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Rubber modified vinyl ester resins of different molecular weights

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The morphology, as well as the related fracture and mechanical behavior of vinyl ester resins (DVER) of different molecular weights cured with styrene (S) and modified with two different liquid rubbers are presented and discussed. The liquid rubbers are: carboxyl terminated poly(butadiene-*co*-acrylonitrile) (CTBN), a common toughening agent for epoxy resins, and an almost unreactive rubber with the DVER and S comonomers, and a reactive rubber (vinyl terminated poly(butadiene-*co*-acrylonitrile), (VTBN). The initial miscibility of the modified systems and the reactivity of the rubber determine the final morphology of the material. This morphology will correspond to a continuous main phase (rich in the DVER-S copolymer) with simple rubber rich inclusions (as in the epoxy-rubber systems) or with inclusions with a complex internal structure, where phase separation occurs as in the low profile modified unsaturated polyester resins. The morphologies developed are strongly dependent on the resin molecular weight as well as on the elastomer added. In spite of the initially higher compatibility of the S-DVER-CTBN system with respect to the S-DVER-VTBN system, the reactivity of the vinyl-ended elastomer leads to a much finer distribution of the elastomeric phase. In particular, the low molecular weight resin cured with S and modified with 10% of CTBN leads to a cocontinuous structure with microvoids that generates a material of low density and poor mechanical and fracture properties. On the other hand, the use of VTBN as additive leads to a more compact morphology, with gradual reduction of the mechanical performance of the modified resins and improved fracture behavior. *© 2002 Kluwer Academic Publishers*

1. Introduction

Most of the published results on modified thermosets refer to the mechanisms that govern the "toughening" of modified epoxy resins with liquid elastomers [1, 2]. In these materials, the phase separation generates a morphology of dispersed elastomeric particles in the continuous phase formed by the crosslinked epoxy. Other thermosets, such as unsaturated polyesters (UPR) and vinyl ester resins (DVER) have been less studied, although some results are available in the literature [3–6]. Studies of the modification of UPR-S and DVER-S systems have been carried out using different elastomeric additives with different degrees of initial miscibility to obtain an effective "toughening" of the network.

Low profile additives (LPA) have been used to control the volumetric contraction in UPR [7, 8]. In this case, the final morphologies are totally different. The systems can be homogeneous at the beginning of the reaction, but as the reaction advances, the formed copolymer, UPR-S, presents partial miscibility in the mixture and it begins to separate forming nodules in whose interior the density of crosslinking increases quickly [9–11]. At the same time that the UPR and the S react, the monomeric phase gets rich in the liquid elastomer, and at the end of the curing reaction, the material is constituted by copolymer rich regions consisting of the aggregated nodules already formed, and elastomer rich regions. Depending on the quantity of LPA used, the final morphology may be that of a matrix with elastomeric inclusions (irregular or spherical), or it may contain regions of co-continuous structure. Finally, due to the different volume shrinkage of the phases during cure, microvoids or cavities are formed that coexist with the co-continuous structure of the heterogeneous material. The compensation of the volumetric contraction of the cured resin takes place at the cost of the formation of these cavities [9–11].

In a DVER-S system, the addition of CTBN (carboxyl terminated acrylonitrile-butadiene copolymer) generates a morphology like that developed in low profile additive (LPA) - UPE modified systems. The addition of a more reactive elastomer, such as VTBN (vinyl

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terminated acrylonitrile-butadiene copolymer), leads to a very different and more compact final morphology. Consequently, the mechanical and fracture behavior of the resulting modified thermosets are also different [4, 6].

The studies reporting on the mechanical properties of this type of materials are mainly focused on the fracture [4–6]. In general, an increase in toughening is reported with the addition of the elastomer, but with the reduction of the mechanical properties, such as modulus and yield stress [4, 11, 12]. In particular, the authors have previously analyzed the mechanical behavior of a modified low molecular weight DVER resin cured with styrene and related its properties to the initial miscibility of the systems and the further phase separation induced by polymerization [11].

In this work, the effect of the molecular weight of vinyl ester resins modified with elastomeric additives, terminated in carboxylic groups (CTBN) and vinyl groups (VTBN), and crosslinked with styrene is analyzed. The mechanical and fracture properties are explained as a function of morphology, which is determined by the molecular weight of the initial resin and the reactivity of the added elastomers.

2. Experimental

2.1. Materials and sample preparation

Two divinylester resins of low and high molecular weight, DVERL and DVERH, were synthesized by reacting epoxy resins, diglicidyl ether of bisphenol A (DGEBA MY 790, Ciba Geigy, equivalent weight 176.2 g/eq. and DGEBA Araldite GT 6071, Ciba Geigy, equivalent weight 450–465 g/eq.), with methacrylic acid (Norent Plast S.A., laboratory grade reagent) using triphenylphosphine as catalyst (Fluka A.G., analytical reagent). The final conversion reached was higher than 93% in both cases. The molecular weights were measured by gel permeation chromatography (GPC) using a polystyrene calibration. Synthesized DVERs were stabilized with 300 ppm of hydroquinone. A commercial DVER resin (PALATAL A 430, BASF AG) was also used in the study. The molecular weights of the three resins are shown in Table I.

The two liquid rubbers used as modifiers were copolymers of butadiene and acrylonitrile (BF Goodrich Co.), which had either carboxyl end groups (CTBN, 1300 × 8) or vinyl end groups (VTBN, 1300 × 8). Table I summarizes the characteristics of the components used in this study.

Crosslinking reaction of all the DVER samples was realized by addition of styrene in a weight proportion of DVER: $S = 55:45$, an usual commercial formulation. The cure reaction was carried out at 50°C and the samples were further postcured at 170°C for 1 hour. The reaction was initiated by an amine-accelerated system using benzoyl peroxide (Luzidol 75%, Akzo Chemicals S.A.) as initiator and N, N-dimethyl aniline (Akzo Chemicals S.A.) as promoter. All the materials were used as received.

In order to make samples for compression testing, the reactive mixture of monomers (with or without additives) was injected into glass cylinders of 6 mm diameter previously sprayed with a silicone release agent. Compression specimens were carefully machined from the cylinders up to achieve the final dimensions (length/diameter = 1.5–2) with parallel upper and lower bases.

Plates for bending tests (3 mm thickness) and fracture measurements (6 mm thickness) were obtained by casting the mixtures into a mould consisting of two glass plates coated with a silicone release agent, spaced by a rubber cord and held together with clamps.

2.2. Electronic microscopy

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 OsO_4 (immersed in OsO_4 solution during 7 days). Then a thin slice was obtained by microtoming the specimen and observed by TEM. Only the unreacted C=C bonds are stained by this technique and since the DVER and S reacted through the unsaturations, only less reactive internal unsaturations of the liquid rubbers become stained. Electronic microscopy was carried out using a Jeol JSM 35 CF scanning microscope and a JEOL 100 CX transmission electron microscope.

2.3. Physical and mechanical tests

The density of the cured copolymers with different compositions of elastomeric additives was determined by picnometry, with immersion of the samples in distilled degassed water at 20°C.

Dynamic mechanical tests were performed using a Perkin Elmer 7e on rectangular bars of 2 ± 0.1 mm thickness and 3 ± 0.1 mm width. A three point bending geometry was used with a span of 15 mm, at a frequency of 1 Hz and at a heating rate of 10°C/min. The applied static stress was 0.5 MPa and the dynamic stress 0.1 MPa.

Flexural modulus and strength were measured using three points bending geometry, according to ASTM D 790-86 specifications, using an electromechanical INSTRON Universal Testing Machine model 4467.

Compression test specimens were deformed between metallic plates lubricated with molybdenum disulphide

TABLE I Molecular weights of the reactants and modifiers

	Styrene (S)	DVER L (Synthesized)	DVER C (Commercial)	DVER H (Synthesized)	CTBN (1300 × 8)	VTBN (×33)
Mn (gr/mol)	104	583	1015	1236	3600	3600
Mw (gr/mol)	104	606	1766	2662	6501	6498
Mw/Mn	1.0	1.04	1.74	2.15	1.81	1.81

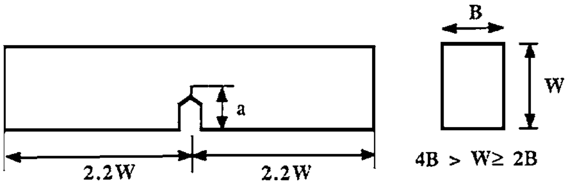


Figure 1 Schematic of the fracture specimen geometry.

TABLE III Mechanical properties of the neat DVER-S copolymers

	E_f (GPa)	σ_{yc} (MPa)	K_{IC} (MPa/m$^{1/2}$)
DVER L-S	4.04 ± 0.16	114 ± 3	0.72 ± 0.05
DVER C-S	2.74 ± 0.22	88 ± 3	0.83 ± 0.13
DVER H-S	3.46 ± 0.05	102 ± 3	0.96 ± 0.09

in a hydraulic INSTRON Universal Testing Machine Model 8501 according to ASTM D 695-85.

Fracture mechanics measurements were made at room temperature, in three-point bending mode at a crosshead displacement rate of 10 mm/min using the Universal Testing Machine mentioned above. Test specimens were prepared by cutting rectangular bars from the slabs using a diamond saw. Central V-shaped notches were machined in the bars, then a razor blade was positioned in the notch and gently tapped to induce the growth of a natural crack ahead the blade. The samples tested were those showing a total crack length, a, in the range of $0.45 < a/W < 0.55$, where W is the width of the specimen (Fig. 1). The span to width (S/W) and the thickness to width (B/W) ratios were kept equal to 4 and 0.5, respectively. The stress intensity factor at the onset of crack growth, K_{IC}, was calculated following the ESIS Protocol recommendations using single edge notched specimens (SEN) [13]. The total crack length a was measured from the fracture surface, using a profile projector with a magnification of 10×.

3. Results and discussion

3.1. Neat copolymers DVER-S

3.1.1. Dynamic mechanical properties above and below the glass transition temperature

Table II includes the values of the glass transition temperature, T_g, and storage modulus, E', at the glass and rubbery states measured in dynamic mechanical tests (DMA) for the neat DVER-S copolymers. It also includes the density of the copolymers measured by picnometry at 20°C. The glass transition temperature was measured at the maximum in $\tan\delta$, the E' in the rubbery region was measured at $T = T_g + 60°\text{C}$ and the E' in the glassy state was measured at room temperature. The trend observed in the T_g values correlates very well with the crosslinking density expected for these networks. Since the resins are vinyl terminated, they are crosslinked through these final groups to another molecule containing double bonds (ie. another resin molecule or, with a higher probability, to a styrene molecule). Therefore, the resin with the lowest molecular weight of the series (at S : DVER ratio = 45 : 55 by weight) leads to the copolymer with the highest crosslinking density, and thus with the highest T_g. Consequently, the lowest T_g is reported for the network obtained with the highest molecular weight resin. Using the same reasoning, the E' in the rubbery region (measured at $T = T_g + 60°\text{C}$) increases as the molecular weight of the resin decreases, since it is a function of the crosslinking density of the network.

TABLE II Physical and dynamic mechanical properties of the neat DVER-S copolymers

	Density (g/cm^3)	T_g (°C)	E' glass (GPa)	E' rubber (MPa)
DVERL-S	1.145 ± 0.005	115.3	3.2	48.9
DVERC-S	1.127 ± 0.002	92.3	1.8	24.1
DVERH-S	1.132 ± 0.005	77.2	2.5	12.2

On the other hand, the modulus in the glassy region, at room temperature, shows a different trend. It is well known that below the glass transition, the physical properties of amorphous polymers are generally little dependent on the temperature [14]. Moreover, as the density increases the separation between adjacent chain segments decreases and the Van der Waals forces between intermolecular atoms increase, that is the cohesive energy of the material increases and this leads to an increase in the elastic modulus [15]. As it can be seen in Table II, the values of E' glass are best correlated to the values of the densities measured for the copolymers.

Table III includes the results obtained for the neat DVER-S tested in flexion, compression and fracture. The overall flexural response of these thermosets is in the linear range with essentially no plastic deformation under the conditions of the test. Again, the results of the flexural modulus show a good correlation with the density of the materials.

During the compression tests the crosslinked materials show a first linear region followed by plastic deformation until they finally break, a behavior typical of thermosets that show yield phenomena only in compression. Yield stress values are reported in Table III.

The stress intensity factors, K_{IC}, measured in this work are comparable to those found in the literature (0.75–1.12 MPa/m$^{1/2}$) for commercial DVER-S systems [4, 6] obtained from resins of similar molecular weights (Mn $\sim$ 1100) and styrene concentrations (45 wt%). The values of the stress concentration factor, K_{IC}, reported in Table III show that samples are tougher the larger the molecular weight of the initial DVER. This observation is not new in the literature of thermosets. Other authors have previously investigated the effect of the molecular weight between crosslinks, M_c, on the fracture behavior of crosslinked resins. They found that an increment in M_c produces an increment on the fracture toughness of the material [16], although in some cases this change is followed by a slow decrease after passing through a maximum [17]. Since only the terminal groups of the DVER are reactive, the value of M_c correlates with the molecular weight of the initial DVER and explains the observed trend.

3.2. Modified networks

3.2.1. Morphology

The observation by SEM and TEM of the neat DVER-S networks indicates that they constitute homogeneous systems that fracture in a brittle way without showing any special features in the fracture surfaces [11]. However, the morphologies of the modified systems can vary very broadly depending on the molecular weight of the resin and the type and concentration of the elastomer. The final properties of the modified networks depend strongly on the morphology of these materials. The components are initially miscible in the case of the low molecular weight resin, but they form heterogeneous systems in the other two cases. This last feature is the usual situation in commercial modified DVER systems. The components are thoroughly mixed by mechanical means, but the high molecular weight resin systems (DVERC and DVERH) remain as heterogeneous systems formed by a continuous DVER-S rich phase and a discontinuous elastomer rich phase.

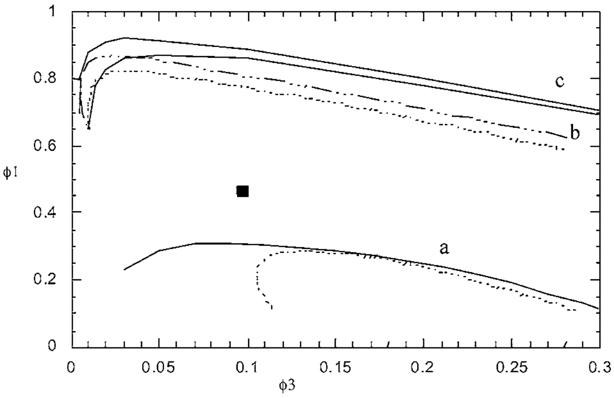


Figure 2 Calculated quasiternary phase diagram at 50°C, showing binodal curves (continuous lines) and spinodal curves (dashed lines); (a) DVERL-S/CTBN, (b) DVERC-S/CTBN, and (c) DVERH-S/CTBN. Solid point represents a 55%DVER-45% S/10% CTBN sample composition (by weight). $\phi 1$ and $\phi 3$ represent the volume fractions of styrene and CTBN, respectively.

This feature can be easily understood using a ternary phase diagram as shown in Fig. 2. The calculations have taken into account the polydispersity of the resins and the interaction parameters between the three componentes of the mixtures [12] at the curing temperature. The point representing the initial system composition is in the one-phase region for DVERL-S/CTBN, but it is clearly in the two-phase region for the other two systems. Thus, depending on the molecular weight of the original resin, their molecular weight distribution and the type and concentration of elastomeric modifier utilized, one or two phase material results. Similar plots were obtained for VTBN indicating that it is initially less soluble in the DVERL-S mixture than the CTBN elastomer [12]. However, the systems remain homogeneous for the DVERL system and heterogeneous for the other two resin systems.

3.2.2. Copolymers modified with CTBN: effect of the resin molecular weight

3.2.2.1. Low molecular weight. The morphology generated in the CTBN modified copolymers prepared from the low molecular weight resin (DVERL) has been discussed in a previous paper [11]. The system is initially homogeneous, but at low CTBN concentrations (≤ 5 wt%), CTBN is separated during curing in the form of irregular inclusions in the main phase, the rigid DVER-S matrix. This morphology was confirmed by TEM and SEM of the fracture surfaces. However, at high concentrations (5 to 10 wt%) a cocontinuous structure develops which spans the whole sample (Fig. 3).

Fig. 3 shows the TEM micrograph, obtained from the OsO_4 stained samples, of the DVERL-S copolymer with 10% CTBN. The material shows a uniform nodular morphology constituted by linked nodules with diameters in the range of 1–5 μm (clear gray areas). The nodules are formed of DVERL-S crosslinked copolymer. Surrounding the nodular microstructure there is a

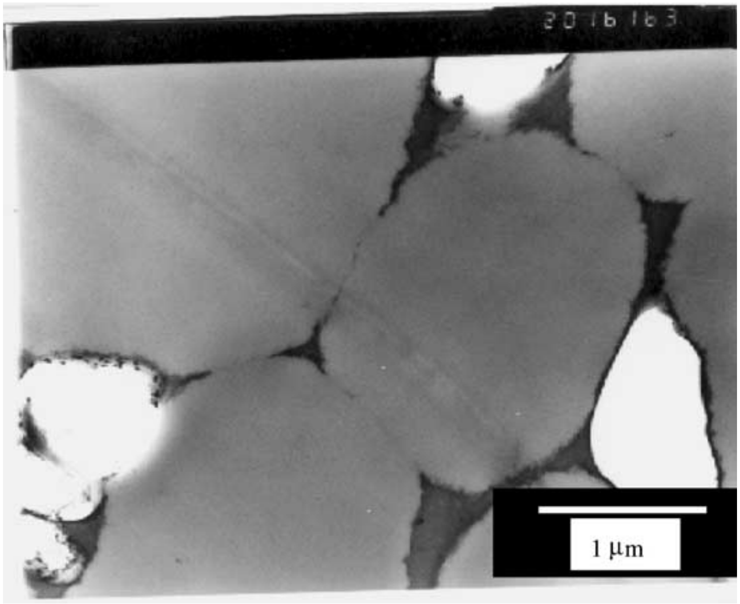
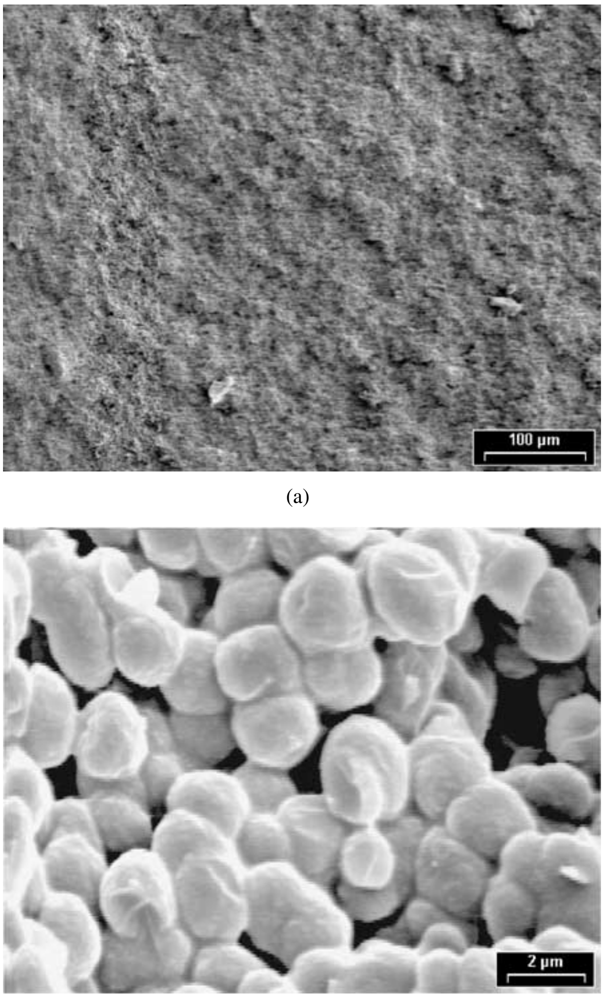


Figure 3 TEM of the DVERL-S/10% CTBN. Line represents 1 μm.



(a)

(b)

Figure 4 SEM of fracture surfaces. (a) DVERL-S/10%CTBN at 200× and (b) DVERL-S/10%CTBN at 7800×.

continuous minor phase rich in the CTBN liquid rubber as shown by the dark gray areas. White areas correspond to the microvoids formed during the curing of the samples. This morphology is the result of the phase separation originated by the "polymerization induced-phase separation" mechanism, occurring from an initially homogeneous solution.

Fig. 4a and b shows SEM micrographs of the fracture surface of the DVERL-S networks modified with 10% of CTBN at two different magnifications. The nodular microstructure is clearly visible and it spans the whole sample. Actually, the fracture surfaces of these specimens were rough even to the naked eye and the material showed poor adhesion between the phases. Similar structures have been previously described for UPE-S with 10% by wt. of PVAc [3, 18].

3.2.2.2. High molecular weight resins. The materials prepared from the high molecular weight resins present two main regions: one corresponds to a rich DVER-S region with or without rubber inclusions; the other shows the nodular DVER-S formation surrounded by elastomer. Fig. 5 shows a TEM micrograph of this type of material, where the nodular region can be observed. There are copolymer formations of irregular form and also some evidence of microvoiding (white areas).

Fig. 6a and b shows the fracture surfaces for the DVERC-S/CTBN samples at 5 and 10 wt% of elastomer. The nodular regions appear as large spherical domains, "islands", of different sizes (between 20–60 μm) included in the main DVERC-S rich region. These domains were originated at the start of the reaction. Initially two macrophases were present: a CTBN-rich phase, which will be the minor phase in the final material and a CTBN-poor phase, which will form the majority of the continuous phase. Curing in the separated macrophases occurs as independent reactions. The phase separation process induced by polymerization takes place at different rates in each of the two initially homogeneous macrophases. Inside the "islands", rich in CTBN, a nodular structure is generated in much the same way as in the DVERL-S modified system, with a continuous phase rich in the elastomer. Outside these domains, the continuous DVERC-S rich phase undergoes phase separation forming very small well dispersed CTBN spherical particles, as discussed later on this paper.

Features typical of brittle fracture are observed in the main region. Comparison of Fig. 6a and b shows that the concentration of "islands" increases as the overall concentration of CTBN in the formulation increases. The fracture surface of the DVERH-S/5%CTBN is shown in Fig. 6c. There are less "river marks" in the main phase of this material, probably as a consequence of the higher molecular weight of the resin.

Fig. 7a and b is larger magnifications of the DVERC-S and DVERH-S systems modified with 5% CTBN. These micrographs show that the main copolymer rich phase has small rubber inclusions in the DVERC-S network, which are not observed in the high molecular weight system, an observation also true for the systems containing 10% of CTBN. The number of these rubber particles increases with the amount of added CTBN, as it could be expected. Taking into account the initial miscibility of the modified systems, one could conclude that for the DVERH-S system, more elastomer is concentrated in the "island" regions and less is left in the main phase from the beginning of the reaction. Therefore, essentially no simple inclusions are observed in the main phase for this network. Besides, the lower molecular weight tail of the DVERH distribution is most probably segregated towards the elastomer rich phase. Since the resin contains a small low molecular weight fraction, less resin is concentrated in the "islands". Initial miscibility and segregation of the resin would contribute to the formation of small not fully conneted nodules in the CTBN rich phase.

3.2.3. Copolymers modified with VTBN: effect of the resin molecular weight

The behavior of the systems DVER-S-VTBN is more complex because the VTBN is vinyl end functionalized and cannot be considered inert during the copolymerization reaction. The reactive mixture behaves as a quaternary system with three monomers, DVER, S

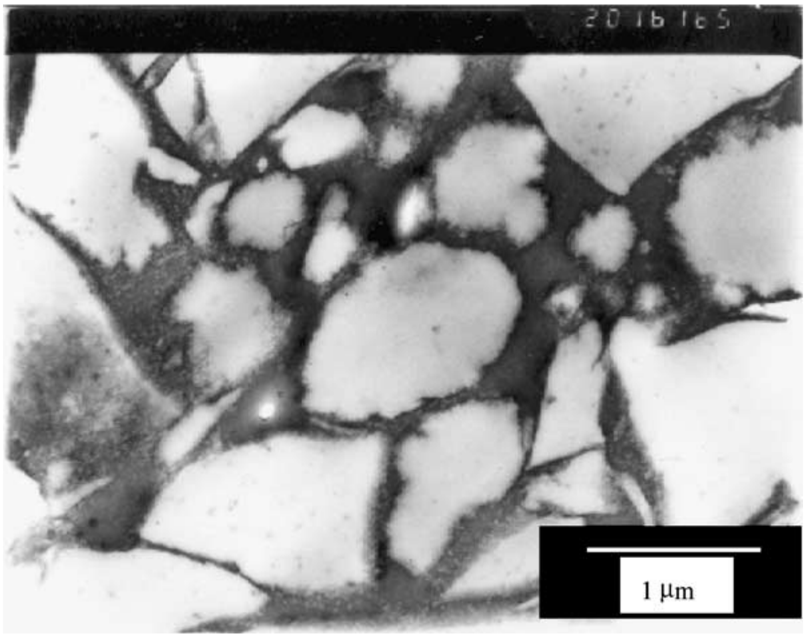


Figure 5 TEM of the DVERC-S/10% CTBN. Line represents 1 μm.

and VTBN, and a terpolymer generated by the copolymerization of the three monomers. The elastomer rich blocks of the copolymer segregate during the reaction, generating elastomer-rich regions and DVER-S rich regions. However, this segregation is not as neat and clear as in the CTBN case because the blocks are chemically linked.

Fig. 8a, b and c shows the scanning micrographs of the 10% VTBN modified systems. The use of the low molecular weight resin generates the same type of granular morphology throughout the whole sample. The fracture surface is rough, but without major changes in the fracture plane. A larger magnification of the DVERL-S/10% VTBN surface (Fig. 9a) allows to distinguish that the granular topography is formed by the existence of continuous brittle regions (copolymer rich regions) and continuous regions with nodular structure, where the block elastomer is partially segregated surrounding copolymer rich nodules.

For the two higher molecular weight systems, the surface shows steps in the fracture plane, some voids and almost circular regions with no apparent internal structure, which are more easily observable in the commercial system.

The micrograph in Fig. 9b shows the DVERC-S rich phase with cavities that indicate the presence of rubber inclusions. To the right of the micrograph there is a portion of one of the circular structureless regions (probably single phase regions). The same magnification for the VTBN modified DVERH-S is shown in Fig. 9c. The same type of structureless regions appear in this material, although much reduced in size. Besides, there are no rubber inclusions in the main phase of the network. The reduced size of the separated phase in the VTBN modified systems as compared to the CTBN systems is obviously due to the reactivity of the former and the inert behavior of the latter with respect to the copolymerization reaction.

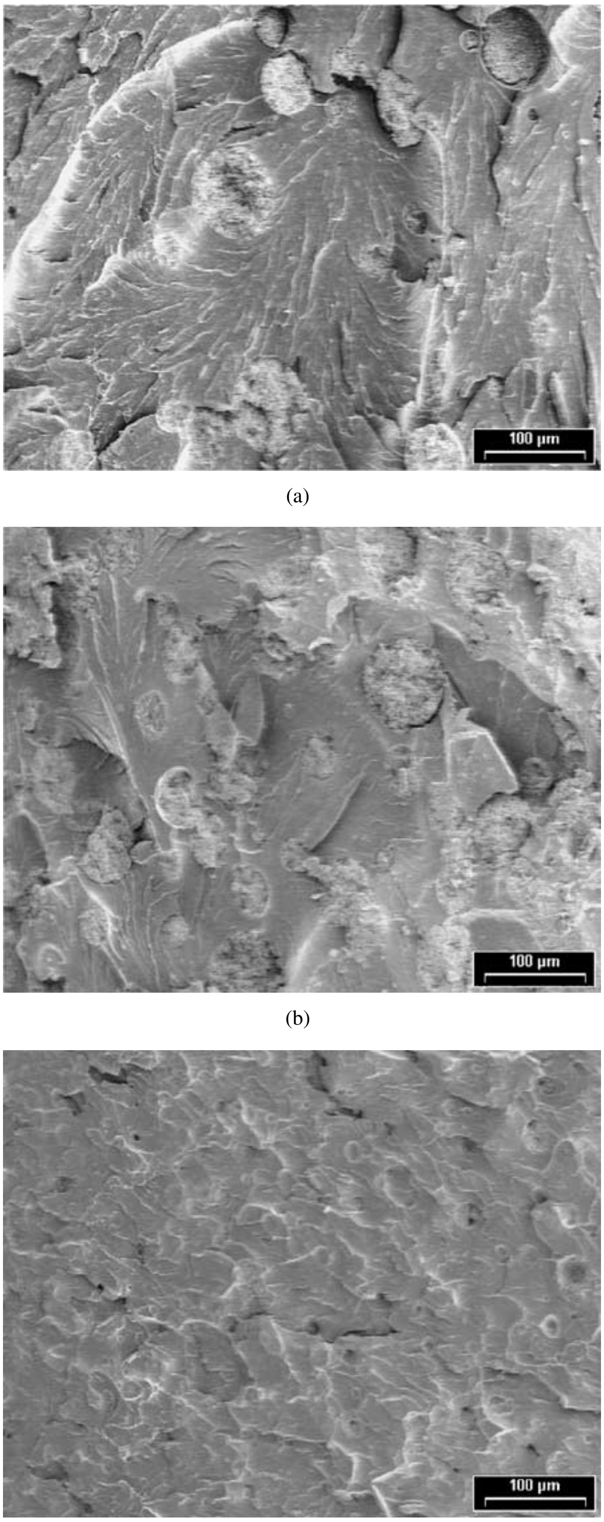
TABLE IV Dynamic mechanical properties of the modified networks at different concentrations of the elastomers

	T_g (°C)	E' rubber (MPa)	E' glass (GPa)	Density (g/cm^3)
5% CTBN				
DVERL-S	125.4	37.3	2.26	1.077 ± 0.012
DVERC-S	87.8	16.5	2.02	1.098 ± 0.003
DVERH-S	83.5	11.6	2.65	1.115 ± 0.003
10% CTBN				
DVERL-S	149.2	22.1	1.65	0.975 ± 0.010
DVERC-S	90.9	16.0	1.41	1.087 ± 0.005
DVERH-S	79.1	10.7	2.43	1.106 ± 0.005
5% VTBN				
DVERL-S	107.2	43.9	2.77	1.130 ± 0.002
DVERC-S	93.2	22.7	1.44	1.118 ± 0.001
DVERH-S	76.1	13.1	2.06	1.124 ± 0.004
10% VTBN				
DVERL-S	122.3	43.8	2.23	1.124 ± 0.002
DVERC-S	90.6	25.93	1.97	1.101 ± 0.017
DVERH-S	83.26	12.1	2.20	1.103 ± 0.002

3.2.4. Dynamic mechanical analysis

The thermomechanical transitions of the networks modified with different amounts of additives, CTBN and VTBN, were determined from dynamic mechanical tests. The materials present two transitions, one at low temperatures (−30 to −50°C) and the other at high temperatures, which corresponds to the glass transition temperature of the DVER-S network. Both temperatures are measured as the temperatures of the maxima in tan δ. Table IV includes a summary of the main DMA results obtained for the neat and modified networks. The data are presented to facilitate the analysis of the effect of the molecular weight of the initial resins.

The glass transition temperature of the main phase (copolymer DVER-S) decreases with the molecular weight of the original resin. For the DVERL-S system the width of the glass transition is particularly large at

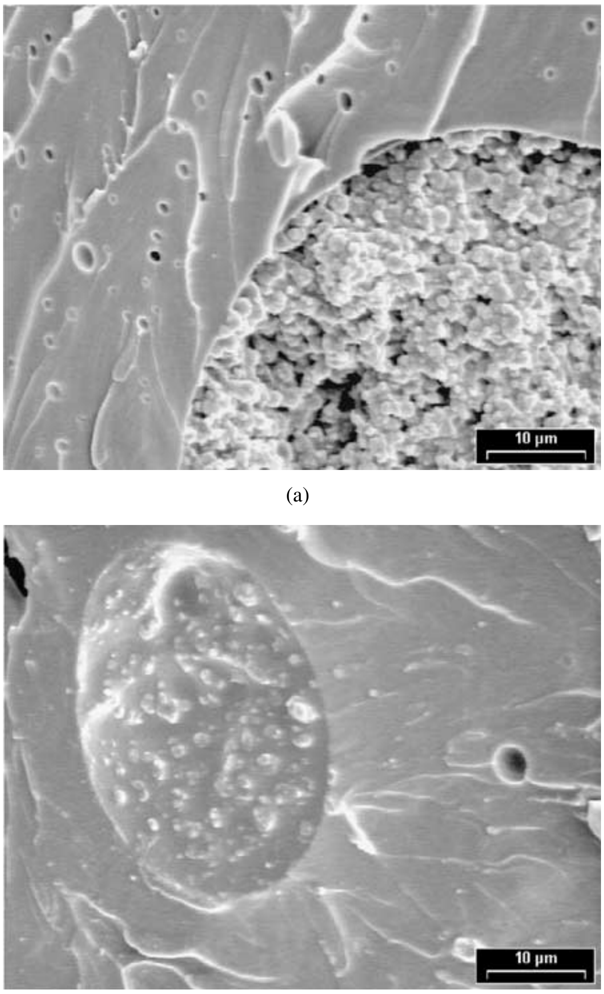


(a)

(b)

(c)

Figure 6 SEM of fracture surfaces. (a) DVERC-S/5%CTBN at 200×, (b) DVERC-S/10% CTBN at 200×, and (c) DVERH-S/5%CTBN at 200×.



(a)

(b)

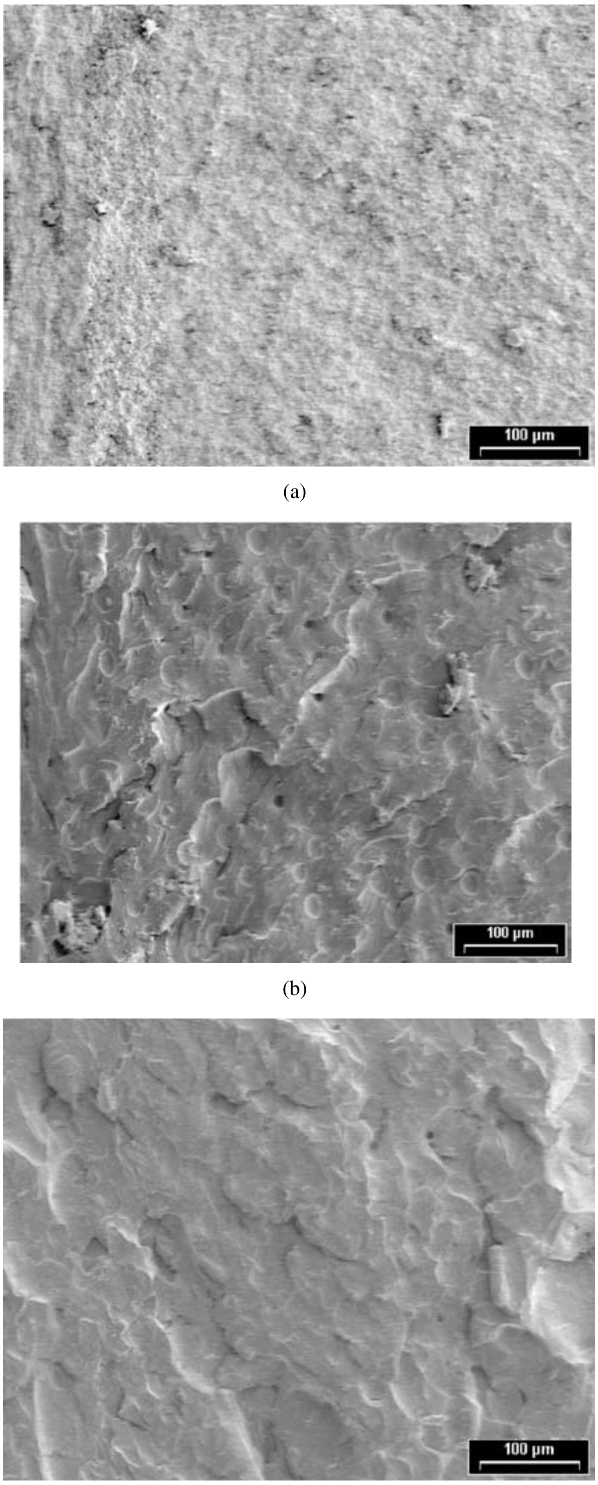
Figure 7 SEM of fracture surfaces. (a) DVERC-S/5%CTBN at 2000× and (b) DVERH-S/5% CTBN at 2000×.

the 5% CTBN and 10% VTBN, concentrations at which the change in the type of morphology occurs for these two systems. In some cases the addition of elastomer produced an increment in the T_g of the modified network. The explanation is the partial migration of the styrene to the rubber-rich phase. During cure the probability of direct reaction between DVER double bonds (or through shorter S-S links) is increased, leading to a more rigid network and thus to a higher T_g. The reduced concentration of styrene in the main phase leads to reduced segment mobility in that region.

The values of the rubber storage modulus, E' rubber, also decreases with the molecular weight of the original resin, indicating that it depends mainly on the crosslinking density of the system. Again, the exception is the DVERL-S/10% CTBN that has a too low modulus, due to the cocontinuous structure of this sample. Since the CTBN rich phase is also continuous in this sample, the low modulus of the elastomer would influence in a larger degree the final property than it does in the other cases (discontinuous elastomeric phase), with the additional detrimental effect of the presence of microvoids.

On the other hand, the values of the densities of the modified copolymers follow the trend already discussed for the neat systems, that is $\rho_{\text{DVERL-S}} > \rho_{\text{DVERH-S}} > \rho_{\text{DVERC-S}}$. The clearest exception to this trend is DVERL-S/10% CTBN where generalized microvoiding was observed and already discussed.

The analysis of the values of the E' glass is more complex than the analysis for the storage modulus above the glass transition temperature, there exists general trends only when the morphologies of the systems are similar. That is, when two samples exhibit different types of morphology, the general trend is not obeyed.

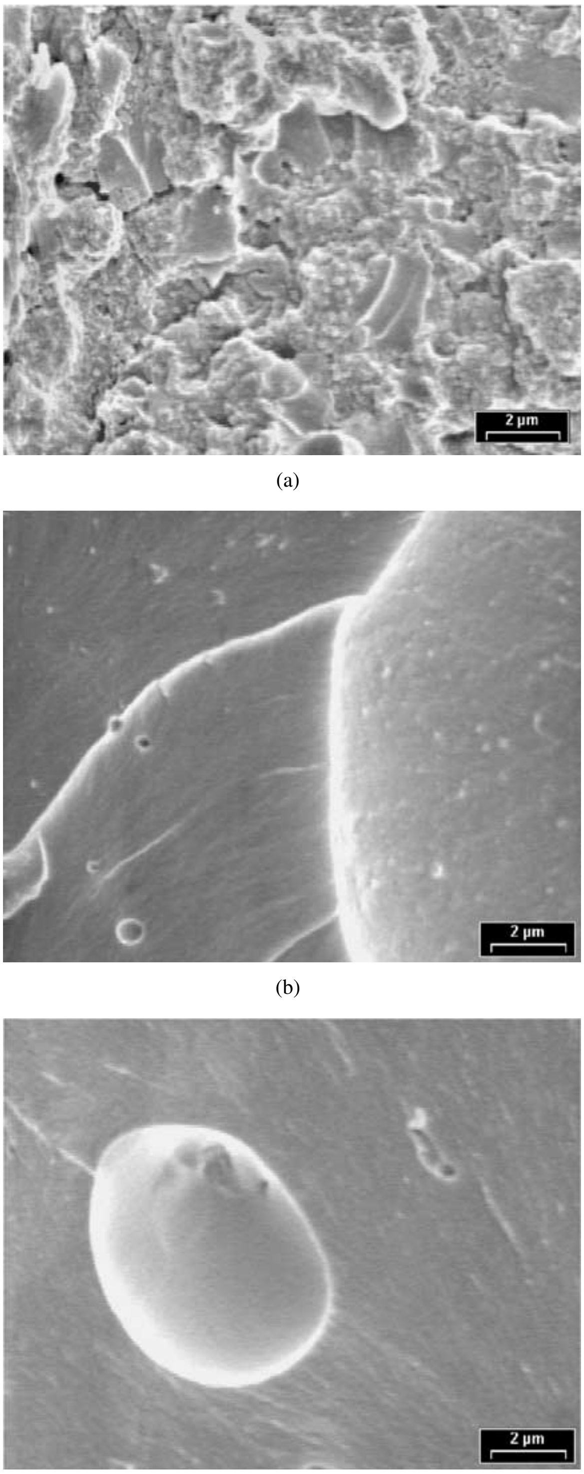


(a)

(b)

(c)

Figure 8 SEM of fracture surfaces. (a) DVERL-S/10%VTBN at 200×, (b) DVERC-S/10% VTBN at 200×, and (c) DVERH-S/10% VTBN at 200×.



(a)

(b)

(c)

Figure 9 SEM of fracture surfaces. (a) DVERL-S/10%VTBN at 7800×, (b) DVERC-S/10% VTBN at 7800×, and (c) DVERH-S/10% VTBN at 7800×.

If the morphology corresponds to a continuous matrix (with or without inclusions) as in the neat systems and all the 5% VTBN modified networks, it is seen that:

$$E'\text{glass DVERL-S} > E'\text{glass DVERH-S} > E'\text{glass DVERC-S.}$$

In all the other cases is still valid that E' glass DVERH-S > E' glass DVERC-S, which present similar morphologies (a continuous main phase with separated different regions).

The networks generated from DVERL-S need a more detailed analysis : DVERL-S/5%VTBN was included in the previous analysis; DVERL-S/10% VTBN shows a structure with nodular regions and copolymer-rich regions, and apparently both regions are continuous. The result is the reduction of the modulus:

$$E' \text{ glass DVERL-S} \sim E' \text{ glass DVERH-S} > E' \text{ glass DVERC-S.}$$

TABLE V Physical and mechanical properties of the networks modified with different concentrations of CTBN

	Density (g/cm^3)	E_f (GPa)	σ_y (MPa)	K_{IC} (MPa/m$^{1/2}$)
DVER L-S				
5	1.075 ± 0.012	2.81 ± 0.18	69.1 ± 1.3	0.80 ± 0.05
10	0.975 ± 0.010	1.13 ± 0.02	42.7 ± 4.1	0.30 ± 0.03
DVER C-S				
5	1.098 ± 0.003	2.14 ± 0.03	69.7 ± 1.0	1.53 ± 0.09
10	1.085 ± 0.005	1.75 ± 0.07	53.5 ± 0.6	1.82 ± 0.05
DVER H-S				
5	1.113 ± 0.003	2.85 ± 0.03	69.6 ± 5.1	1.49 ± 0.13
10	1.105 ± 0.005	2.38 ± 0.03	51.9 ± 3.0	1.41 ± 0.33

TABLE VI Physical and mechanical properties of the networks modified with different concentrations of VTBN

	Density (g/cm^3)	E_f (GPa)	σ_y (MPa)	K_{IC} (MPa/m$^{1/2}$)
DVER L-S				
5	1.130 ± 0.002	3.30 ± 0.19	76.6 ± 2.4	1.31 ± 0.05
10	1.122 ± 0.002	2.68 ± 0.06	64.8 ± 2.2	1.46 ± 0.10
DVER C-S				
5	1.119 ± 0.001	2.44 ± 0.03	67.5 ± 1.3	1.61 ± 0.09
10	1.100 ± 0.018	2.20 ± 0.06	60.0 ± 3.1	1.85 ± 0.17
DVER H-S				
5	1.124 ± 0.004	2.79 ± 0.02	69.7 ± 2.8	1.66 ± 0.33
10	1.103 ± 0.002	2.50 ± 0.02	60.4 ± 3.1	1.80 ± 0.24

At 5% CTBN, E' glass DVERL-S < E'glass DVERH-S. The first system shows the nodular morphology throughout the entire sample, while the second one shows nodular discontinuous regions immersed in a continuous copolymer region.

At 10% CTBN, E' glass DVERC-S < E' glass DVERL-S < E' glass DVERH-S. The modulus of the DVERL-S/10% CTBN is the low in the series due to the global nodular structure and microvoiding (Table IV).

3.2.5. Physical and mechanical properties of the modified networks

The density average values of the modified copolymers are reported in Tables V and VI. The systems modified with VTBN show a slight decrease in density with the addition of the elastomer. The changes are gradual and follow an identical trend for the three different resins. In general, the addition of CTBN generates materials with lower density than those modified with VTBN, a consequence of the microvoiding observed in CTBN modified systems. The drop in density is dramatic in the case of the low molecular weight system, where microvoiding occurs throughout the whole material. Voids notoriously affect the mechanical behavior of the modified networks. By using the rule of mixtures the theoretical density of the material with additives can be calculated and the conclusion is that there is a small but not negligible amount of voids in the materials. In general the fraction of voids increases when the DVER molecular weight decreases and the rubber concentration increases. The calculated void fractions $\rho_{\text{rubber}} = 1.06\ \text{g/cm}^3$, for both elastomers) were between 0.4 and 1.9% for the VTBN modified resins and between 1.3 and 5.7% for the CTBN modified networks. The sample with the largest fraction of voids is DVERL-S/10% CTBN. In this case, the calculated void fraction is 14.2%, hence the mechanical properties are reduced.

From the results presented in Tables V and VI, it is evident that as the amount of additive is increased the densities of the materials are reduced as are the flexural moduli, E_f, and the yield stresses in compression, σ_y. In particular, the mechanical properties of the DVERL-S/10% CTBN show a large drop with respect to the samples with lower CTBN content, due to the large amount of microvoiding in this sample and the resulting reduced cohesion of the material. Moreover, the fracture properties are also negatively affected because such a large percentage of voids in the sample act as points of failure in the material. The material becomes very brittle and crack growth progresses easily through the whole sample.

As observed in Tables V and VI all the modified materials show better fracture properties than the neat systems, with the exception of the DVER L-S with 10% of CTBN. In general the increment in toughening of the modified networks is accompanied by a decrease in the rigidity of the material. The resins of higher molecular weight show a similar behavior with slightly better properties for the DVERC-S system.

A behavior similar to that described here has been reported by Huang *et al.* [19] for unsaturated polyester-styrene and additives such as polyvinylacetate (PVAc) and polyurethane (PU). They found a maximum in the fracture toughness with the addition of 5% of PVAc or with 10% of PU. Those systems also showed microvoid formation and a cocontinuous structure around the maximum in toughness, indicating that the presence of disperse microvoids was more efficient to improve toughness than microvoids confined to a single dispersed phase [8]. The toughness increment was related to the crack tip blunting produced in the matrix due to the presence of the microvoids, which delay the crack propagation. A larger concentration of additives, increases the microvoid concentration and at some point the concentration is so high that an adverse effect is observed and the crack propagates through the plane of voids. These two contrary effects produce a maximum in the properties, which is clearly visible in the DVER L-S presented in this work, where the phase separation and microvoid formation is more generalized.

Summarizing, the K_{IC} value increases with the percentage of additive in the case of the two higher molecular weight resins, where microvoid formation represents a relatively low volume fraction of the material, contributing to the crack blunting and reducing the rate of crack propagation. This effect may be also responsible of the behavior of the DVER L-S system modified with VTBN, but in the case of the CTBN modification of this network the generation of microvoids is too high and K_{IC} drops because of the propagation of the crack through the voids.

The present behavior is also in agreement with the model presented for Kinloch and Williams, originally proposed for epoxy networks with rubber inclusions [20]. From the analysis of the correlation between K_{IC} with σ_y, they concluded that the toughening observed was the result of the crack tip blunting in the matrix, consequence of the lower σ_y values. Again, the exception to this conclusion is the DVERL-S system with 10% CTBN, which is obviously due to the fact that it does not correspond to the physical model of a matrix with second phase-inclusions considered by Kinloch [11].

4. Conclusions

The room temperature mechanical properties of the materials (neat and modified) showed good correlation with the densities of the materials whenever a continuous main phase is present. In those cases, properties such as flexural modulus or yield stress in compression are higher for the low molecular weight derived networks, followed by the networks prepared from high molecular weight and the commercial (intermediate molecular weight) resins. The materials with lower modulus are tougher.

The addition of elastomers produces toughening of the networks, but at the same time a reduction of their mechanical properties. There is a continuous decrease of the flexural modulus and compression yield stress of the materials as more VTBN is added, but there is a dramatic drop of properties in the case of the DVERL-S/10% CTBN. The reason for this different behavior is the generated morphology, that in the latter case corresponds to a nodular two phase microstructure that spans the whole sample. Although VTBN leads to initially less compatible systems, it produces a finer phase separation due to its terminal reactive groups, through which it is incorporated (co-reacted) to the DVER-S network.

On the other hand, the rubber storage modulus and the glass transition temperature of these materials show a good correlation with the crosslinking density of the network, as it should be expected. The addition of VTBN produced minor changes in the values of the rubber modulus and the same is true for the T_g values. However, the width of the transition was increased in some cases (related to the change in the type of morphology of the material).

The addition of CTBN produced larger changes as the amount of CTBN was increased and the molecular weight of the resin was reduced. In general, the addition of this elastomer reduced the E' glass values more than the addition of VTBN. On the other hand, an increment of the T_g values was observed in some cases indicating that the styrene has passed to the elastomer rich phase, reducing its concentration in the main phase. This lower concentration of styrene reduced the mobility of the polymeric segments in the main phase and thus, T_g increased.

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