

Epoxy-Based Divinyl Ester Resin/Styrene Copolymers: Composition Dependence of the Mechanical and Thermal Properties

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ABSTRACT: Epoxy-based divinyl ester resins (DVER) were obtained by reacting diglycidyl ether of bisphenol A (DGEBA) with methacrylic acid (MA) and characterized by FTIR and $^1\text{H-NMR}$ spectroscopies and gel permeation chromatography (GPC). The densities and viscosities of the DVER in styrene (S) solutions were measured at different temperatures, 25, 40, and 60°C and compositions, 3.4 to 100% by weight of styrene. Dynamic mechanical measurements (DMA) and differential scanning calorimetry (DSC) were used to determine the glass transition temperatures of the homopolymers and the DVER/S copolymers: 20, 40, 60, and 80% by weight of styrene. The values obtained are in the range limited by the homopolymers glass transition, 100°C for polystyrene and 173°C for the cured DVER. The data were well fitted if two contributions to the glass transition are taken into account: the “linear copolymer” contribution (Fox eq.) and the “crosslinking” contribution (Nielsen model). Uniaxial static compression tests were carried out to determine the modulus, yield stress, and ultimate stress in samples with different compositions. All the mentioned properties decrease with an increase in the styrene concentration in the final copolymer. It was found that the volumetric contraction during curing increases with styrene concentration. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1059–1066, 1997

Key words: divinyl ester resins; styrene copolymers; glass transition; mechanical properties; dynamic mechanical properties

INTRODUCTION

An important amount of the composite materials currently manufactured are obtained from thermoset resins. Epoxy-based divinyl ester resins (DVER) 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} These resins are commercially attractive, with respect to the unsaturated polyesters,

because of their toughness, lower viscosity, and chemical resistance. These divinylesters also possess some advantageous characteristics including excellent reactivity due to terminal vinyl unsaturations, improved elongation, good acid resistance, and better wetting and bonding to glass reinforcements. They have an epoxy backbone structure with terminal unsaturated vinyl groups that can be cured by copolymerization with vinyl monomers, usually styrene or acrylic esters, in analogy with the unsaturated polyesters.^{1,2}

Most of the studies of synthesis, characterization, and properties of these materials have been realized in industrial laboratories,^{1,2} and only recently some kinetic studies of the curing reac-

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tion^{3,4} and of the fracture mechanics of the cross-linked copolymers^{5,6} have been published. The different measurements were usually done on commercial resins, typically crosslinked with 45% by weight of styrene.³⁻⁶

Contrary to the unsaturated polyester behavior,⁷ divinyl ester resins form homogeneous solution with styrene in all compositions, which allows one to obtain cured copolymers with thermal and mechanical properties that vary between those of the homopolymers, the pure cured divinyl ester resin, and the polystyrene. Besides, it is possible to vary the initial viscosity of the reactive system changing the composition of the comonomer feed, the only restriction being the final properties of the cured copolymer. This may be particularly important in resin transfer molding (RTM) processes, where the viscosity of the reactive mixture can be varied in a narrow range to completely fill the mold to obtain perfect pieces.

This article deals with the synthesis and characterization of epoxy-based divinyl ester resins from DGEBA and methacrylic acid, as well as the study of the copolymer composition dependence of the thermal and mechanical final properties with the styrene comonomer.

EXPERIMENTAL

Synthesis of the Divinyl Ester Resin

A divinyl ester resin was synthesized from the reaction of an epoxy resin, diglycidyl ether of bisphenol A (DGEBA MY 790, Ciba Geigy, equivalent weight 176.2 g/equiv) with methacrylic acid (Norent Plast S.A., laboratory grade reagent) and triphenylphosphine (Fluka A.G., analytical reagent) as the catalyst.⁸ The reaction was carried out using a stoichiometric ratio of 1.25 mol of acid to 1 mol of DGEBA, 0.5 g of catalyst per hundred grams of DGEBA and 1000 ppm of hydroquinone to avoid the thermal polymerization of the vinyl groups. A stainless steel reactor with a low velocity stirrer, temperature control, and nitrogen purge was used for the synthesis. The temperature was maintained at 70°C during the first 30 min of the reaction to avoid sudden increments of temperature due to the high initial reaction rate, then it was stepped to and kept at 100°C until the final conversion was reached, usually higher than 93%. The total time for the synthesis was approximately 4.5 h.

Conversion was monitored by the titration of

residual acid groups with an alcoholic KOH solution and by FTIR spectroscopy performed on samples taken at different reaction times. Excess methacrylic acid was washed out from the synthesis product with distilled water. The remaining water was extracted under vacuum at 60°C, using a rotavapor apparatus. The final product was stored in a refrigerator, after addition of 500 ppm of hydroquinone.

The obtained resins were characterized analytically by determining the saponification index, and using FTIR and ¹H-NMR spectroscopies and by GPC chromatography.

Density and viscosity of the liquid solutions prepared in styrene (Perlinac S.A., laboratory grade reagent) with different overall compositions were determined using a precision balance for densities Becker and Sons and a Brookfield viscosimeter, respectively.

Preparation and Testing of Cured Copolymers

The final properties of the DVER/Styrene copolymers were determined using thermal, compression, and dynamic mechanical tests.

Thermal tests were realized in a Shimadzu DSC-50 calorimeter, with In calibration. Scans were run at 10°C/min.

Compression specimens were obtained from samples molded in glass tubes of 5 mm of internal diameter coated with silicone release agent. The curing cycle for these samples was 2 h at 50°C, 1.5 h at 80°C, and finally postcuring at 150°C for 2 h. Cylinders were cut with a height/diameter ratio of 1.5 to 2.0 (ASTM D695M). The top and bottom faces were carefully machined to be parallel and the dimensions were measured with a caliper up to 0.01 mm. The tests were carried out at crosshead speed of 0.5 mm/min and room temperature using an Instron 8501 universal testing machine.

Dynamic mechanical tests were carried out in a Perkin-Elmer DMA 7e apparatus using the three-point bending fixture and specimens of transversal area 2 × 3 mm², and a span of 15 mm. All temperature scans of the DMA tests were done at a frequency of 1 Hz and applying a static stress of 0.5 MPa and a dynamic stress of 0.3 MPa. The specimen bars used for these tests were cut from plaques obtained by curing of the comonomers between two plane glasses previously treated with the silicone release agent. The curing cycle was the same used to obtain the compression specimens. The concentration of the comonomers was

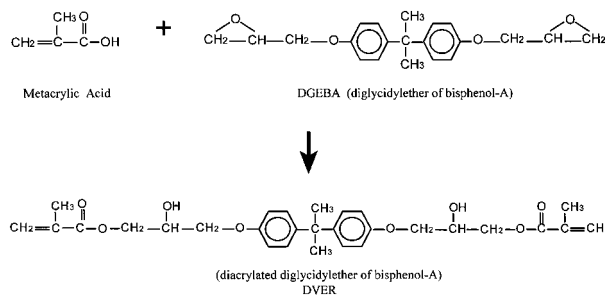


Figure 1 Schematic of the DVER synthesis reaction.

varied between 3.4 to 100% by weight of styrene, using 2% by weight of benzoyl peroxide (Lucidol 75%, Akzo Chemicals S.A.). The minimum styrene concentration, 3.4%, results from the dissolution of the initiator in styrene before utilization.

The density of the cured copolymers were determined at 20°C using picnometry.

RESULTS AND DISCUSSION

Resin Formulation and Characterization

Figure 1 shows a schematic of the synthesis of DVER from the reaction of DGEBA and methacrylic acid.

FTIR spectra of samples taken at different reaction times show an increment of the intensity in the 3300–3600 cm^{-1} absorption band, which corresponds to the stretch $\nu(\text{O—H})$ of the formed alcohol groups and a reduction of the intensity of the 950 and 856 cm^{-1} bands corresponding to the epoxy group. A FTIR spectrum of the DVER is shown in Figure 2, the corresponding peak assign-

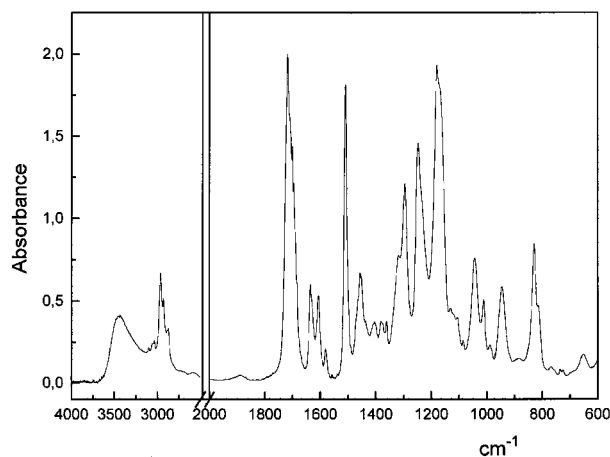


Figure 2 FTIR spectrum of the DVER resin.

Table I Band Assignment for the Infrared Absorption of DVER Resin

Assignment	Band Position (cm^{-1})
$\nu(\text{OH})$ m	3428
$\nu(\phi\text{-H})$ m	3037
$\nu(\text{CH}, \text{CH}_2, \text{CH}_3)$ m	2963
$\nu(\text{C}=\text{O})$ s	1718
$\nu(\text{C}=\text{C})$ vinyl m	1635
$\nu(\text{C}=\text{C})$ ϕ m	1607
$\nu(\text{C}=\text{C})$ ϕ s	1509
$\delta(\text{CH}, \text{CH}_2, \text{CH}_3)$ m	1457
$\nu(\text{C}—\text{O}) + \nu(\text{C}—\text{C})$ s	1296
$\nu(\phi—\text{O})$ s	1248
$\delta(\phi—\text{H})$ in plane s	1181
$\nu(\phi—\text{O}—\text{C})$ m,s	1044
$\delta(\phi—\text{H})$ in plane m	1011
$\delta(\text{C}=\text{C})$ vinyl m	945
$\delta(\phi—\text{H})$ out of plane m,s	829

ν , stretching; δ , deformation; ϕ , aromatic ring; s, strong; m, medium.

ments are included in Table I, and are based in previous publications on epoxy resins.^{9,10}

Figure 3 shows a $^1\text{H-NMR}$ spectrum of DVER, where the two doublets at 7.13–7.03 ppm and 6.80–6.70 ppm (marked as B and C) correspond to the aromatic hydrogens, the 6.10 ppm and 5.53 ppm peaks correspond to the vinyl hydrogens (D), the peaks in the region between 4.40–3.80 ppm correspond to the five hydrogens related to the reacted epoxy (F), the 1.90 ppm correspond to the methyl hydrogens of the methacrylic acid (E), and the 1.56 ppm peak correspond to the methyl hydrogens of the bisphenol A (A). The peaks at 1.90 and 1.56 ppm have similar intensities, in agreement with a high reaction conversion between epoxy groups and carboxylic acid.

Elution volumes measured from GPC runs, using polystyrene calibration, allowed to calculate the resin molecular weight, $M_n = 583$, with a polydispersity index, $M_w/M_n = 1.04$. The expected theoretical value is 546 for complete conversion of the epoxy groups and absence of secondary reactions. The average saponification value determined for the three synthesized DVER is 197.5 mg KOH/g DVER. There is a good agreement with the theoretical value of 186.8 mg KOH/g DVER calculated assuming complete conversion during the synthesis. The differences between calculated and experimental values indicate a negligible presence of secondary reactions.

Curve B in Figure 4 represents the densities of

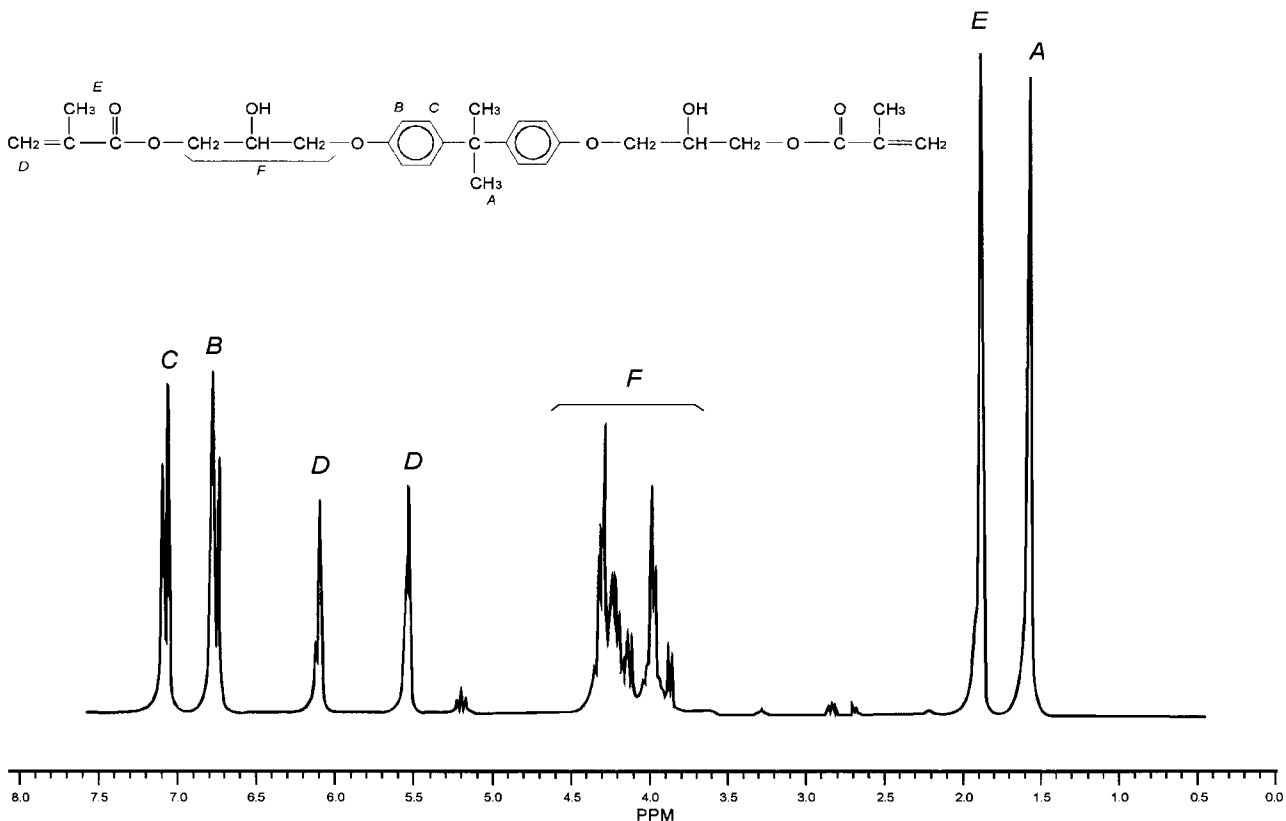


Figure 3 $^1\text{H-NMR}$ spectrum of the DVER resin and band assignment.

the unreacted mixtures DVER–styrene at 20°C calculated according to the rule of mixtures:

$$1/\rho_{\text{mixt.}} = w_S/\rho_S + w_{\text{DVER}}/\rho_{\text{DVER}} \quad (1)$$

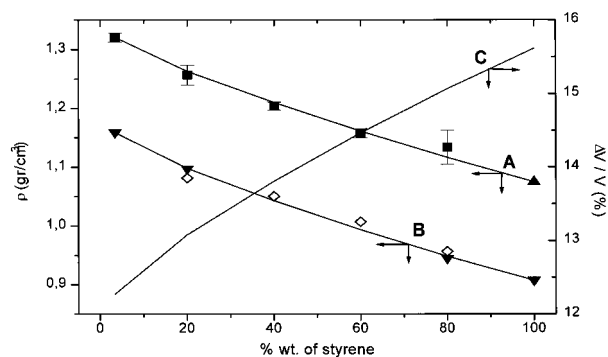


Figure 4 Densities of the DVER-S mixtures and the corresponding copolymers, as a function of the weight fraction of styrene (%) at 20°C . DVER-S mixtures: (\diamond) values obtained by picnometry, (∇) values obtained with the density balance. DVER-S copolymers: (\blacksquare) values obtained by picnometry, (\blacktriangle) literature data. Curves A and B: mixing rules. Curve C: volumetric contraction as percent of the initial volume.

where w_S , w_{DVER} , ρ_S , ρ_{DVER} , are the weight fractions and densities of styrene and resin, respectively, at the temperature of the mixtures. Experimental points are very well fitted in this way.

The viscosities of the DVER–styrene mixtures are reported in Table II at 25, 40, and 60°C . Each value represents the average of at least six measurements carried out at different shear rates. The values of viscosity for the styrene homopolymer were obtained from literature.¹¹

Cured Copolymer

Volume Contraction

The density of the cured copolymers at different styrene concentrations is shown in Figure 4, it includes experimental values obtained by picnometry and the literature value for the styrene homopolymer. The continuous line was calculated using the rule of mixtures, as before:

$$1/\rho_{\text{COP}} = w_{\text{HDVER}}/\rho_{\text{HDVER}} + w_{\text{HS}}/\rho_{\text{HS}} \quad (2)$$

where ρ_{COP} is the density of the cured copolymer;

and w_{HDVER} , ρ_{HDVER} and w_{HS} , ρ_{HS} are the weight fractions and the densities of the homopolymers, DVER, and S, respectively.

For a given composition, the difference between the specific volume of the liquid mixture of the comonomers and that corresponding to the cured copolymer represents the volumetric contraction due to the copolymerization.

$$\Delta V = 1/\rho_{\text{mixt.}} - 1/\rho_{\text{COp}} \quad (3)$$

The percentage of volume decrease, $\Delta V/V_{\text{mixt.}}\%$, as a function of copolymer composition, calculated from the experimental density values (A and B), is shown as curve C in Figure 4. ΔV increases with increasing styrene concentration in the copolymer, although this variation is small, 12 to 15%, for the whole concentration range. These results are similar to those published for styrene crosslinked polyester resins, which are between 14 and 17%.^{12,13}

Glass Transition

Table III shows the experimental values of the glass transition temperatures, $T_{g\text{COp}}$, of the cured copolymers measured with DMA and DSC techniques (columns 2 and 3, respectively) for different styrene concentrations (column 1). The reported values correspond to the middle point of the transition as measured from the thermograms, and to the maximum in $\tan \delta$ from the DMA runs. As it should be expected for a homogeneous material, only one transition is seen for each copolymer composition. Increasing styrene concentration in the copolymer reduces the glass transition temperature from 173°C for the DVER homopolymer to 100°C corresponding to the polystyrene. As a comparison, matrices of similar structure present glass transitions in that same temperature range. Commercial unsaturated

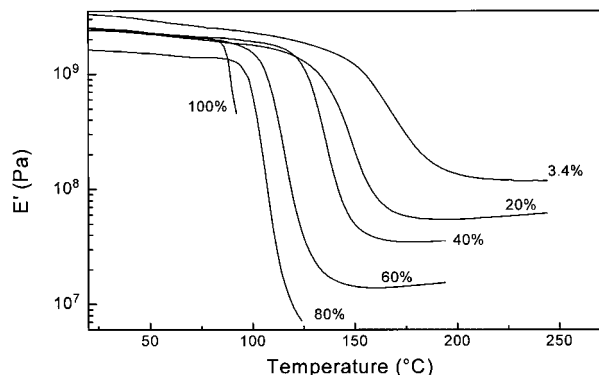


Figure 5 Storage modulus as a function of the temperature for the DVER-S copolymers of different compositions.

polyester resins crosslinked with styrene have glass transition temperatures that vary from 110°C for a general purpose resin to 140°C for a high-performance isoftalic resin.¹⁴ Some epoxy-amine systems that present transitions in that temperature range are¹⁵: DGEBA-EDA ($T_g = 106^\circ\text{C}$), DGEBA-mPhA ($T_g = 157^\circ\text{C}$), DGEBA-TMHMD ($T_g = 107^\circ\text{C}$), DGEBA-IPD ($T_g = 157^\circ\text{C}$).

Glass transition temperatures were also determined using dynamic mechanical measurements. The results were in very good agreement with DSC results.

Figures 5 and 6 show the storage modulus and $\tan \delta$ versus temperature obtained from samples with different styrene composition. The glassy storage modulus is not much affected by the composition of the material, while the rubbery modulus changes from that of the DVER homopolymer to a negligible value for the polystyrene melt. This observation is in good agreement with the known fact that increasing crosslinking density (decreasing S concentration) the network strands become shorter and the range of magnitudes of modulus

Table II Viscosities of the DVER-S Mixtures

Styrene (wt %)	Viscosity of the Mixture DVER-S (cp)		
	25°C	40°C	60°C
3.4	$3.17 \pm 0.01 \cdot 10^5$	$2.84 \pm 0.03 \cdot 10^4$	$2.89 \pm 0.08 \cdot 10^3$
20	$1.26 \pm 0.06 \cdot 10^3$	$2.98 \pm 0.08 \cdot 10^2$	82.8 ± 5.6
40	39.2 ± 1.5	23.0 ± 1.6	9.4 ± 1.5
60	9.2 ± 1.1	6.53 ± 0.75	4.6 ± 0.2
80	4.57 ± 0.06	2.77 ± 0.25	2.35 ± 0.35
100	0.705	0.58	0.469

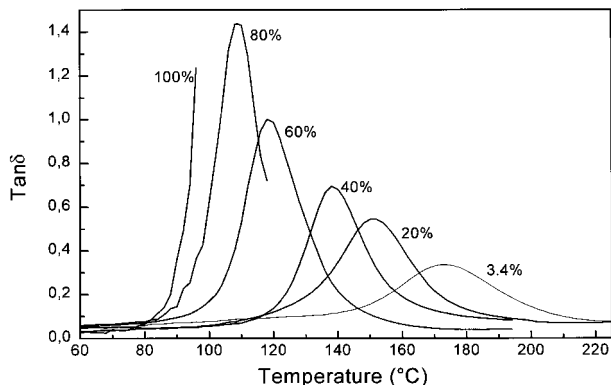


Figure 6 $\tan \delta$ as a function of the temperature for the DVER-S copolymers of different compositions.

encompassed by the transition zone becomes narrower, involving a change only from $3 \cdot 10^9$ Pa to $1.2 \cdot 10^8$ Pa for the 3.4% S copolymer. The plots of $\tan \rho$ versus temperature are more revealing of the structure of the different networks. Increasing the amount of styrene in the copolymer not only reduces the temperature of the glass-rubber transition, but also reduces the width of the peak and increases the height. At the smallest composition of styrene (3.4%) the transition is very wide, indicating that various relaxation mechanisms are active in that temperature interval. As the amount of styrene in the copolymer is increased, the free volume in the resultant networks increases and so does the chain mobility. Because the height of the $\tan \delta$ peak is related to the amount of the material undergoing the transition, the peak is higher for high percentages of styrene in the copolymer. Besides, because of the increased chain mobility, the activation energy of the process diminishes and the temperature at the maximum of $\tan \delta$ is reduced.

To analyze the results obtained, the Nielsen model was considered. He proposed that the copolymer T_g can be considered as the sum of two contributions: (a) the "linear copolymer" contribution, T_{gLCop} , where the system is assumed to be formed by hypothetical linear molecules of high molecular weight formed by the random copolymerization of DVER and S, with a composition equal to that of the real copolymer; (b) the "crosslinking" contribution, $k\nu$, originated by the crosslinkage of the "linear macromolecules." This depends on the composition through the density of elastically active chains, ν , that connect crosslinking points of functionality, $f = 4$, resulting from the DVER monomer incorporated to the copoly-

mer. These two contributions appear in the equation proposed by Nielsen.¹⁶

$$T_{gCop} = T_{gLCop} + k\nu \quad (4)$$

The "linear copolymer" contribution can be calculated for the different compositions using the Fox equation.¹⁷

$$1/T_{gLCop} = w_{LHDVER}/T_{gLHDVER} + w_{HS}/T_{gHS} \quad (5)$$

where w_{LHDVER} and w_{HS} are the weight fractions of DVER and S in the copolymer, $T_{gLHDVER}$ is the glass transition temperature of the hypothetical linear DVER homopolymer, and T_{gHS} , which corresponds to high molecular weight polystyrene. T_{gHS} was measured using polystyrene samples synthesized in our laboratory. The value reported in Table III is in good agreement with literature data.¹¹ T_{gLCop} cannot be experimentally determined; thus, the value corresponding to the linear polyphenoxy homopolymer was used. This polymer, which has a chemical structure similar to that of the DVER, show the glass transition at 355 K, as reported by Pascault and Williams.¹⁸ These authors also report the values of the "linear copolymer" contribution for other thermosets with similar structures to that of the cured DVER, for example, for DGEBA-3DCM and DGEBA-DDM the published values are 356 and 355 K, respectively.

To obtain the "crosslinking" contribution, the number of elastically active chains per volume of copolymer, ν , was calculated, assuming that the reaction is random and complete conversions achieved:

$$\nu = 2w_{DVER} \cdot \rho_{Cop} / M_{DVER} \quad (6)$$

where M_{DVER} and w_{DVER} are the DVER molecular weight and its weight fraction in the copolymer,

Table III Glass Transition Temperatures of the DVER-S Copolymers

Styrene (wt %)	$T_{g_{cop.}}$ (DMA) (°C)	$T_{g_{cop.}}$ (DSC) (°C)
3.4	173	173.5
20	150.3	151.2
40	138	138.6
60	126.6	130.6
80	109	105.9
100	—	98

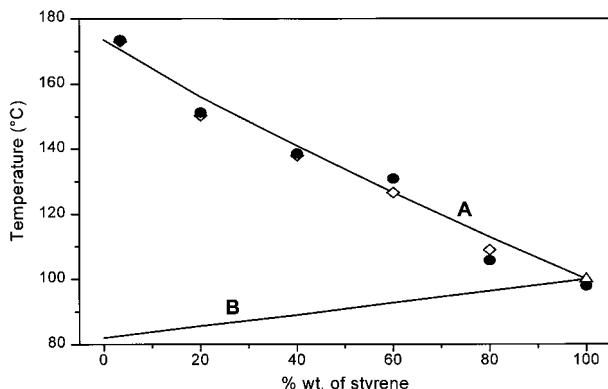


Figure 7 Glass transition temperature of DVER-S copolymers as a function of the composition: (\diamond) values measured with a DMA, (\bullet) values measured with a DSC, (\triangle) literature data. Curve A: Nielsen equation. Curve B: "linear copolymer" contribution.

respectively, ρ_{COP} is the density of the cured material.

The value of the parameter k fitted from the experimental data was $2.18 \cdot 10^4 \text{ } ^\circ\text{C cm}^3 \text{ mol}^{-1}$, which is in the usually accepted range,¹⁹ $1.2 \cdot 10^4 < k < 4.1 \cdot 10^4$.

Figure 7 shows the experimental values for T_g measured by DSC and DMA as a function of the styrene weight concentration in the copolymer, curve B represents the "linear copolymer" contribution calculated by eq. (5), and curve A represents the Nielsen model eq. (4), the difference between ordinates corresponds to the "crosslinking" contribution.

Compression Tests

Tensile tests are usually carried out to characterize the materials; however, these being glassy copolymers, compression tests are more adequate. Figure 8 shows the true stress versus deformation in compression tests, measured for samples made with different mass concentration of styrene.

At room temperature, polystyrene homopolymer deformed inhomogeneously and the specimen failed at nil plastic deformation with brittle fracture. The rest of the tests curves showed considerable plastic deformation before the fracture took place. At high styrene concentration, the styrene chains formed are crosslinked through the DVER molecules; thus, the inhomogeneous shear deformation changes from very localized to a more diffuse region, which leads to the observed behavior. As the amount of DVER increases the crosslinking density of the copolymer increases and the plastic deformation is reduced.

All samples show stress softening, a general behavior of amorphous glassy polymers, followed by stress hardening. The values of yield stress reported in Table IV refer to the intrinsic property of the polymer measured as the maximum of the true stress vs. nominal strain ($\Delta\varepsilon/\varepsilon_0$), which is related to the start of yielding of the material. The yield stress increases with the crosslinking density of the material, as it was expected. Similar trend was observed for the compression modulus and ultimate stress. The data of the modulus show a maximum at 20% of styrene, which could not be explained. The measured values are comparable to those of commercial resins reported in the literature ($E = 2.8$ to 3.3 GPa).^{5,6} The ultimate stress shows a plateau at low styrene concentration (approx. 186 MPa). All the results are the average of five runs.

CONCLUSIONS

Divinyl ester resins were synthesized from an epoxy resin with an excess of methacrylic acid. The chemical and spectroscopic characterization of the resins show an elevated conversion of the epoxy groups, and a negligible occurrence of secondary reactions of polymerization of vinyl groups during the synthesis.

DVER is miscible with styrene in all concentrations, and the viscosities and densities of the solutions were measured for the whole range of concentrations.

There is a volumetric contraction of the material during the crosslinking reaction from 12 to 15% as the styrene concentration is increased from 3.4 to 100% by weight.

The copolymer glass transition temperatures

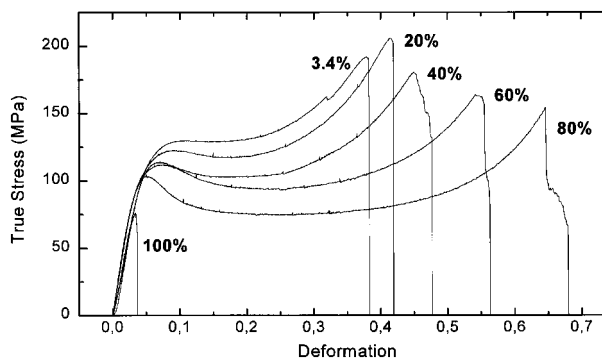


Figure 8 True stress versus deformation curves for uniaxial compression tests at different copolymer compositions.

Table IV Uniaxial Compression Values of Yield Stress, Modulus, and Ultimate Stress for DVER-S Copolymers

Styrene (wt %)	Yield Stress (MPa)	Elastic Modulus (MPa)	Ultimate Stress (MPa)
3.4	127.38 ± 3.36	3002.35 ± 140.35	185.95 ± 11.99
20	125.95 ± 3.62	3232.64 ± 89.26	186.62 ± 18.28
40	111.03 ± 0.79	2904.93 ± 96.81	159.99 ± 18.10
60	110.06 ± 4.30	2872.32 ± 107.03	147.94 ± 14.00
80	100.02 ± 2.52	2702.26 ± 126.27	135.95 ± 10.59
100	—	2592.25 ± 85.54	85.67 ± 4.18

vary from 173°C for the pure DVER homopolymer, to 100°C for pure polystyrene.

The yield stress and compression modulus increase and the plastic deformation decreases with the increasing amount of DVER in the copolymer.

The high values of T_g , compression modulus, yield stress, and ultimate stress of these copolymers at the different compositions indicate that the applications could use formulations with compositions different from 45% w/w styrene, which is commonly used.

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