. Impact strength was measured according to ASTM D256 with unnotched specimen. Heat deflection temperature was measured

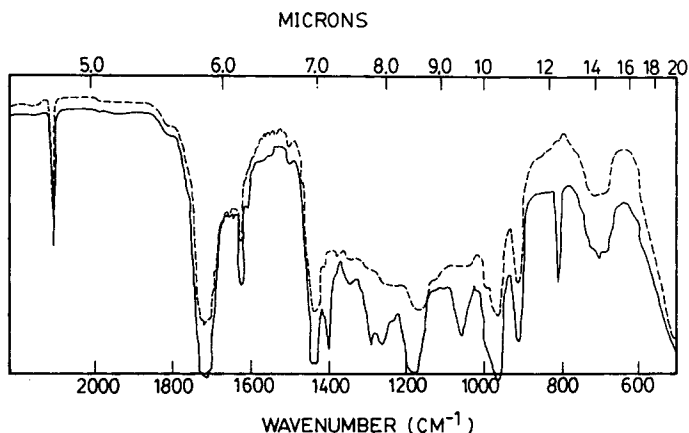


Fig. 1. Infrared absorption spectra of Hycar VTBNX 1300 × 23 (—) before cure; (---) after cure.

according to ASTM D648 under a load of 264 psi. Hardness was measured according to ASTM D2240 with a Shore D durometer.

RESULTS AND DISCUSSION

Characterization of Vinyl Esters and VTBN

The reaction between acrylic acid and DGEBA was followed by determining the acid number of the reactant, which was reduced to a value of 4.3–4.5 in 5 h, corresponding to a 98% completion of reaction based on the amount of the acid used. In addition, the prepared vinyl esters were further characterized by near infrared spectroscopy in which the epoxy functional group showed an absorption peak at $1.65 \mu\text{m}$.¹⁹ This peak completely disappeared in the spectra of the vinyl esters.

The terminal vinyl group in Hycar VTBNX was characterized as the acrylate by NMR spectroscopy. The signals of the three protons attached to the acrylic double bond occurred at 5.79, 6.14, and 6.37 ppm, same as the signals from the acrylic vinyl ester.

Polymerization of Vinyl Esters and VTBN

The polymerization of the vinyl esters and VTBN under the specified curing conditions was investigated by infrared spectroscopy. Figure 1 shows the spectra of VTBN taken before and after the cure of the resin on sodium chloride disks. A comparison of the spectra showed the disappearance of the absorption peak at 810 cm^{-1} in the spectrum of the cured sample. This peak was derived from a C—H bending vibration of the acrylic double bond.²⁰ Its disappearance indicated that the double bonds were polymerized. On the other hand, the spectra of cured acrylic and methacrylic vinyl esters, given in Figures 2 and 3, showed residual peaks or shoulders at 810 cm^{-1} and 1630 cm^{-1} , indicating the presence of residual double bonds from incomplete reaction. These results may be expected from a glass effect of the cured resin.

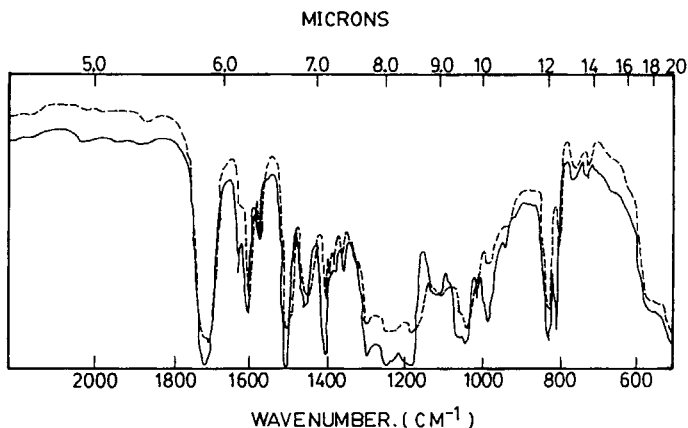


Fig. 2. Infrared absorption spectra of acrylic vinyl ester (—) before cure; (---) after cure.

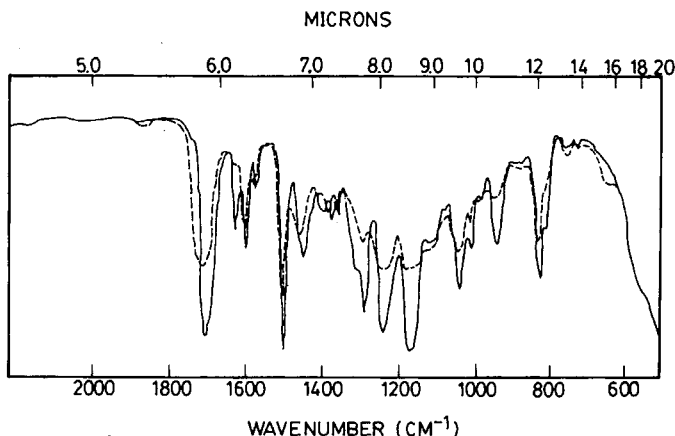


Fig. 3. Infrared absorption spectra of methacrylic vinyl ester (—) before cure; (---) after cure.

The absorption peak at 1630 cm^{-1} in Figure 1 was derived from both the acrylic double bonds and the olefinic double bonds in VTBN. Using relative intensities of the nitrile group at 2240 cm^{-1} as a reference, the absorption intensity of this peak was reduced almost by one third during the cure of the resin. Since the acrylic double bonds constituted only 3.8% of the total double bonds in VTBN, this result indicated an extensive copolymerization of the internal double bonds or pendant vinyl groups in VTBN during the process of cure.

Morphology

Discrete domains of VTBN can be discerned in the electron micrographs of the modified vinyl esters shown in Figure 4. The size of the rubber particles was estimated on the order of 10 nm in diameter which was too small for optimal results in toughness improvement.^{21,22} Smith²³ has shown that in multicomponent cross-linked polymers, the domain sizes of the dispersed phase are small, typically in the range of 20–100 nm, due to a restriction on

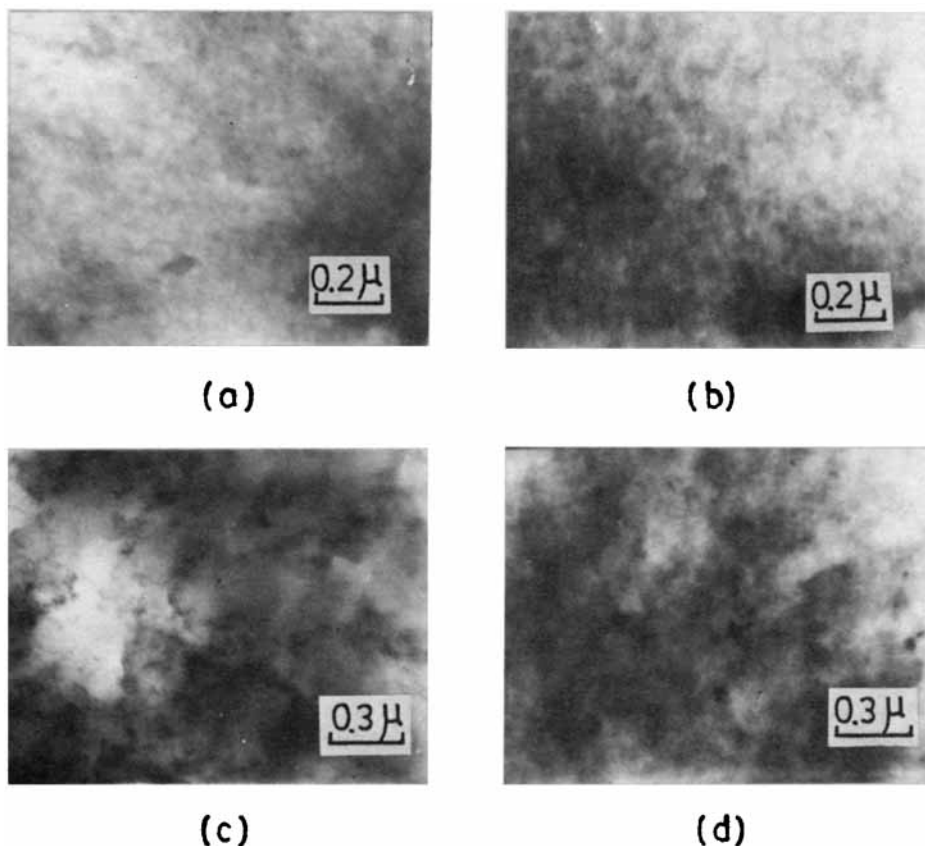


Fig. 4. Electron micrographs of VTBN-modified vinyl ester. (a) acrylic vinyl ester with 5 phr VTBN; (b) acrylic vinyl ester with 15 phr VTBN; (c) methacrylic vinyl ester with 5 phr VTBN; (d) methacrylic vinyl ester with 15 phr VTBN.

the mobility of the rubber chains by the crosslinks formed during the phase separation. In the present systems, both the vinyl esters and VTBN were tetrafunctional. The mixed resin gelled at an early stage of reaction. This prevented the aggregation of the rubber molecules into large domains. In this respect, the present results are similar to that of ATBN, an amine-terminated poly(butadiene-co-acrylonitrile), modified epoxy resin. The rubber particles formed in the latter system were limited to a size of ca. 20 nm.²⁴

Dynamic Mechanical Properties

The dynamic mechanical properties of the modified methacrylic vinyl esters were measured with a rheometric dynamic spectrometer in the temperature range of -160°C to 240°C . The results are shown in Figures 5 through 7 for the storage modulus, loss modulus, and loss tangent, respectively. The spectra of the cured methacrylic vinyl ester showed three distinct transition regions. One occurred around -90°C , possibly from the β -relaxation of the epoxy unit.²⁵ One occurred around 160°C from the main polymethacrylate chains. The remaining one occurred around 80°C , possibly from the ester side groups.

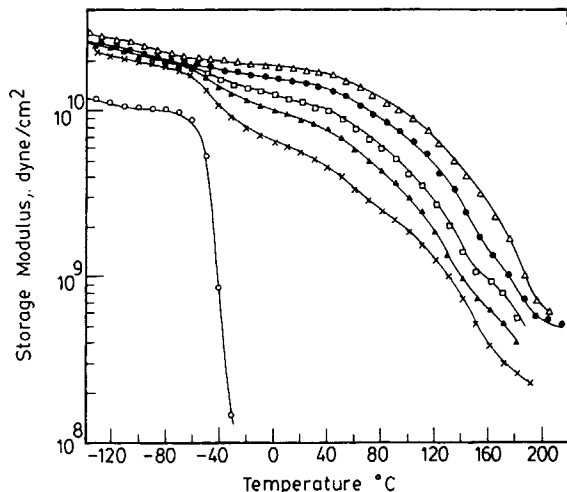


Fig. 5. Storage modulus of VTBN-modified methacrylic vinyl ester; (Δ) methacrylic vinyl ester; (\bullet) MVE + 10 phr VTBN; (\square) MVE + 20 phr VTBN; (\blacktriangle) MVE + 30 phr VTBN; (\times) MVE + 50 phr VTBN; (\circ) VTBN.

On the other hand, cured VTBN showed a single transition at -37°C from the loss tangent. The transition peaks of both components were retained in the spectra of VTBN-modified vinyl ester sample, a confirmation of phase separation between the components.

The transition temperature of the rubber phase is, in general, raised to a higher temperature due to a restriction on the motion of the rubber molecules in a glassy matrix. In the present systems, the transition temperature of the rubber phase was lowered from a value of -37°C to values of -45° to -50° in samples containing 50 phr and 30 phr of VTBN, respectively (cf. Fig. 7). These results could be attributed to a difference in cross-linking density in the

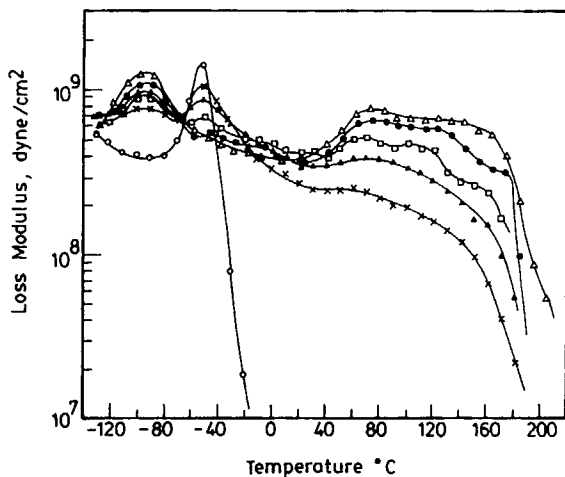


Fig. 6. Loss modulus of VTBN-modified methacrylic vinyl ester. Notations as in Fig. 5.

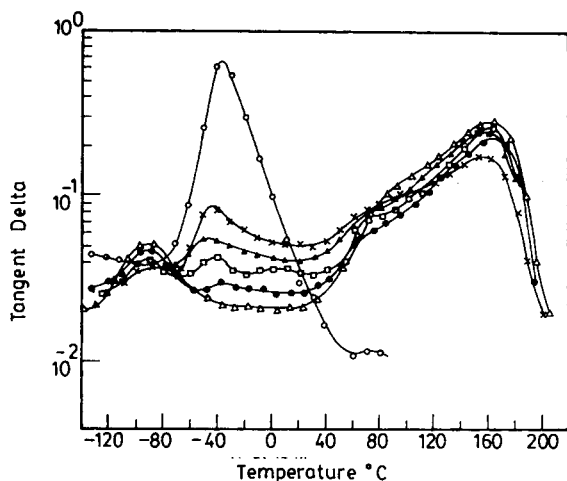


Fig. 7. Tangent delta of VTBN-modified methacrylic vinyl ester. Notations as in Fig 5.

rubber phase. As described earlier, infrared spectroscopy gave evidence of extensive copolymerization of the olefinic double bonds in VTBN during the cure of the resin. However, the chance of copolymerization of these double bonds was progressively diminished in the presence of an increased amount of methacrylic double bonds due to a significant difference in reactivity between them. This would yield a less cross-linked rubber phase with a lower transition temperature at reduced concentrations of VTBN. On the other hand, the effect of the glassy matrix on the motion of the rubber molecules became dominant at low VTBN content, and the transition temperature of the rubber phase was again raised as shown from the experimental results in Figure 7.

Mechanical Properties

The tensile strength of the vinyl esters in Figure 8 showed an increase upon incorporation of VTBN, and reached a maximum at approximately 10 phr of

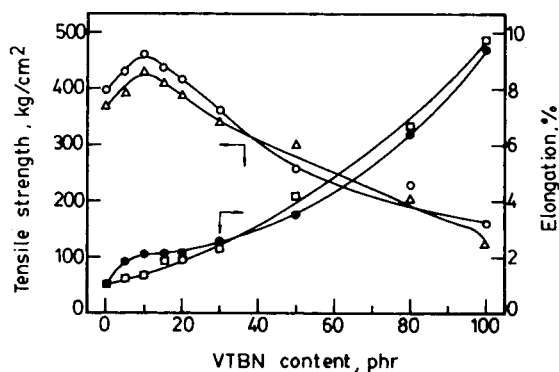


Fig. 8. Tensile strength and elongation of VTBN-modified vinyl esters; ($-\Delta-$) and ($-\square-$) for the methacrylic vinyl esters; ($-\circ-$) and ($-\bullet-$) for the acrylic vinyl esters.

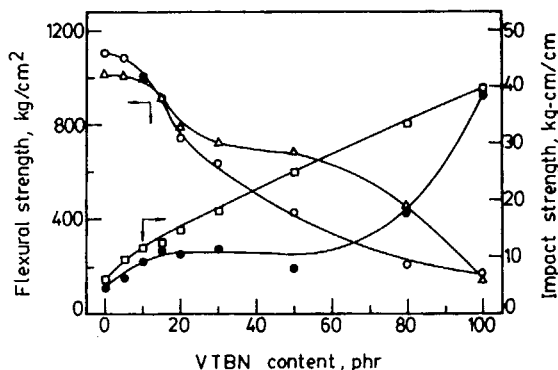


Fig. 9. Flexural strength and impact strength of VTBN-modified methacrylic vinyl ester. Notations as in Fig. 8.

VTBN with a 15% increase in value. Such results were observed in polymer blends with good compatibility.²⁶ In the present systems, both the vinyl esters and VTBN had a calculated solubility parameter of 9.6. A limited miscibility between the components might be expected even though the systems were not compatible.

Both vinyl esters had low extensibility with an elongation of 1.1% at break. This value was increased by the addition of the rubbery VTBN, and the results from the two vinyl esters were very similar over a wide range of compositions. Except at low VTBN content, the acrylic vinyl ester showed a more pronounced increment in extensibility than the methacrylic vinyl ester did.

Figure 9 shows the flexural strength and impact strength of the modified vinyl esters. The results revealed some significant differences in mechanical behavior between them. While the flexural strength of the methacrylic vinyl ester remained unchanged up to a VTBN content of 10 phr, that of the acrylic vinyl ester was reduced progressively with the amount of VTBN added. The impact strength of both vinyl esters was increased by two- to threefold with the addition of VTBN up to 10–15 phr. Beyond that, the two vinyl esters gave entirely different results. The methacrylic series showed a continued increase in impact strength with an increased amount of VTBN, whereas the acrylic series showed no change in the range from 15 to perhaps 60 phr of VTBN. At a VTBN content of 100 phr, the flexural strength and impact strength, together with heat deflection temperature shown below, of both vinyl esters became the same. These results signified a phase inversion in the systems since VTBN, being lighter in density, became the major component by volume.

The hardness of both vinyl esters given in Figure 10 was almost the same, and the values were not seriously affected by the addition of the rubber component, especially at low VTBN contents. On the other hand, the heat deflection temperature (HDT) of the methacrylic vinyl ester was 25–30°C higher than that of the corresponding acrylic vinyl ester with or without VTBN modification. Until the rubber content reached 100 phr, the HDT of both vinyl esters became nearly the same due to a possible phase inversion as mentioned above.

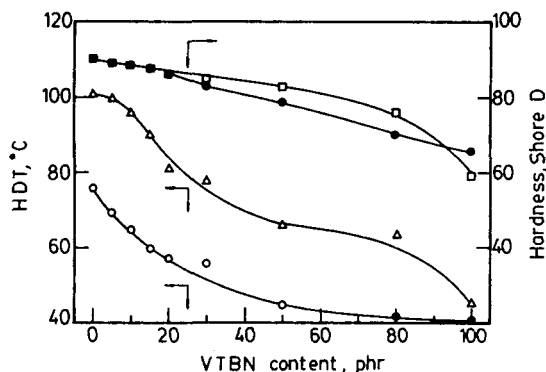


Fig. 10. Heat deflection temperature and hardness of VTBN-modified methacrylic vinyl ester. Notations as in Fig. 8.

In contrast to the results obtained from the methacrylic vinyl ester, the addition of a small amount of VTBN to the acrylic vinyl ester caused a sharp reduction in heat deflection temperature and increase in elongation. These results suggested a partial miscibility between the components in the latter system. The added VTBN produced a "softening" effect in the acrylic resin.

In conclusion, modification of the vinyl esters with VTBN gave a moderate improvement in toughness. This result was limited by the size of the rubber domains formed in the cross-linked resin. In terms of the thermal and mechanical properties, better results were obtained from the methacrylic vinyl ester. For instance, by the addition of say 10 phr VTBN, a 15% increase in tensile strength and a two- to threefold increase in impact strength can be achieved without changes in other properties.

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