

Poly(methyl methacrylate)-Modified Vinyl Ester Thermosets: Morphology, Volume Shrinkage, and Mechanical Properties

Walter F. Schroeder, Julio Borrajo, Mirta I. Aranguren

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata–National Research Council for Science and Technology (CONICET), Avenida Juan B. Justo 4302, (7600) Mar del Plata, Argentina

Received 25 April 2007; accepted 29 June 2007

DOI 10.1002/app.27006

Published online 4 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermoset materials obtained from styrene/vinyl ester resins of different molecular weights modified with poly(methyl methacrylate) (PMMA) were prepared and studied. Scanning electron microscopy and transmission electron microscopy micrographs of the fracture surfaces allowed the determination of a two-phase morphology of the modified networks. Depending on the molecular weight of the vinyl ester oligomer, the initial content of the PMMA additive, and the selected curing temperature, different morphologies were obtained, including the dispersion of thermoplastic-rich particles in a thermoset-rich matrix, cocontinuous structures, and the dispersion of thermoset-rich particles in a thermoplastic-rich matrix (phase-inverted structure). Density measure-

ments were performed to determine the effect of the PMMA-modifier concentration and curing temperature on the volume shrinkage of the final materials. The development of cocontinuous or thermoplastic-rich matrices was not too effective in controlling the volume shrinkage of the studied vinyl ester systems. The evaluation of the dynamic mechanical behavior, flexural modulus, compressive yield stress, and fracture toughness showed that the addition of PMMA increased the fracture resistance without significantly compromising the thermal or mechanical properties of the vinyl ester networks. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4007–4017, 2007

Key words: blends; fracture; mechanical properties

INTRODUCTION

A significant number of composite materials currently manufactured for structural applications are made from thermoset resins. Epoxy-based vinyl ester (VE) resins were developed to incorporate the generally superior cast-resin properties of epoxies with the ease of fiber reinforcement processing during conventional fabrication routes of composite materials.^{1,2} Although these materials give a better overall performance than that offered by the more common unsaturated polyester (UP) resins, they still have poor resistance to crack propagation and present high volume shrinkage that occurs during polymerization. The addition of fillers and reinforcements partially alleviates the volume shrinkage, but the phenomenon is not completely inhibited.³

To improve the toughness of thermoset resins, two methods may be selected: the addition of a plasticizer and the amplification of deformation mechanisms by the generation of a heterogeneous structure. The first option is usually discarded because the addition of a low glass-transition temperature component to the formulation not only affects the fracture behavior of the system but also greatly reduces the thermal and mechanical performance of the thermoset. The second option has been applied with more success by the addition of preformed particles^{4–6} or by *in situ* formation of the particles with a technique called polymerization-induced phase separation. This method consists of preparing a reactive homogeneous mixture of thermoset precursors [e.g., VE and styrene (St)] and the modifying additive. As the reaction proceeds, the reacted VE–St copolymer becomes incompatible with the unreacted liquid mixture, and phase separation occurs. The developed two-phase structure influences the thermal, mechanical, and fracture properties of the obtained material. Although most reported studies on VE modification concern the use of rubber additives, in which the generation of a second elastomeric phase takes place in the thermoset matrix, the improvement in toughness is inevitably accompanied by a significant loss in the elastic modulus and

Correspondence to: M. I. Aranguren (marangur@fi.mdp.edu.ar).

Contract grant sponsor: National Research Council for Science and Technology.

Contract grant sponsor: National Agency for the Promotion of Science and Technology.

Contract grant sponsor: National University of Mar del Plata.

Journal of Applied Polymer Science, Vol. 106, 4007–4017 (2007)
© 2007 Wiley Periodicals, Inc.

yield strength.^{7,8} Therefore, the use of thermoplastics possessing a high modulus, a high glass-transition temperature, and a high level of toughness has attracted attention in recent years.

UP resins, like VE, are usually copolymerized with St monomer via free-radical crosslinking reactions to form a three-dimensional network. The cure of UP resins is accompanied by a high degree of polymerization shrinkage (normally 7–10%). Thermoplastics are used in blends with UP resins to improve the surface quality of molded parts, reducing the overall resin shrinkage during the curing step.^{9,10} These modifiers are called low-profile additives (LPAs), and the purpose of their inclusion is to compensate for the shrinkage of the resin at a minimum cost to the other properties. One of the most commonly used thermoplastics is poly(vinyl acetate) (PVAc), which has been reported to fulfill the low-profile requirement; it consists of a UP–St reacted copolymer and a thermoplastic modifier phase-separating during polymerization, forming a cocontinuous structure.^{11,12} Tensile stresses arising from internal thermal and curing contractions in the presence of mechanical constraints (e.g., a closed mold) provoke cavitation in the weak PVAc-rich phase. These cavities compensate for the shrinkage of the part, leading to a good copy of the mold's surface.

Although the degree of miscibility between an epoxy-based VE resin and a thermoplastic additive has been cited as a significant characteristic for achieving a suitable morphology to obtain a low-profile effect,¹³ no detailed studies of the initial miscibility of the modified system and the influence of the cure conditions on the phase-separation process are available in the literature.

A thermodynamic analysis of the initial solubility of an St/VE/poly(methyl methacrylate) (PMMA) system, its evolution during cure, and the nature of the developed phases were the subjects of a previous article.¹⁴ In this work, an analysis of the morphologies obtained with different PMMA concentrations and curing conditions, as well as the resulting volume shrinkage and final properties of the modified thermosets, is presented and discussed.

EXPERIMENTAL

Materials and sample preparation

Two VE resins were selected for this work. A VE monomer of a low molar mass (VE_L) was synthesized through the reaction of a diglycidyl ether of bisphenol A epoxy resin (DER 332, Dow Chemical Co., Freeport, TX; epoxy equivalent weight = 175 g/equiv) with methacrylic acid (Norent Plast S.A., Buenos Aires, Argentina; laboratory-grade reagent) and triphenylphosphine (Fluka A.G., Buchs, Switzerland;

analytical reagent) as a catalyst. The final conversion, monitored by titration of the residual acid groups and by Fourier transform infrared (Genesis II, Mattson, Madison, WI), was higher than 97%, and the final product was stabilized with 500 ppm hydroquinone. The second VE was a commercial resin (VE_C; Derakane Momentum 411-350; Dow Chemical). The molar masses of both VEs were measured by size exclusion chromatography (SEC; model 440, Waters, Milford, MA) with PLgel columns (Phenomenex; Torrance, CA) of 100, 500, 10³, 10⁴, and 10⁶ Å in distilled tetrahydrofuran (Laboratorios Cicarelli, Buenos Aires, Argentina; analytical reagent) with a flow rate of 1 mL/min and with polystyrene calibration. The densities of both VEs were determined with a precision balance (Becker and Sons, New Rochelle, NY).

Table I summarizes the characteristics of all the components used in this work.

Crosslinking reactions were carried out, with a VE/St ratio of 55 wt % to 45 wt % maintained (Poliresinas San Luis S. A., San Luis, Argentina; laboratory-grade reagent), with 2 wt % benzoyl peroxide (Luzidol 75%, Akzo Chemicals S.A., Buenos Aires, Argentina) as an initiator and 0.4 wt % *N,N*-dimethylaniline (Akzo Chemicals) as a promoter of the cure reactions at 40°C. All materials were used as received.

The PMMA modifier was supplied by Aldrich Chemical Co. (Milwaukee, WI). The average molar masses were measured by SEC (ALC 244, Waters) with Shodex columns (A 802, 803, 804, 805, and 806/S) with both refractive-index and specific-viscosity detection on line (model 200, Viscotek, Houston, TX). Average molecular weights were determined with universal calibration (Table I).

The modified samples were prepared by the addition of PMMA in a proportion of 5–20% with respect to the total weight. The PMMA particles were initially dissolved in St and then were mixed with the VE and remaining St to reach the final composition.

TABLE I
Characterization of the Components

	St	VE _L (synthesized)	VE _C (commercial)	PMMA
M_n (g/mol)	104	600 ^a	950 ^a	41,500 ^a
M_w/M_n	1.00	1.06	2.05	1.93
Density at 25°C (g/cm ³)	0.91 ^b	1.16 ^b	1.16 ^b	1.19 ^c

M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Measured by SEC with tetrahydrofuran as the solvent at 1 mL/min.

^b Measured with a precision balance for densities (Becker and Sons).

^c Taken from the supplier's catalogue (Aldrich Chemical Co.).

To make samples for compression testing, a reactive mixture of the monomers (with or without the PMMA modifier) was injected into a glass cylinder 6 mm in diameter that was previously sprayed with a silicone release agent. After removal from the molds, the compression specimens were carefully machined to reach the final dimensions (length/diameter = 1.5–2) and to obtain perfect parallelism for the upper and lower base surfaces.

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

Electron microscopy

Specimens fractured in liquid nitrogen were further sputter-coated with gold–palladium (Vacuum Desk II, Denton, San Antonio, TX) at 5–10 Pa and 45 mA for 30 s. The fracture surfaces of the samples were observed with a scanning electron microscope (JSM 6460 Lv, JEOL, Akishima, Japan) at a 15-kV accelerating voltage.

Samples to be studied by transmission electron microscopy (TEM) were sectioned in an LKB ultramicrotome with a diamond knife. The rigidity of the obtained materials was high enough to prepare high-quality, ultrathin sections at room temperature. The section thickness was 60 nm for all studied samples to compare the different morphologies. This study was performed on a transmission electron microscope (100 CX, JEOL, Akishima, Japan) operated at 80 kV.

Physical and mechanical testing

The densities of the unreacted liquid mixtures (neat St–VE and St–VE containing different amounts of the PMMA modifier) were measured by weighing techniques with a density balance (precision = 10^{-4} g/cm³; Becker and Sons) at room temperature ($25 \pm 0.5^\circ\text{C}$). This method is based on Archimedes principle and requires the calibration of the balance with degassed and distilled water at room temperature. On the other hand, the densities of the cured materials were obtained with cylindrical specimens and careful machining of parallel bottom and top faces. The density values were obtained from the weights of the specimens and the volume calculated from their measured dimensions (ASTM D 1895-89). The reported values are the averages of the densities measured for five different specimens. The standard deviation was in all cases lower than 0.005 g/cm³.

Dynamic mechanical tests were performed with a PerkinElmer (Norwalk, CT) 7e on rectangular bars 2 ± 0.1 mm thick and 3 ± 0.1 mm wide. 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 $5^\circ\text{C}/\text{min}$. The applied static stress was 0.5 MPa, and the dynamic stress was 0.35 MPa.

Mechanical tests were carried out with a model 4467 electromechanical universal testing machine (Instron, Canton, MA). Flexural moduli were measured with a three-point bending geometry according to ASTM D 790M-93 specifications. Compression test specimens were deformed between metallic plates lubricated with molybdenum disulfide according to ASTM D 695-91, which corresponds to the compressive properties of rigid plastics.

Fracture mechanics measurements were made at room temperature with a three-point bending geometry at a crosshead displacement rate of 10 mm/min with the Instron model 4467 universal testing machine. Test specimens were prepared by rectangular bars being cut from slabs with a diamond saw. Central V-shaped notches were machined in the bars, and then a razor blade was positioned in the notch and gently tapped to induce the growth of a natural crack ahead the blade. The crack length was measured post mortem in a Praxi profile projector (Aro S.A., Buenos Aires, Argentina) with a $20\times$ magnification. The critical stress intensity factor at the onset of crack growth (K_{IC}) was calculated according to the ASTM D 5045-93 specifications with single-edge-notched specimens.

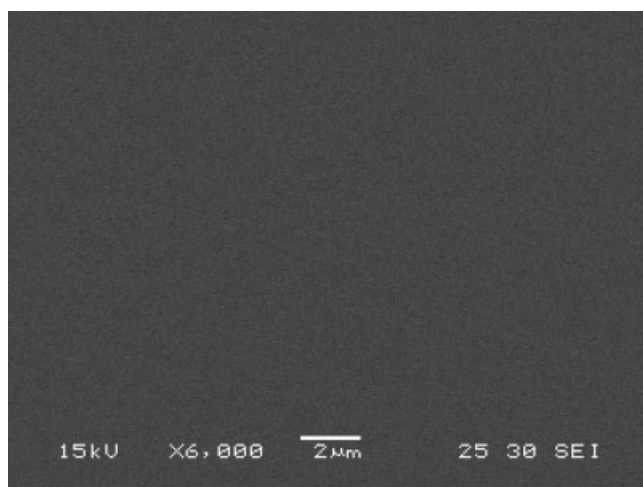
RESULTS AND DISCUSSION

Morphological characterization

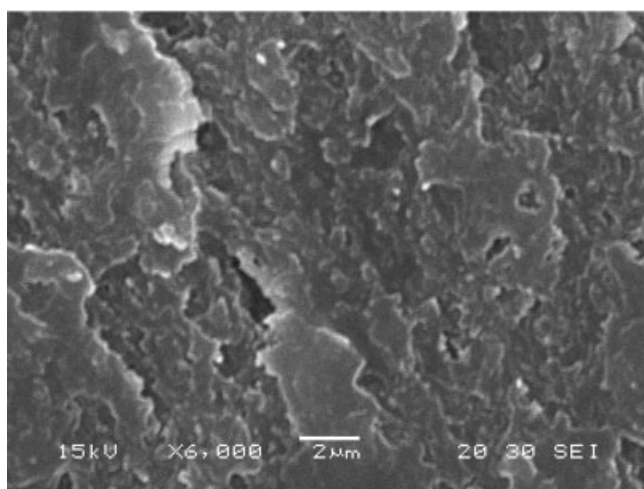
The morphologies of the final cured materials showed differences depending on the molecular weight of the VE, the content of the PMMA modifier in the formulation, and the curing temperature selected. These differences had a correlation with the final properties of the materials, as discussed in the following sections.

The observation by scanning electron microscopy (SEM) and TEM of the neat St–VE_L and St–VE_C networks cured at 40 and 80°C indicated that they constituted homogeneous systems that fractured in a brittle way without showing any special features of the fracture surfaces. This can be observed in Figure 1(a), which shows an unmodified St–VE_L system cured at 80°C . A practically flat fracture surface was obtained that showed no phase-separation feature, and this was in agreement with the transparent, yellow macroscopic aspect of that sample.

PMMA-modified specimens were translucent, with the opacity increasing gradually with the thermoplastic content. These features of the samples obviously had a correlation with the morphology generated by the polymerization-induced phase-separation



(a)



(b)

Figure 1 SEM micrographs of the fracture surfaces of St-VE_L samples cured at 80°C: (a) an unmodified sample and (b) a sample containing 10 wt % PMMA.

mechanism. The thermodynamic analysis of the initial miscibility of the St-VE-PMMA system and its evolution during curing, which was reported by the authors in a previous article,¹⁴ allowed the explanation of the nature and origin of these phases in the observed morphologies. Briefly, it consisted of aggregates of irregular nodular particles of the St-co-VE copolymer surrounded by the PMMA-rich phase.

Figure 1(b) shows the SEM morphology of the material obtained from St-VE_L modified with 10 wt % PMMA and cured to 80°C. A very irregular fracture surface consisting of aggregates of irregular nodular particles can be observed. As shown, these nodules were formed by the St-co-VE crosslinked copolymer, and surrounding the nodular aggregates and confined to the interstitial space between them was the PMMA-rich phase. Although the materials obtained with different amounts of PMMA (between 5 and

20 wt %) presented similar morphological features, the level of separation of the dispersed PMMA phase and the irregularity of the fracture surface increased with the amount of the thermoplastic in the initial formulation. These obtained morphologies were similar to those presented in previous studies on St-VE thermosets modified with elastomers^{7,15} and UP resins modified with different thermoplastics,^{3,16,17} all of them in the range of 5–15 wt % modifier. It has been previously reported that this type of morphology generated in elastomer-modified VE resins leads to materials of low interfacial cohesion and reduced mechanical and thermal properties.⁷ In this case, because of the better properties of the thermoplastics at room temperature, this problem was somehow alleviated.

The samples obtained from the St-VE_L system modified with 5–15 wt % PMMA cured at 40°C presented SEM morphologies very similar to that of the same formulation cured at 80°C. This indicates that the final morphology of these materials was not too sensitive to the curing temperature in the range studied.

On the other hand, the samples obtained from the higher molecular weight VE resin (St-VE_C) modified with PMMA presented clearly different morphologies depending on the selected curing temperature. Figure 2 shows an SEM micrograph of a sample obtained from St-VE_C containing 20 wt % PMMA and cured at 80°C. Although the sample had a rough fracture surface resulting from phase separation, this process was not as developed as in the modified materials previously analyzed [Fig. 1(b)]. Although thermodynamic considerations would predict a more defined phase separation for this system,¹⁴ the experimental finding indicated that the phase-separa-

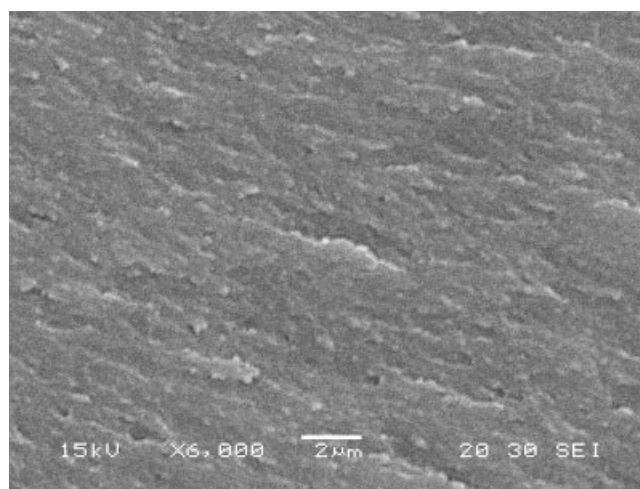
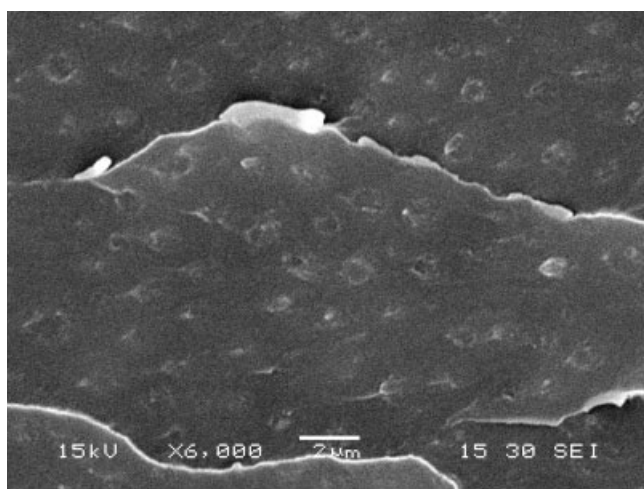
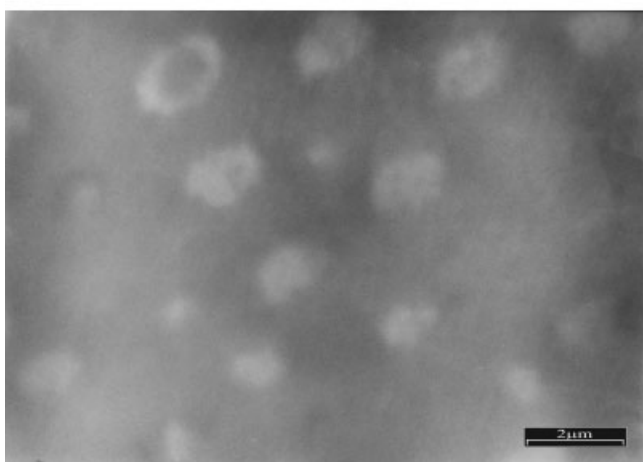


Figure 2 SEM micrograph of the fracture surface of an St-VE_C sample modified with 20 wt % PMMA and cured at 80°C.



(a)



(b)

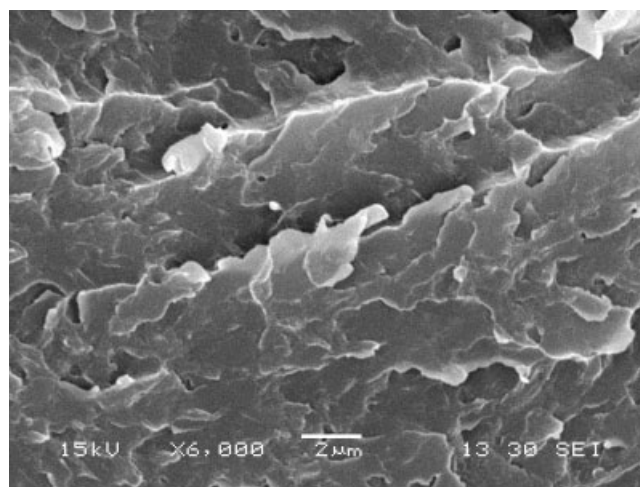
Figure 3 Micrographs of an St-VE_C sample modified with 5 wt % PMMA and cured at 40°C: (a) SEM and (b) TEM (10,000×).

tion process during the reaction was quickly arrested by diffusion restrictions that prevented species segregation. The level of separation of the dispersed PMMA phase and the irregularity of the fracture surface decreased still more in those formulations containing a lower initial amount of PMMA.

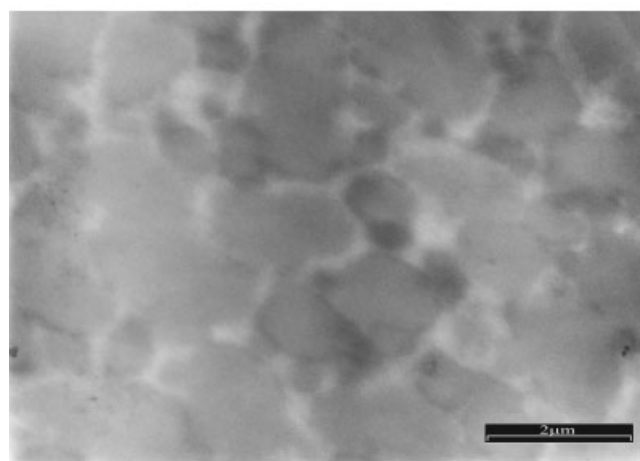
The samples obtained from the St-VE_C systems modified with 5–15 wt % PMMA and cured at 40°C presented different morphologies depending on the amount of the modifier in the initial mixture. Figure 3(a) shows the SEM morphology of the material modified with 5 wt % PMMA; a smooth fracture surface containing dispersed spherical domains with diameters in the range of 0.7–1.2 µm can be observed. Figure 3(b) is the TEM image of the same sample and shows that the phase rich in the St-co-VE crosslinked copolymer, which looks dark gray in the image,¹⁴ was the principal continuous phase, whereas the dispersed domains (light gray) were

rich in PMMA. Inside these domains, dark gray regions indicating the presence of the copolymer can be observed. This suggests that a secondary polymerization-induced phase separation took place inside the PMMA-rich phase.^{4,18}

Figure 4(a) is an SEM micrograph of the sample obtained from St-VE_C modified with 10 wt % PMMA and cured at 40°C. A very irregular fracture surface clearly different from that obtained with 5 wt % PMMA [Fig. 3(a)] was obtained. The TEM micrograph of the same sample [Fig. 4(b)] shows a cocontinuous phase morphology with interconnected irregular nodular aggregates of the St-co-VE copolymer surrounded by the thermoplastic modifier. Figure 5(a,b) shows SEM and TEM micrographs of the St-VE_C system modified with 15 wt % PMMA and cured at 40°C, respectively. The images show essentially a morphology of inverted phases, in which the



(a)



(b)

Figure 4 Micrographs of an St-VE_C sample modified with 10 wt % PMMA and cured at 40°C: (a) SEM and (b) TEM (10,000×).

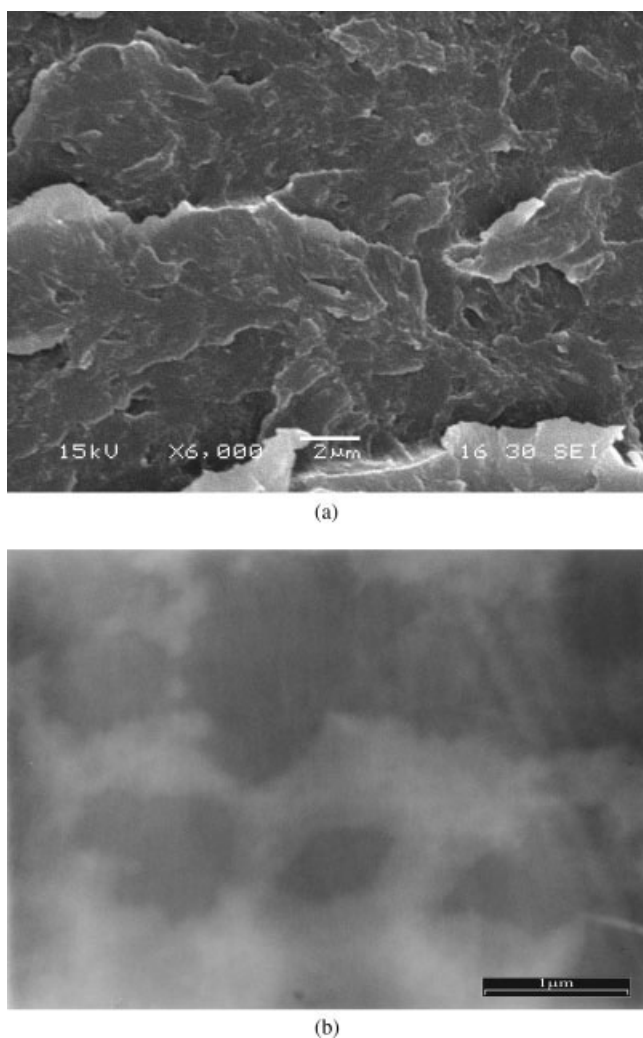


Figure 5 Micrographs of an St-VE_C sample modified with 15 wt % PMMA and cured at 40°C: (a) SEM and (b) TEM (20,000×).

irregular aggregates of the copolymer were practically dispersed in a thermoplastic matrix.

Volume shrinkage

VE resins, as well as UP resins, suffer nonnegligible volume shrinkage during crosslinking.^{13,19} This is due to the fact that elastomeric or, more recently, thermoplastic modifiers are added to the reactive mixture to reduce the overall volume shrinkage and to improve the dimensional stability of the molded parts (LPAs). It is known that the action of an LPA is based on the formation of a two-phase structure, which promotes the formation of microvoids that compensate for the crosslinking shrinkage.^{11,12,20}

To study the effect of the PMMA concentration on the volume shrinkage control in the VE_L and VE_C systems, a density measurement method was used in this work. The percentage of volume shrinkage

during crosslinking was calculated according to the following equation:

$$\text{Volume change (\%)} = \left(\frac{\rho_L}{\rho_C} - 1 \right) \times 100$$

where ρ_L is the density of the liquid mixture before the crosslinking reaction and ρ_C is the density of the cured material.

Figure 6 shows the final volume change versus the thermoplastic modifier concentration in the VE_L and VE_C systems cured at 80°C; it can be observed that the volume shrinkage was larger during the curing of neat St-VE_L (10.22%) than in the case of neat St-VE_C (8.24%) because of the higher crosslinking density of the network formed from the lower molecular weight resin. As the concentration of PMMA increased, there was an effective reduction of the material shrinkage. At 20 wt % PMMA, the percentage of the volume change was reduced to 7.85% for VE_L and to 6.85% for VE_C. For PMMA considered simply as a filler, the calculated effect on the volume change of both modified VE resins is shown as dashed lines in Figure 6. These behaviors were calculated by the estimation of the densities of the cured PMMA-filled samples with a simple rule of mixtures considering the additivity of the volumes of the unmodified thermoset and the PMMA modifier.

When the concentration of the thermoplastic additive was low, the effect of PMMA approached that of a filler. At PMMA concentrations between 15 and 20 wt % for VE_L and between 10 and 20 wt % for VE_C, the effect of PMMA on the volume shrinkage

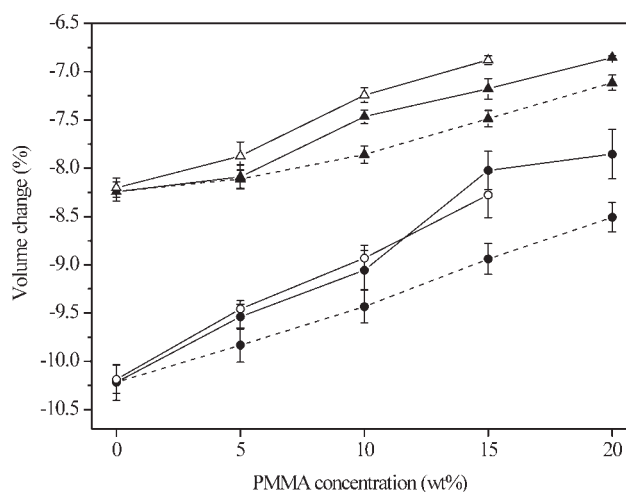


Figure 6 Final volume change versus the PMMA concentration for both VE systems: (●) experimental data for VE_L cured at 80°C, (▲) experimental data for VE_C cured at 80°C, (○) experimental data for VE_L cured at 40°C, (△) experimental data for VE_C cured at 40°C, (-●-) calculated behavior considering PMMA as a filler for VE_L and (-▲-) calculated behavior considering PMMA as a filler for VE_C.

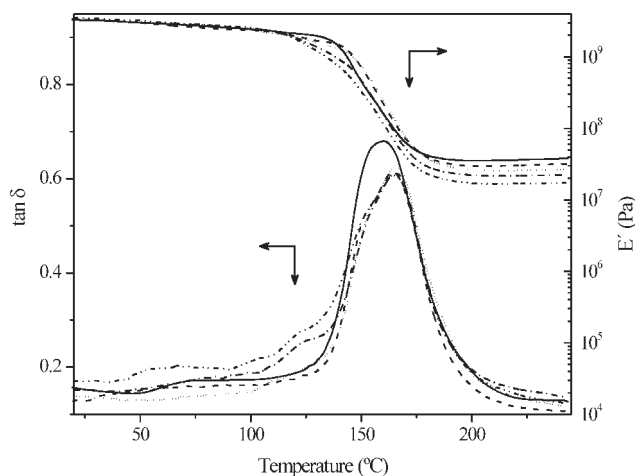


Figure 7 Dynamic mechanical behavior as a function of temperature for neat and PMMA-modified St-VE_L thermosets cured at 80°C: (—) an unmodified system, (---) a modified system with 5 wt % PMMA, (· · ·) a modified system with 10 wt % PMMA, (- · -) a modified system with 15 wt % PMMA, and (- · · -) a modified system with 20 wt % PMMA.

was slightly better than that of a filler, and the difference between the two behaviors did not increase markedly with increasing PMMA content. These results are in agreement with those reported by Cao and Lee,¹³ who used a polyurethane-based polymer as a low-shrinkage additive for a VE resin based on methacrylated bisphenol A and cured at 35°C.

Figure 6 shows that samples obtained from St-VE_L modified with 0–15 wt % PMMA and cured at 40°C presented volume shrinkage very similar to that of the same formulations cured at 80°C, and this is in agreement with the observation of the previous section that the final morphology of these materials was not too sensitive to a curing temperature between 40 and 80°C.

On the other hand, the samples obtained from St-VE_C modified with 10 or 15 wt % PMMA and cured at 40°C presented slightly better shrinkage control than that obtained for the same formulations cured at 80°C (Fig. 6). As analyzed previously, samples with 10 or 15% PMMA presented cocontinuous [Figs. 4(a,b)] and PMMA-rich matrix [Figs. 5(a,b)] morphologies, respectively, whereas the same formulations cured at 80°C showed morphologies with the phases very little segregated. Thus, with an increase in the degree of phase separation during curing, only small improvements in the control of volume shrinkage were obtained. Again, in the sample containing 5 wt % PMMA, the thermoplastic acted almost like a filler.

The overall shrinkage reduction obtained for both analyzed VE systems with PMMA as a modifier was much smaller than that reported for UP resins with a thermoplastic such as PVAc as an LPA; there, the

volume shrinkage of the neat St-UP thermoset (9%) was reduced up to 4.5% with the addition of 4% PVAc.^{9,11} It is very important to underline that cocontinuous or LPA-rich matrix morphologies, which are essential for thermoplastics to be effective as shrinkage-control additives (low-profile behavior) in UP resins, have been shown to be inefficient in the VE systems studied.

Dynamic mechanical analysis

Dynamic mechanical responses obtained for the two series of PMMA-modified VE thermosets cured at 80°C are shown in Figures 7 and 8. The use of VEs of different molecular weights led to thermosets with different degrees of crosslinking. The lower molecular weight one (VE_L) generated a network with a higher crosslinking density as the end groups of the shorter chains reacted with the St monomer. The resulting network presented a higher glass-transition temperature than that obtained with the St-VE_C system (160 and 133°C, respectively) and a higher modulus in the rubbery state (36 and 12 MPa, respectively), whereas the tan δ peak was lower because of the lower mobility of the chains in the more cross-linked network.

It can be observed in Figures 7 and 8 that the addition of PMMA modified the dynamic mechanical response. Although in both cases the rubber modulus decreased with the addition of the thermoplastic modifier, the reduction obtained in the VE_L system was greater (from 36 to 17 MPa for 20% PMMA) than that obtained in the VE_C system (from 12 to 8.2 MPa) for the same content of PMMA. This observation suggests that the crosslinking density

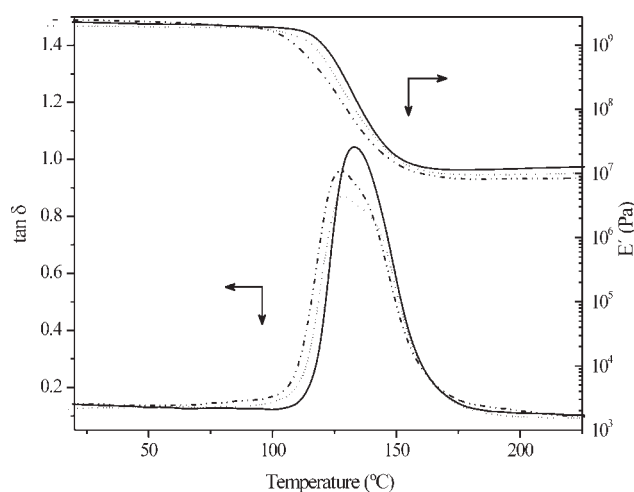


Figure 8 Dynamic mechanical behavior as a function of temperature for neat and PMMA-modified St-VE_C thermosets cured at 80°C: (—) an unmodified system, (· · ·) a modified system with 10 wt % PMMA, and (- · -) a modified system with 20 wt % PMMA.

was more affected in the VE_L system than in the VE_C one by the addition of PMMA. This difference may be associated with the thermoplastic showing a more important diluent effect in the St- VE_L cross-linked phase (reducing network connectivity) than in the St- VE_C system for the same PMMA content.

Figure 7 ($\tan \delta$ vs the temperature) shows that the relaxation of the main phase (copolymer-rich) in the modified systems seemed to be formed by overlapping peaks centered at temperatures closely above and below the glass-transition temperature of the unmodified thermoset. These peaks are believed to correspond to the relaxations of the copolymer formed at St- VE_L ratios that varied as the reaction proceeded as a result of the higher miscibility of St with respect to VE in the PMMA-rich phase.¹⁴ The main change (overlapping peaks of a lower height than $\tan \delta$ of the neat thermoset) occurred with the addition of a minimum concentration of PMMA (5 wt %). A further addition of the modifier did not produce other significant changes. A shoulder at 125°C, which could be observed at 15–20% PMMA, was assigned to the transition of the modifier.

$\tan \delta$ curves of the modified St- VE_C networks (Fig. 8) show two overlapping transitions corresponding to the two formed phases, the transition of the PMMA-rich phase at 127°C and the transition of the thermoset-rich phase at a higher temperature (ca. at 136°C). The observed overlap in the $\tan \delta$ transitions indicates that the two phases were not well segregated in these systems. This is very well supported by the SEM morphologies discussed in a previous section (Fig. 2).

Figure 9 shows the dynamic mechanical responses of the neat and PMMA-modified St- VE_C thermosets cured at 40°C. The unmodified thermoset presented a behavior very similar to that obtained when it was cured at 80°C (Fig. 8). For the sample modified with 5 wt % PMMA, two $\tan \delta$ transitions, corresponding to the two phases formed, appear clearly separated. In addition, the rubber modulus for this sample was practically the same as that of the neat thermoset. These observations suggest that the two phases were kept well separated during copolymerization and that the crosslink density of the main phase did not vary significantly with the modifier addition. Because the position of the relaxation of the copolymer-rich phase did not change as more PMMA was added, it is apparent that the St- VE_C ratio was kept essentially constant during the reaction. These observations are supported by the morphologies shown in Figure 3, in which a dispersion of PMMA-rich particles in a practically neat thermoset matrix can be observed. The sample containing 15 wt % PMMA also showed two $\tan \delta$ transitions clearly separated in agreement with the phase-inverted morphology shown in Figure 5. For this sample, the peak corre-

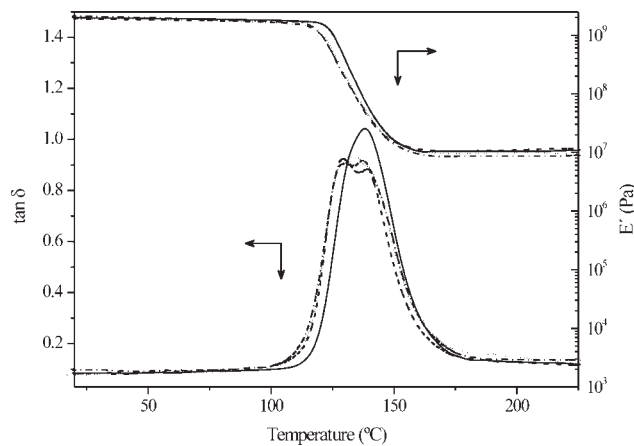


Figure 9 Dynamic mechanical behavior as a function of temperature for neat and PMMA-modified St- VE_C thermosets cured at 40°C: (—) an unmodified system, (---) a modified system with 5 wt % PMMA, (· · ·) a modified system with 10 wt % PMMA, and (- · -) a modified system with 15 wt % PMMA.

sponding to the relaxation of the PMMA phase was slightly higher than that observed in the 5 wt % PMMA sample. This feature was in agreement with the global compositions of the materials. On the other hand, for the sample containing 10 wt % PMMA, which presented a cocontinuous phase morphology (Fig. 4), the two relaxation peaks were not resolved.

Although the PMMA concentrations used in the St- VE_C systems were as high as those used in the St- VE_L system (Fig. 7), the height of the PMMA-phase transition peak was much higher, and this suggested that the PMMA chains were less restricted during the relaxation because the phases were more separated or because PMMA was trapped in a less crosslinked network.

The dynamic mechanical responses of the neat and PMMA-modified St- VE_L thermosets cured at 40°C showed glass-transition temperatures for the PMMA-rich and thermoset-rich phases, $\tan \delta$ curve shapes, and rubber moduli very similar to those shown in Figure 7 for the same formulation cured at 80°C. Again, this is in agreement with the morphologies of these materials, which were not too sensitive to the curing temperature in the studied range.

Mechanical properties

The obtained thermoset composites showed the typical behavior of this type of material; they broke in the initial linear region when tested under flexural forces, and they could yield under compression.

Table II shows the results obtained from the mechanical tests for both VE systems modified with different PMMA contents and cured at 80°C. The flexural moduli of the two neat VE systems were quite similar

TABLE II
Mechanical Properties of the Two VE Systems Modified with PMMA
and Cured at 80°C

PMMA (wt %)	Flexural modulus (GPa)		Compressive yield stress (MPa)		K_{IC} (MPa·m ^{1/2})	
	St-VE _L	St-VE _C	St-VE _L	St-VE _C	St-VE _L	St-VE _C
0	3.54 ± 0.02	3.51 ± 0.02	120.0 ± 1.0	114.2 ± 1.0	0.63 ± 0.04	0.86 ± 0.06
5	3.58 ± 0.01	3.56 ± 0.04	118.3 ± 1.5	110.6 ± 1.3	0.79 ± 0.05	1.01 ± 0.10
10	3.62 ± 0.02	3.60 ± 0.02	115.4 ± 1.8	111.1 ± 1.8	1.10 ± 0.06	1.13 ± 0.06
15	3.67 ± 0.04	3.57 ± 0.02	116.8 ± 2.2	114.8 ± 0.8	0.95 ± 0.05	1.09 ± 0.04
20	3.68 ± 0.05	3.55 ± 0.03	121.2 ± 2.0	114.1 ± 0.5	1.04 ± 0.16	1.27 ± 0.12

in light of the experimental error. The addition of PMMA to the St-VE_L network (formulated from the low-molecular-weight resin) produced a small but consistent increase in the modulus measured at room temperature. The values of the moduli of the modified St-VE_C networks (formulated from the high-molecular-weight resin) also showed small differences, but the values did not follow a simple trend.

Previous studies on St-VE copolymers modified with elastomers^{7,21} showed a reduction in the modulus with the addition of a modifier. This reduction was important in those cases because of the low modulus of the elastomeric phase. In fact, the study of the modification of thermosets with thermoplastics has been justified as a response to this unfavorable effect of rubber modifiers.

To carry out a suitable analysis of these results, the flexural modulus of the used neat PMMA was measured. A plate of PMMA was made by compression molding, and then test specimens were prepared and tested under the same experimental setup used for the modified VE materials. The obtained flexural modulus for the neat PMMA was 3.41 ± 0.07 GPa. Therefore, the flexural moduli of the materials based on both VE resins modified with PMMA were slightly higher than those of the unmodified thermosets or the neat PMMA. In the case of the low-molecular-weight-derived thermosets, the rule of mixtures for the calculation of the modulus (parallel and series models for two-phase systems) was applied.²² As could be expected, the calculated moduli (which followed a decreasing trend) were all below the experimental data, which followed an increasing trend (Fig. 10).

Table III shows the results obtained from the mechanical tests for both VE systems modified with different PMMA contents and cured at 40°C. Very small variations were observed in the flexural moduli of both St-VE thermosets when the curing temperature was changed from 80 to 40°C. However, the addition of PMMA to the VE_C system produced an apparent slightly decreasing trend when the curing temperature was 40°C.

Stress-strain curves of both neat St-VE thermosets cured at 80°C in a uniaxial compression test are

shown in Figure 11. The elastic moduli of the two materials (defined as the slope of the initial linear region) were very similar, in agreement with the results obtained in the flexural tests. The thermoset prepared with VE_C showed lower yield stress, higher strain softening after yielding, and higher strain hardening that allowed larger deformation to be achieved before breakage. These differences were the result of the higher molecular weight of the VE_C resin, that is, longer chains between crosslinking points, which led to a less tight network with more mobile chains.

The compressive measurements showed very little influence of the addition of the modifier, as can be observed in Tables II and III. Both tables illustrate that when PMMA was added to any of the VE systems, no significant changes in the compressive yield stress were obtained.

It is important to emphasize that the mechanical properties of the materials modified with thermoplastic PMMA were little affected by the addition of the modifier. Eventually, the modulus of some systems was slightly improved, instead of the usual

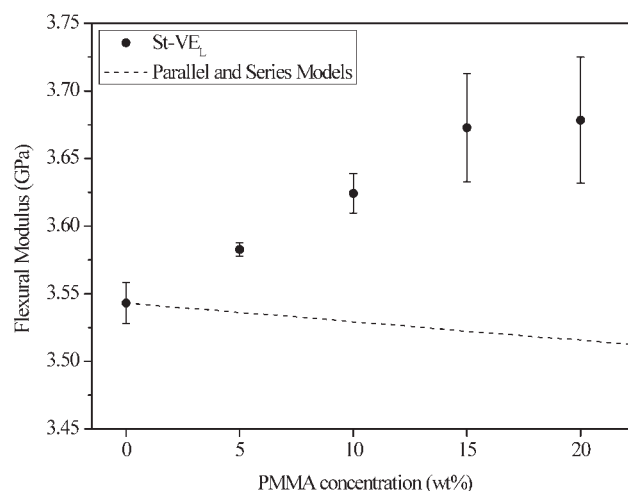


Figure 10 Flexural modulus values obtained for the St-VE_L systems cured at 80°C and predictions of parallel and series models as a function of the PMMA content.

TABLE III
Mechanical Properties of the Two VE Systems Modified with PMMA
and Cured at 40°C

PMMA (wt %)	Flexural modulus (GPa)		Compressive yield stress (MPa)		K_{IC} (MPa.m ^{1/2})	
	St-VE _L	St-VE _C	St-VE _L	St-VE _C	St-VE _L	St-VE _C
0	3.52 ± 0.01	3.48 ± 0.03	117.3 ± 1.8	113.4 ± 0.8	0.65 ± 0.07	0.85 ± 0.05
5	3.54 ± 0.02	3.43 ± 0.04	113.1 ± 1.6	111.5 ± 1.3	1.11 ± 0.13	0.94 ± 0.07
10	3.58 ± 0.02	3.40 ± 0.01	116.2 ± 2.3	109.9 ± 0.7	0.99 ± 0.05	1.36 ± 0.09
15	3.60 ± 0.04	3.38 ± 0.02	120.1 ± 1.5	110.6 ± 1.9	0.83 ± 0.06	1.21 ± 0.14

reduction obtained when elastomers are added to networks.

Fracture behavior

Experimental values of K_{IC} for both unmodified VE systems cured at 80 and 40°C showed an inverse correlation with the yield stress values (Tables II and III). This is the same trend reported in the literature for unmodified epoxy networks and can be explained by the crack tip blunting model.^{23,24}

In general, all PMMA-modified materials showed enhanced fracture properties with respect to those of the pure networks. Table II (materials cured at 80°C) shows that the VE_L system presented a maximum in the fracture resistance for the 10 wt % PMMA sample, for which the K_{IC} value increased by 75% with respect to that of the neat network. On the other hand, in the VE_C system, the largest improvement (48%) was achieved with 20 wt % PMMA, and this was a lower increase than that of the previous case. This difference in toughening was in agreement with the level of phase separation achieved during the reaction. A comparison of Figures 1(b) and 2 shows that in the PMMA-modified VE_C system, the phase-separation

process was not as developed as that in the modified VE_L material. Because of the better developed phase-separated morphology, in the VE_L system, additional toughening mechanisms were activated.

Table III shows the K_{IC} values measured for materials cured at 40°C. The VE_L system presented a maximum in the fracture resistance for 5 wt % PMMA; the K_{IC} value increased 71% with respect to that of the neat network. The largest improvement for the VE_C systems occurred with the addition of 10 wt % PMMA; the K_{IC} value increased by 60%. It is necessary to remember that when the curing temperature of the PMMA-modified VE_C formulations was reduced from 80 to 40°C, an increase in the segregation of species during the phase-separation process was produced, as shown in the microscopy study (Figs. 2–5). The VE_C material modified with 10 wt % PMMA (maximum in K_{IC}) clearly presented a cocontinuous phase morphology [Figs. 4(a,b)], and this indicates that the formation of continuous PMMA-rich and thermoset-rich phases is more efficient in improving the fracture toughness than the formation of structures such as PMMA particles dispersed in a thermoset-rich matrix, or vice versa. In the literature, the existence of a maximum in K_{IC} has been associated with the appearance of cocontinuous phase morphologies, as reported for epoxy networks modified with thermoplastics.^{4,18} The conclusion is that good interfacial adhesion is a necessary requirement for that response.

CONCLUSIONS

The final morphologies of the PMMA-modified St-VE thermosets showed differences depending on the molecular weight of the VE, the PMMA content in the formulation, and the selected curing temperature. The PMMA-modified St-VE_L thermosets (those formulated from the low-molecular-weight resin) led to heterogeneous morphologies, which were not much affected by the curing temperature in the range studied (40–80°C). The samples obtained from the modified St-VE_C thermoset (those formulated from the commercial high-molecular-weight resin) presented different morphologies depending on the selected curing temperature and modifier content.

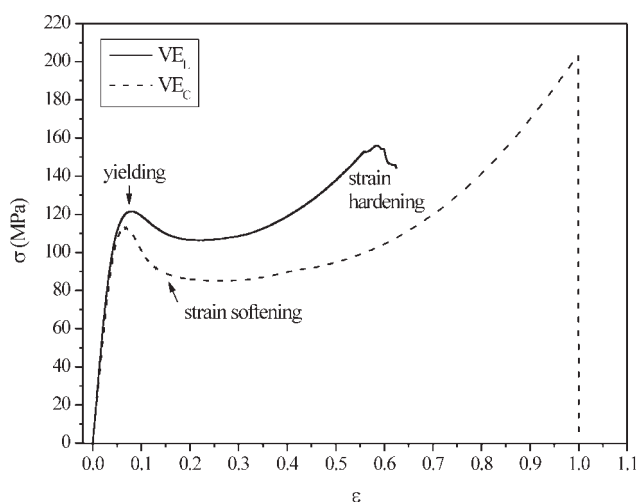


Figure 11 True stress (σ) versus the true strain (ϵ) obtained in a uniaxial compression test of both neat St-VE thermosets cured at 80°C.

Although at 80°C morphologies with phases not completely segregated were obtained, at 40°C, different morphologies could be generated, depending on the amount of the modifier in the initial mixture: they ranged from a dispersion of thermoplastic-rich particles in a thermoset-rich matrix to thermoset-rich particles dispersed in a thermoplastic-rich matrix.

The volume shrinkage reduction obtained in the analyzed VE systems with PMMA as a modifier was much smaller than that reported for UP resins with thermoplastics as LPAs.

Dynamic mechanical tests clearly showed that no major changes appeared in the relaxation temperature of the St-VE copolymer phase when PMMA was added as a modifier. However, the small variations observed in $\tan \delta$ correlated very well with the phase separation observed by SEM and TEM. The evaluation of the flexural modulus and compressive yield stress showed that these mechanical properties were little affected by the addition of the modifier. In contrast to the reduction of the modulus observed with the addition of elastomeric modifiers to thermoset polymers, the addition of PMMA did not have a deleterious effect on the mechanical properties of the St-VE copolymers. The addition of PMMA toughened the St-VE networks, and there was a correlation between the cocontinuous phase morphology and the maximum in the K_{IC} value.

References

1. Zawke, S. H. In *Handbook of Thermosetting Resins*; Goodman, S. H., Ed.; Noyes Publications, NJ, 1986.
2. Li, H.; Burts, E.; Bears, K.; Ji, Q.; Lesko, J. J.; Dillard, D. A.; Riffle, J. S.; Puckett, P. M. *J Compos Mater* 2000, 34, 1512.
3. Huang, Y. J.; Su, C. C. *J Appl Polym Sci* 1995, 55, 305.
4. Pascault, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J. *J Thermosetting Polymers*; Marcel Dekker: New York, 2002.
5. Gryshchuk, O.; Jost, N.; Karger-Kocsis, J. *J Appl Polym Sci* 2002, 84, 672.
6. Karger-Kocsis, J.; Fröhlich, J.; Gryshchuk, O.; Kautz, H.; Mühlaupt, R. *Polymer* 2004, 45, 1185.
7. Auad, M. L.; Frontini, P. M.; Borrajo, J.; Aranguren, M. I. *Polymer* 2001, 42, 3723.
8. Yee, A. F.; Du, J.; Thouless, M. D. In *Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, Chapter 26.
9. Li, W.; Lee, L. J. *Polymer* 2000, 41, 685.
10. Huang, Y. J.; Chu, C. J.; Dong, J. P. *J Appl Polym Sci* 2000, 78, 543.
11. Bucknall, C. B.; Partridge, I. K.; Phillips, M. J. *Polymer* 1991, 32, 636.
12. Lucas, J. C.; Borrajo, J.; Williams, R. J. *J. Polymer* 1993, 34, 1886.
13. Cao, X.; Lee, L. J. *J Appl Polym Sci* 2003, 90, 1486.
14. Schroeder, W. F.; Yáñez, M. J.; Aranguren, M. I.; Borrajo, J. *J Appl Polym Sci* 2006, 100, 4539.
15. Ullet, J. S.; Chartoff, R. P. *Polym Eng Sci* 1995, 36, 3279.
16. Dong, J. P.; Huang, J. G.; Lee, F. H.; Roan, J. W.; Huang, Y. J. *J Appl Polym Sci* 2004, 91, 3369.
17. Huang, Y. J.; Liang, C. M. *Polymer* 1996, 37, 401.
18. Pascault, J. P.; Williams, R. J. *J. In Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 1, Chapter 13.
19. Auad, M. L.; Aranguren, M. I.; Borrajo, J. *J Appl Polym Sci* 1997, 66, 1059.
20. Li, W.; Lee, L. J. *Polymer* 2000, 41, 697.
21. Pham, S.; Burchill, P. J. *Polymer* 1995, 36, 3279.
22. Broutman, L. J.; Krock, R. H. *Modern Composite Materials*; Addison-Wesley: Reading, MA, 1967.
23. Kinloch, A. J.; Williams, J. G. *J Mater Sci* 1980, 15, 987.
24. Huang, Y.; Kinloch, A. J. *Polymer* 1992, 33, 5338.