

Morphology of Rubber-Modified Vinyl Ester Resins Cured at Different Temperatures

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ABSTRACT: The morphologies of styrene (St) crosslinked divinylester resins (DVER) modified with elastomers were analyzed. The primary focus of this study was on the effect of the molecular weight of the resins, the reactivity of the elastomeric modifiers, and the temperature of curing. All of these variables have a strong influence on both the miscibility and the viscosity of the system, affecting the phase-separation process that takes place in the unreacted and the reacting mixture. The selected liquid rubbers were carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN), a common toughening agent for epoxy resins, and an almost unreactive rubber with the DVER; and St comonomers and vinyl-terminated poly(butadiene-*co*-acrylonitrile) (VTBN), a reactive rubber. Different morphologies potentially appear

in these systems: structures formed by DVER–St nodules surrounded by elastomer and spanning the whole sample; dual cocontinuous micron-size domains formed by elastomer-rich or resin-rich domains; and a continuous DVER–St-rich phase with included complex nodular domains. These microstructures can be varied by just changing the nature and concentration of the elastomer, the molecular weight of the resin, or the curing temperature. The appearance of these morphologies is discussed as a function of the above variables. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 274–283, 2003

Key words: elastomers; modified vinyl ester resins; morphology; curing temperature; crosslinking

INTRODUCTION

Modification and toughening of thermoset epoxy resins by the addition of elastomeric modifiers has been widely reported in the literature.^{1–6} On the other hand, modified unsaturated polyesters (UPR) and divinyl ester resins (DVER) have been less studied, although some studies on UPR results are available in the literature and a few publications can also be found on modified DVER.^{7–12} These modifications have been carried out using different elastomeric additives with different degrees of initial miscibility, with the objective of controlling shrinkage during curing and/or obtaining some toughening in the final materials.

To control the volumetric contraction (shrinkage) in UPR–styrene (St) systems, low-profile additives (LPA) have been used.^{13,14} In this case, the final morphologies are totally different. The systems can be homogeneous or heterogeneous at the beginning of the reaction, depending on the initial miscibility.¹⁰ In any case, as the reaction advances, the formed copolymer, UPR–St, becomes partially miscible in the mixture and begins to separate, forming nodules in whose interior the density of crosslinking increases quickly. At the same time that the UPR and the St react, the monomeric

phase becomes rich in the liquid elastomer. Depending on the initial miscibility or partial miscibility of the system, at the end of the curing reaction, the material is constituted by one or two regions, one region presenting a cocontinuous structure of UPR–St nodules surrounded by elastomer, or two regions with UPR–St copolymer-rich domains, and complex elastomer-rich domains. Finally, because of the different volume shrinkage of the phases during the curing, microvoids are formed in the particulated domains. The compensation of the volumetric contraction of the cured resin takes place at the cost of the formation of these cavities.^{12,15,16} In the case of modified DVER–St systems, even fewer studies have been published.^{12,17–20} The final morphologies are quite similar to those described for modified UPR, and one- or two-region morphologies are possible.

Some reports on the effect of the temperature of curing can be found for LPA-modified UPR–St systems. Li et al.²¹ reported on the volume control of LPA-modified UPR cured at 35, 55, and 80°C and found a correlation between final morphologies and dilatometric measurements. Kinkelaar et al.²² reported on the reduction of the size of the resin–St globules at increasing heating rates during curing. The morphologies were related to the fracture properties of the materials. If continuous UPR–St with complex thermoplastic inclusions is the overall morphology, the materials are tougher than the unmodified resins. When the morphology corresponds to a cocontinuous particulated structure, the best volume

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TABLE I
Molecular Weight Characterization of the Resins and Elastomers Used in This Study

Variable	DVER L Synthesized	DVER C Commercial	CTBN 1300 × 8	VTBN ×33
M_n (g/mol)	583	1015	3600	3600
M_w (g/mol)	606	1766	6501	6498
M_w/M_n	1.04	1.74	1.81	1.81

control is obtained together with a large decrease in the toughness of the material. On the other hand, Huang et al.²³ presented results on the effect of the enhanced interaction between a polyurethane and UPR–St compared to polyvinylacetate–UPR–St. A microstructure with smaller size globules and a stronger interface was obtained because of the improved compatibility of the system. Thus, a strong correlation was observed to exist between the observed morphologies and the final properties of the materials.

In particular, a complete thermodynamic study of an unreacted low molecular weight DVER–St–elastomer system was previously presented by the authors,²⁴ whereas the results of the mechanical and fracture prop-

erties of these materials were discussed in other study.¹² In the present work, the study has mainly focused in the effect of the curing temperature on the final morphology of the materials, which is expected to have a profound effect on properties of the materials. The morphology variations obtained by modifying other variables, such as molecular weight of the resin and nature and concentration of the elastomer, are also discussed.

EXPERIMENTAL

Materials and sample preparation

Two divinylester resins of different molecular weight, DVERL and DVERC, were used. DVERL was synthesized by reacting an epoxy resin, diglicidyl ether of bisphenol A (DGEBA MY 790, equivalent weight 176.2 g/eq; Ciba-Geigy, Summit, NJ) with methacrylic acid (laboratory-grade reagent; Norent Plast S.A., Buenos Aires, Argentina) using triphenylphosphine as catalyst (analytical reagent; Fluka Chemie, Buchs, Switzerland). The final conversion was higher than 93% and the resin was stabilized with 300 ppm of hydroquinone. DVERC is a commercial resin (PALATAL A 430;

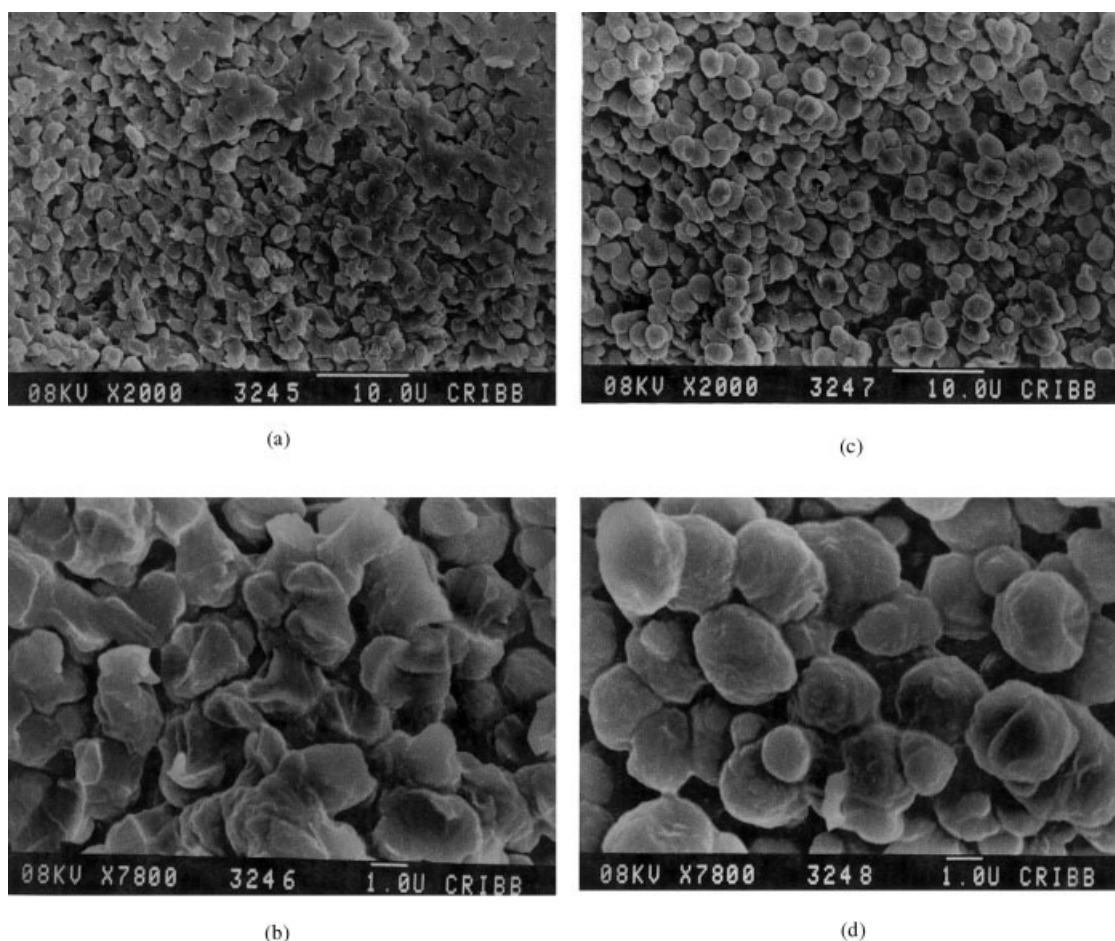


Figure 1 DVERL–St modified with CTBN and cured isothermally at 30°C. 5% CTBN: (a) ×2000, (b) ×7800; 10% CTBN: (c) ×2000, (d) ×7800.

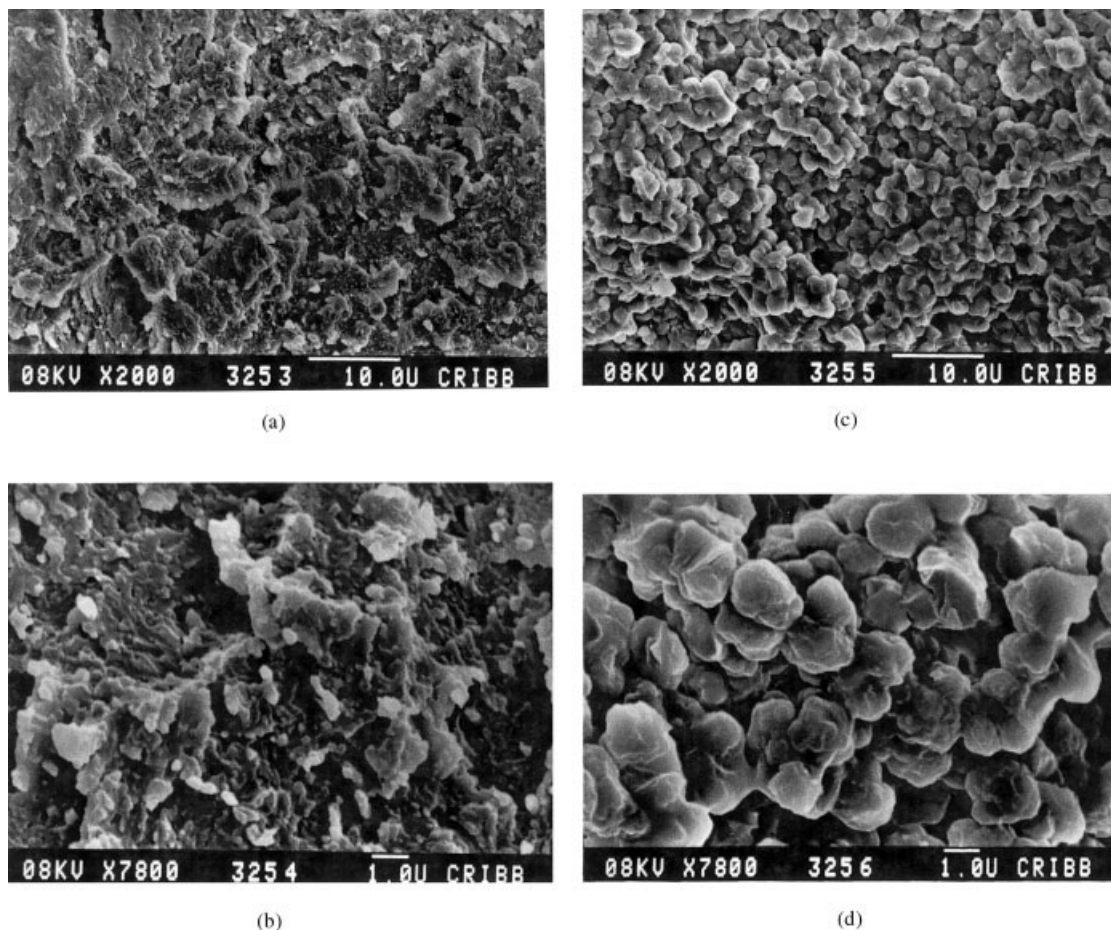


Figure 2 DVERL–St modified with CTBN and cured isothermally at 80°C. 5% CTBN: (a) $\times 2000$, (b) $\times 7800$; 10% CTBN: (c) $\times 2000$, (d) $\times 7800$.

BASF AG, Ludwigshafen, Germany). The molecular weights were measured by gel permeation chromatography (GPC) using a polystyrene calibration. The results are shown in Table I.

The two liquid rubbers used as modifiers were copolymers of butadiene and acrylonitrile (BF Goodrich Co., Cleveland, OH), which had either carboxyl end groups (CTBN, 1300 \times 8) or vinyl end groups (VTBN, \times 33). Table I summarizes the characteristics of these components.

The crosslinking reaction of the DVERs was obtained by addition of styrene in a weight proportion of DVER : St = 55 : 45, a usual commercial formulation. The cure reaction was carried out at 30 or 80°C. The reaction was initiated by an amine-accelerated system using benzoyl peroxide (Luzidol 75%; Akzo Chemicals S.A., Buenos Aires, Argentina) as initiator and *N,N*-dimethyl aniline (Akzo Chemicals S.A.) as promoter. All materials were used as received.

Electron microscopy

Fracture surfaces for microscopy were obtained by bending the molded plaques at liquid nitrogen tem-

peratures. Fractured specimens were gold coated and then observed by scanning electron microscopy (SEM). Samples to be studied by transmission electron microscopy (TEM) were previously stained with OsO₄ (immersed in OsO₄ solution for 7 days). A thin slice was then obtained by microtoming the specimen and observed by TEM. Only the unreacted C=C bonds are stained by this technique and because the DVER and St reacted through the unsaturations, only the less reactive internal unsaturations of the liquid rubbers become stained. Electron microscopy was carried out using a JEOL JSM 35 CF scanning electron microscope (JEOL, Peabody, MA) and a JEOL 100 CX transmission electron microscope.

RESULTS AND DISCUSSION

The observation by SEM and TEM of the neat DVER–St networks indicates that they constitute homogeneous systems that fracture in a brittle way without showing any special features in the fracture surfaces.¹² However, the morphologies of the modified systems can vary very broadly, depending on the molecular weight of the resin, the type, and concen-

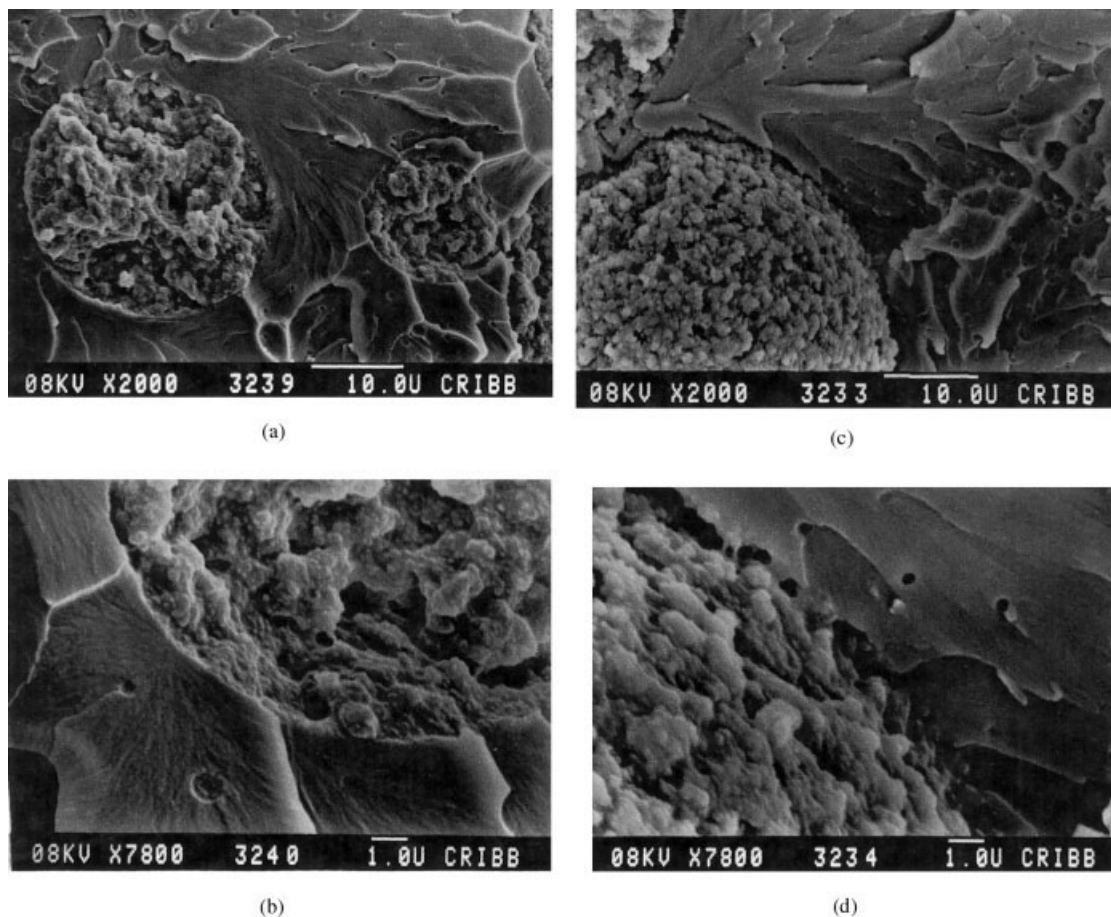


Figure 3 DVERC–St modified with CTBN and cured isothermally at 30°C. 5% CTBN: (a) $\times 2000$, (b) $\times 7800$; 10% CTBN: (c) $\times 2000$, (d) $\times 7800$.

tration of the elastomer and the curing temperature. The components are initially miscible in the case of the low molecular weight resin, but they form heterogeneous systems for the high molecular weight vinyl ester resin. This last feature is the usual situation in commercial modified DVER systems. The components are thoroughly mixed before curing takes place, and the system is formed by a continuous DVER–St-rich phase and a discontinuous elastomer-rich phase.¹⁵ Thus, depending on the molecular weight of the original resin, the type and concentration of the modifier, and the temperature of the reaction, materials of very different morphologies are obtained, and this has a correlation to the varied final properties measured for this type of materials.^{12,22,23}

Copolymers modified with CTBN

Low molecular weight resin, DVERL

Low-temperature cure ($T = 30^\circ\text{C}$). The low molecular weight DVERL–St–CTBN system is miscible and completely transparent before the reaction takes place. As the reaction advances, the formed copolymer presents partial miscibility in the mixture and it begins to sep-

arate, forming nodules in whose interior the density of crosslinking increases quickly. At the same time that the resin and the St react, the monomeric phase becomes rich in the liquid elastomer, and at the end of the curing reaction, the material is constituted by aggregated nodules of copolymer surrounded by the elastomer. Microvoids or cavities are formed as a result of the volumetric contraction of the cured resin that takes place toward the end of the reaction, generating internal stresses on the material.^{12,16,17} The final morphology is the result of the phase separation originated by the “polymerization-induced phase separation” (PIPS) mechanism, occurring from an initially homogeneous solution.

Figure 1 illustrates the St–DVERL–CTBN system cured isothermally at 30°C. The material shows cocontinuous microstructure of DVER–St irregular nodules surrounded by the elastomer. At 5% CTBN [Fig. 1(a) and (b)] the nodules are irregular and highly aggregated, without a clear separation among themselves. At 10% CTBN [Fig. 1(c) and (d)] there is a larger segregation effect of the elastomer (reduced initial miscibility) and the nodules are more spherical and clearly separated. The size of the nodules also appears

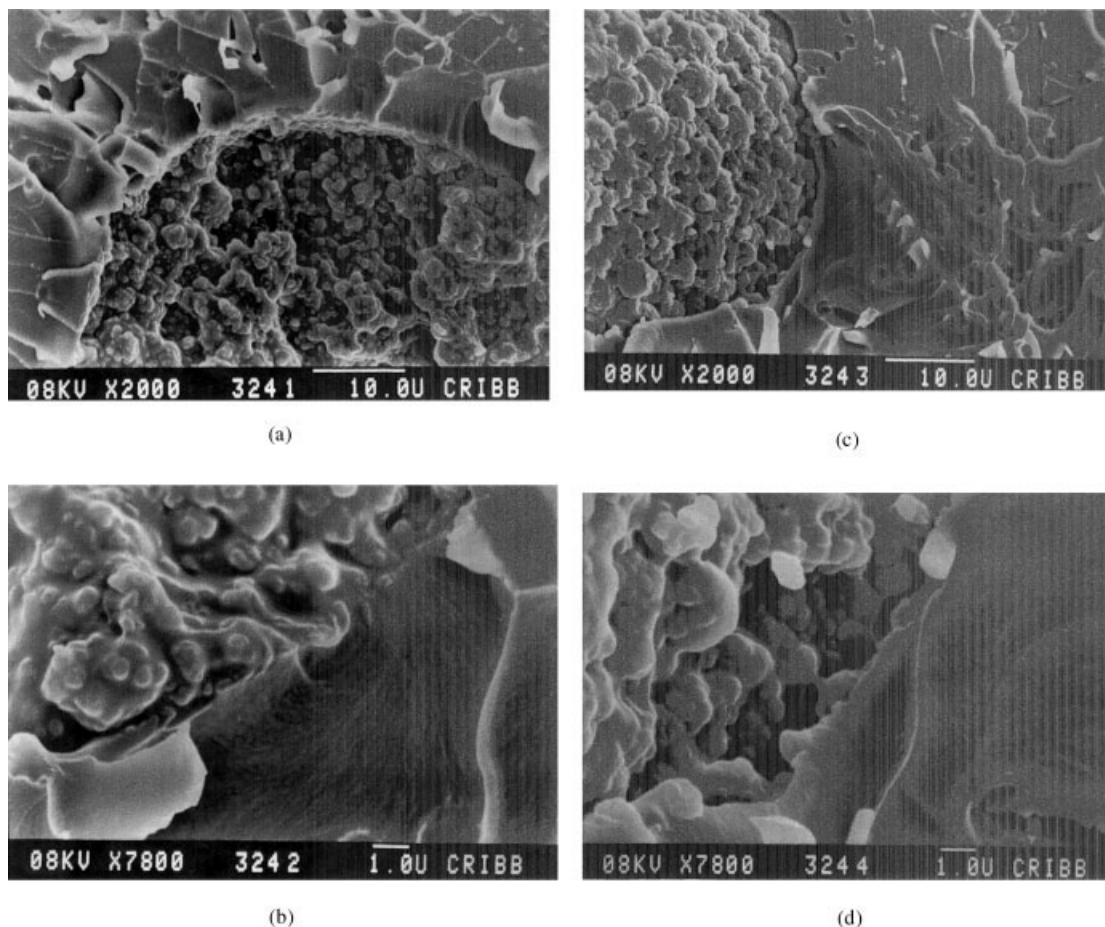


Figure 4 DVERC–St modified with CTBN and cured isothermally at 80°C. 5% CTBN: (a) $\times 2000$, (b) $\times 7800$; 10% CTBN: (c) $\times 2000$, (d) $\times 7800$.

larger at high CTBN concentration (~ 1.5 and ~ 2.5 μm at 5 and 10% CTBN, respectively). According to previous results,¹² the expected properties of these materials are low modulus and resistance, as well as low fracture properties, attributed to the inherent low cohesion between the phases.

High-temperature cure ($T = 80^\circ\text{C}$). Increasing the temperature of the mixture increases the initial miscibility of the system. The result of curing the sample at 80°C is shown in Figure 2(a) and (b) for the St–DVERL–5% CTBN. Although the fracture surface is very rough, no clear nodular structure is visible. The formation of nodule aggregates is incipient and the fracture path is tortuous, which indicates a large energy dissipation during the fracture process. Actually, this morphology has been effectively associated with a maximum in fracture properties for the St–DVERL system modified with varying amounts of CTBN.¹² As the concentration of elastomer is increased, the energy required to fracture the materials increased to 5% CTBN. At higher concentrations, the nodular cocontinuous microstructure appears [even at $T_{\text{cure}} = 80^\circ\text{C}$, Fig. 2(c) and (d)], which is associated with extensive microvoiding, a feature that has a strong negative effect on

the fracture properties of the samples because it induces intrinsic brittleness, with the crack finding an easy path for growing through the sample.^{10,11,12}

Comparison of Figures 1(d) and 2(d) with respect to 1(b) and 2(b) confirms the increasing segregating effect of higher CTBN concentrations, that is, a more clear nodular structure appears at high elastomer concentrations, with deleterious mechanical effects on these formulations.

On the other hand, comparison of Figures 1(d) and 2(d) illustrates the effect of the curing temperature: the lower the temperature, the larger the nodules. This effect had been observed for an LPA-modified UP,²² varying the heating rates of the curing step. At a given concentration, the nodules were smaller at high heating rates and the nodular microstructure appeared at high LP concentration. This is clearly a result of the increased miscibility of the system at higher temperatures. The effect of temperature on the miscibility of the initial ternary system was also observed by Huang and Chen²³ and by Li and Lee¹⁷ for unsaturated polyester–St–LPA systems and an experimental and thermodynamic analysis for the DVERL–St–CTBN elastomer-modified system has been presented and dis-

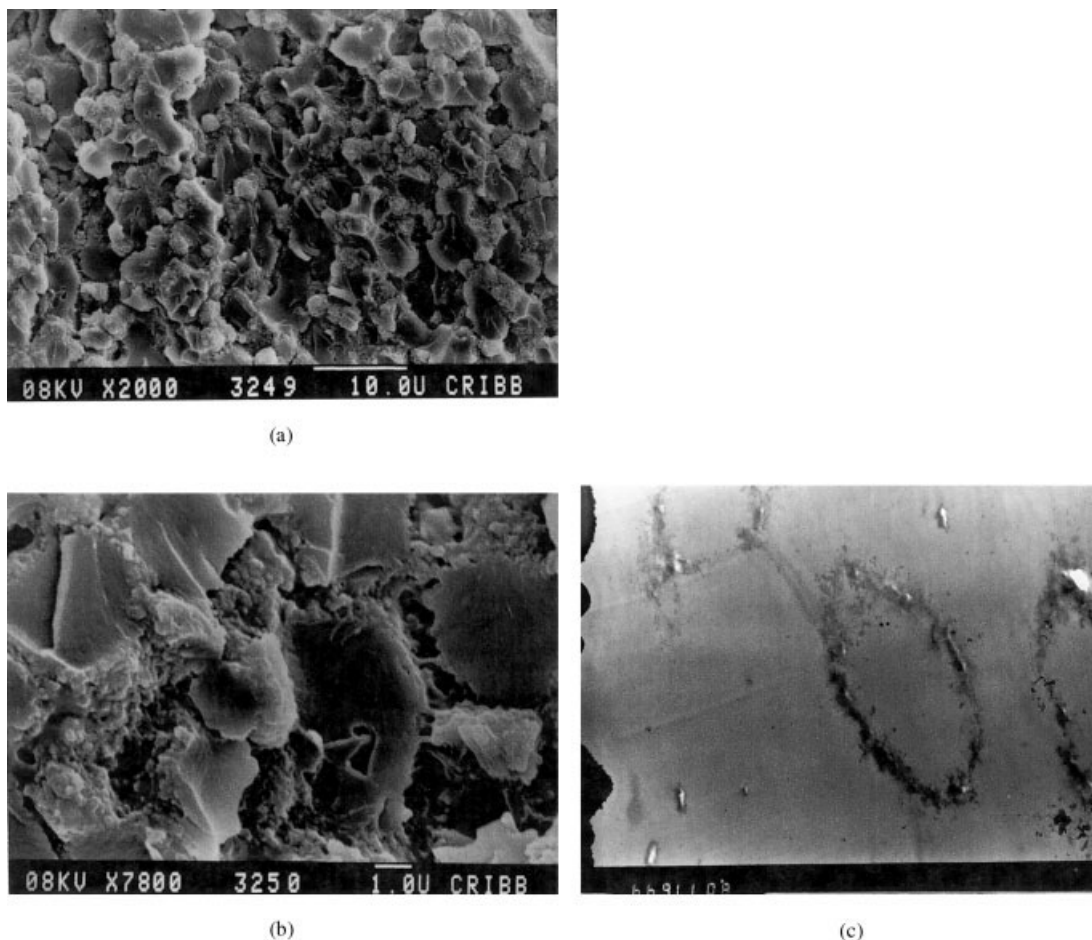


Figure 5 DVERL–St modified with 7.5% VTBN and cured isothermally at 30°C. (a) $\times 2000$, (b) $\times 7800$, (c) TEM (long side of the micrograph represents 8.5 μm).

cussed by Auad et al.,¹² who found good agreement between experimental results and theoretical predictions.

High molecular weight resins

Low-temperature cure. The use of high molecular weight resins leads to a material with two-region morphologies: one corresponds to a rich DVERC–St region with or without rubber inclusions; the other shows an incipient nodular DVERC–St formation surrounded by elastomer.

Figure 3(a)–(d) show different magnifications of the systems prepared at 5–10 wt % of CTBN and at T_{cure} of 30°C. Large, more or less spherical regions appear with a very complex internal structure. These complex domains are formed by incipient DVERC–St nodules not completely developed and highly packed or coagulated. These irregular formations are surrounded, as in the particulated structure discussed above, by the CTBN elastomer. That is, these domains are elastomer-rich regions formed during the mixing step and where the included DVERC–St monomers reacted and

lead to the complex structure observed. Evidence of LPA microvoiding is observed inside these regions. Outside these domains, the continuous phase also undergoes phase separation, forming well-dispersed CTBN spherical particles, or simply incorporating the elastomer as a flexibilizer. Features typical of brittle fracture are observed in the main region.

An increment in the size of the nodular regions with increasing elastomer concentration is observed at low magnification, as it could be expected, because of the increased initial incompatibility of the system. The nodular formation appears as incipient at both concentrations, although nodules show better definition at 10% CTBN. Inspection of the continuous phase allows observation of the presence of small spherical inclusions of the type observed in epoxy-modified systems. However, in Figure 3(b) (down left) a small inclusion is observed that shows internal two-phase composition. Thus, at least some of the small inclusions in the main phase are also complex elastomer-rich domains. This morphology type is typical of LPA–UP–St systems and mainly contributes to control the volume shrinkage during curing, although some

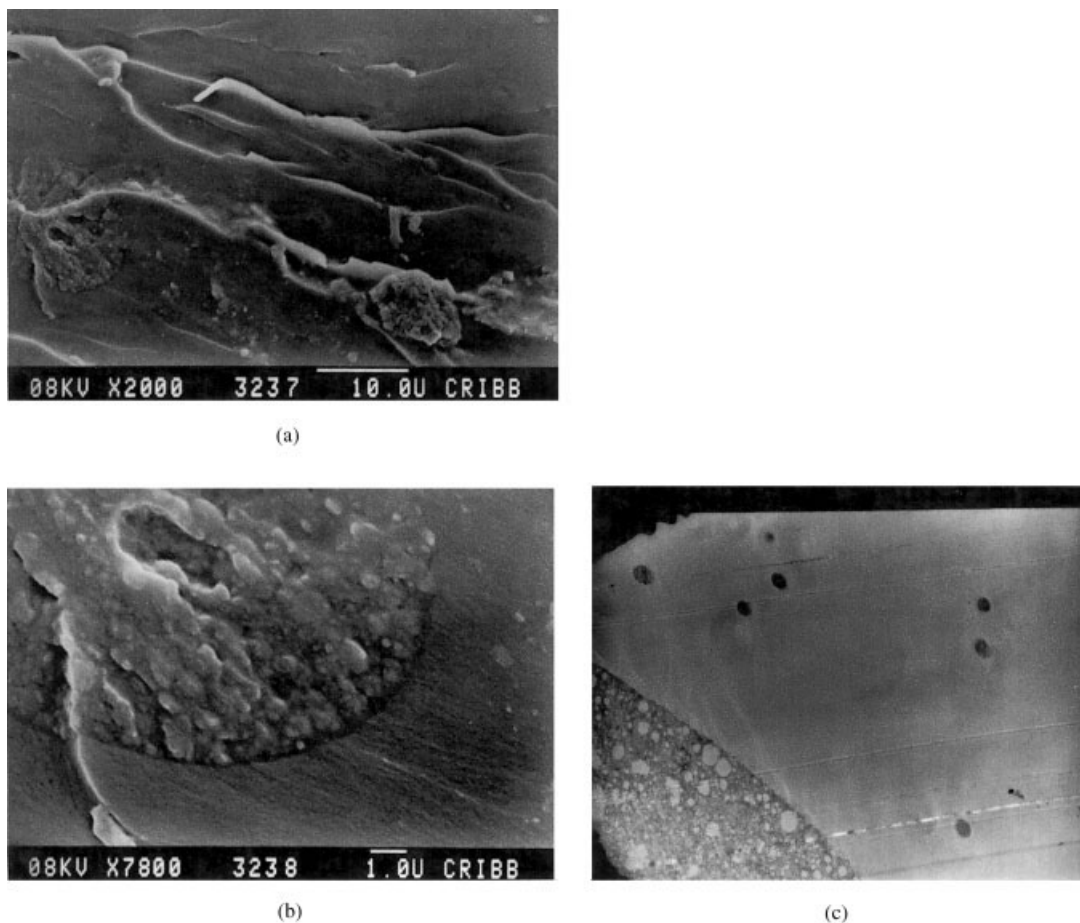


Figure 6 DVERL–St modified with 7.5% VTBN and cured isothermally at 80°C. (a) $\times 2000$, (b) $\times 7800$, (c) TEM (long side of the micrograph represents 8.5 μm).

toughening is also obtained.^{10,25} As observed in other multiphase systems, small particulate domains with complex structure are expected to lead to materials with better properties. Instead, large inclusions can act as point of failure in the material.

High-temperature cure. The use of a high-temperature cure (80°C) increases the initial miscibility, but also increases the reaction rate. Thus, it is expected that phase separation may at some point be impeded by the rapid increment of the system viscosity. This seems to be the present case, according to Figure 4(a)–(d). Figure 4(a) and (c) are low-magnification SEM micrographs of the fracture surfaces of DVERC–St modified with 5 and 10% CTBN, respectively. It is clear that the continuous phase (DVER–St-rich) is undergoing a more plastic deformation before fracture than the samples obtained at $T_{\text{cure}} = 30^\circ\text{C}$. This indicates that more elastomer is retained in the main phase at this cure temperature. Phase separation is not as complete as it was at the lower temperature and the elastomer remains dissolved in the DVERC–St phase and flexibilizes that phase. This effect was previously reported in UPR–St systems.⁸ Because of the matrix flexibilization added to the two-phase mor-

phology, one would expect that the materials cured at high temperature present better fracture behavior, although at the cost of decreased rigidity.

On the other hand, the nodular formation inside the elastomer-rich domains is not completely developed. The nodules are incipient and, although the CTBN remains surrounding the globules, these do not grow as in the DVERL system because of the higher viscosity of the DVERC–St system.

At both temperatures of curing there is a clear interface between the two main regions and microvoiding is observed in the interior of the complex elastomer-rich domains.

Use of a reactive modifier, VTBN

The behavior of the systems modified by VTBN is more complex because the elastomer is vinyl end functionalized and can coreact during the copolymerization. The reacting mixture is composed of the three monomers, DVER, St, and VTBN, and a terpolymer generated by the copolymerization of the three.

The blocks of the copolymer that are rich in the elastomer can segregate during the reaction, generat-

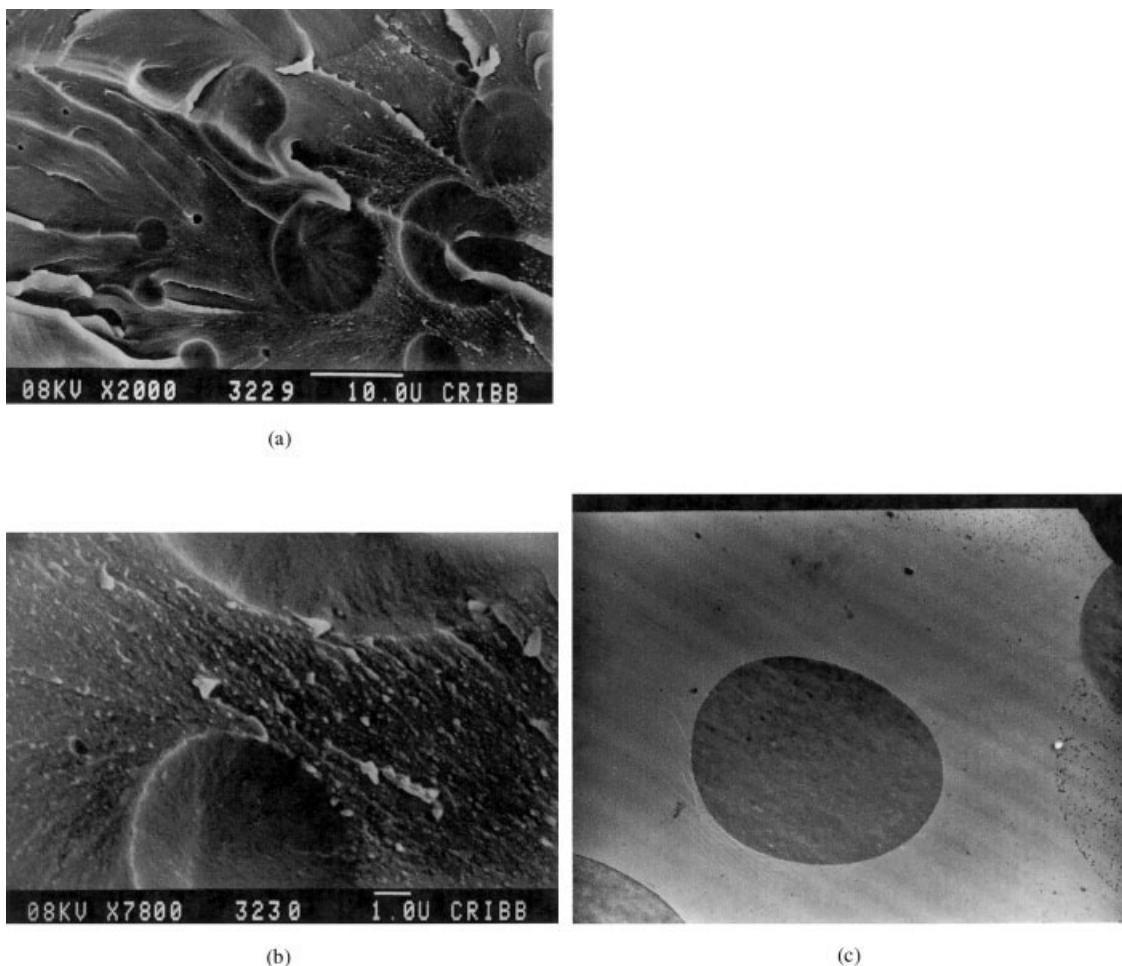


Figure 7 DVERC–St modified with 7.5% VTBN and cured isothermally at 30°C. (a) $\times 2000$, (b) $\times 7800$, (c) TEM (long side of the micrograph represents 8.5 μm).

ing elastomer-rich regions and DVER–St-rich regions. However, this segregation cannot be as neat and well defined as in the CTBN case because of the existence of covalent bonds between the blocks.

Figure 5(a) and (b) show the fracture surfaces of the VTBN-modified DVERL–St system at 7.5% of elastomer. In this range of concentrations the DVERL–St system cured at 30°C with CTBN addition showed a particulated morphology throughout the entire sample [Fig. 1(a)–(d)]. As explained above, VTBN is a reactive elastomer and although it has a lower initial miscibility in the DVERL–St mixture than that of CTBN,¹⁵ it can coreact with the vinyl ester styrene molecules and so the final degree of separation is reduced.

Consequently, Figure 5(a) and (b) show a cocontinuous structure of micron-size domains rich in the DVER–St copolymer and domains of nodular microstructure, which are rich in VTBN. Both types of regions are cocontinuous throughout the sample. A larger magnification obtained by TEM [Fig. 5(c)] allows observation of the elastomer net (darker region) surrounding DVERL–St-rich regions.

If a higher temperature is used during curing ($T = 80^\circ\text{C}$) the final microstructure is markedly changed [Fig. 6(a)–(c)]. In this case, the morphology of a continuous DVERL–St phase with small complex inclusions and larger nodular domains is recovered, although with particular characteristics. The interphase is more diffuse than in any of the CTBN-modified systems [Fig. 6(a)] and, because the magnification in Figure 6(b) is so great, the smaller inclusions are difficult to observe. This feature is correlated with the reactivity of the VTBN that copolymerizes at the interface. The mechanical study of this system cured at 80°C indicated a reduction in the modulus of the VTBN-modified material (with respect to the neat system) and improved fracture behavior. Because phase separation is not as complete as in the CTBN-modified systems, a critical elastomer concentration above which the properties decay does not exist. This is the result of the better cohesion between phases of the VTBN-modified systems.¹² Similarly, Huang et al.²³ reported on the effect of improved compatibility of additive and UPR–St systems. They observed a stronger interface with less segregation of species, which

led to improved impact strength of the system, but lower modulus because of the flexibilizing effect of the elastomer in the main phase.

The formation of nodules inside the particulated domains is not clear from the observation of the SEM micrographs. However, TEM confirms the existence of nodules and shows that a wide distribution in nodule size occurs inside these regions [Fig. 6(c), down left]. The same micrograph shows that the small inclusions in the main phase are not pure elastomer, but that a fine internal microstructure is also present.

The use of a higher molecular weight resin leads to different final morphologies. At the low curing temperature (30°C), SEM shows a two-phase morphology [Fig. 7(a) and (b)]. The main phase, DVER–St-rich region, shows some roughness, which was not present in the low molecular weight system, perhaps attributable to some coreacted VTBN. However, there are micron-size domains that show no internal microstructure. Use of TEM [Fig. 7(c)] allows us to conclude that these are elastomer-rich domains with apparently no internal microstructure. This type of morphology was previously reported for a similar commercial system.⁸ As in that case, evidence of stretching and tearing of the elastomer from the outside edge in is observed at the two magnifications of the fractured surface.

By increasing the curing temperature, the size of the separated domains is reduced (enhanced initial miscibility) and the internal complex microstructure is again recovered [Fig. 8(a) and (b)]. The size of the domains changes from 10 to 20 μm to 1–3 μm for the samples cured at 30 and 80°C, respectively. As in the case of the DVERL–St system, the interface is diffuse. As previously discussed for the CTBN system, the presence of small complex elastomeric-rich domains is expected to produce a material with better properties than those containing large pure elastomer inclusions.

CONCLUSIONS

Nonreactive modifier (CTBN). The use of a low molecular weight resin resulted in better initial compatibility and lower initial viscosity of the system and led to a final cocontinuous particulated morphology that spanned the whole sample.

Use of a high molecular weight resin, which is more viscous and partially miscible with the elastomer, led to a two-region morphology: DVER–St-rich domains and particulated complex domains rich in the elastomer.

Curing at high temperatures increased the initial compatibility of the system and led to smaller, more irregular nodules in the particulated domains and to modified resin–St-rich domains. These last regions were more flexible than the neat thermoset and

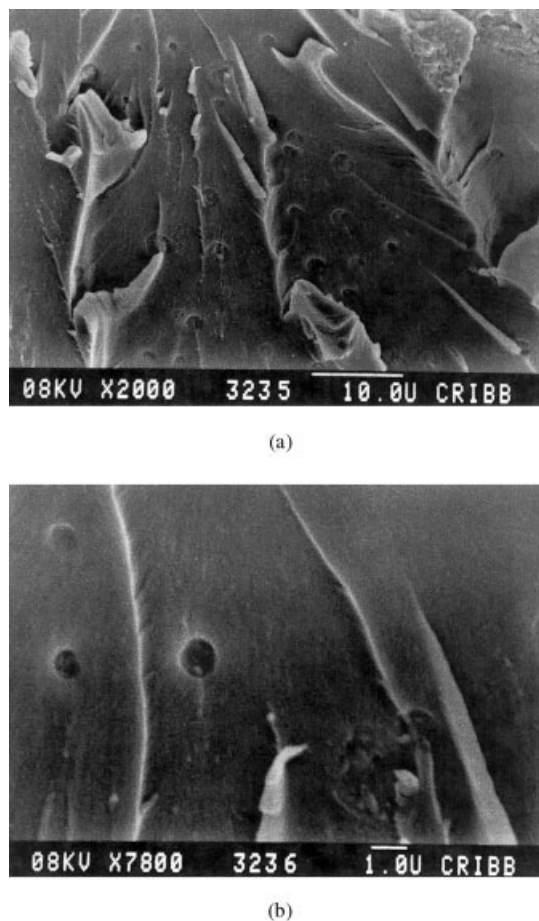


Figure 8 DVERC–St modified with 7.5% VTBN and cured isothermally at 80°C. (a) $\times 2000$, (b) $\times 7800$.

showed evidence of plastic deformations before fracture.

Reactive modifier (VTBN). Although the use of VTBN, a coreactant in the resin–St reaction, initially reduced the miscibility of the system DVER–St–elastomer (with respect to the use of the more compatible CTBN), it finally led to phase-separated systems with stronger and more diffuse interfaces and varied morphologies.

When the low molecular weight resin was used, low-temperature curing led to a cocontinuous structure formed by micron-size domains of resin–St-rich and particulated elastomer-rich phases.

The high-temperature cure, on the other hand, led to particulated domains in a DVER–St-rich continuous phase. However, microvoiding was not as clear as it was in the CTBN-modified systems and the interface was diffuse, as a result of the reduced segregation of the species.

High molecular weight resins cured at low temperature produced clear phase separation with spherical domains rich in the elastomer. Fracture in the main phase, however, showed some roughness, indicating that it was not a neat DVER–St copolymer. Elastomer-

rich regions seemed to fail by stretching and tearing of the particles from outside in.

Curing at high temperature has an important effect in reducing the size of the complex elastomer-rich domains, which are even difficult to detect because of the increased miscibility and copolymerization at the domain edges.

A good control of the copolymerization process in this type of modified systems will help to obtain a desired morphology and thus to achieve the required final properties: cocontinuous microstructures with microvoiding for better volume control, or two-phase dual structures with a more or less flexibilized main phase for toughening the thermoset copolymer. The control of the reaction temperature, the selection and concentration of the additive, and the molecular weight of the divinylester resin are all variables that allow tailoring of the required material.

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