

Relationship Between the Network Morphology and Properties of Commercial Vinyl Ester Resins

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ABSTRACT: Two commercial vinyl ester resins, Derakane 411-350 (resin D) and Derakane 411-350 Momentum (resin M), were characterized. Despite the large quantity of publications in the literature about vinyl ester resins, few experimental results have been reported for resin M. The effect of the styrene content on the mechanical properties and morphological structure was studied. An increase in the styrene content produced a network with a low storage modulus in the rubber state and a glass-transition temperature. The apparent average molecular weight between crosslink points and glass-transition temperature were slightly higher for resin D than for resin M. The Fourier transform infrared

spectra and molecular weight distributions were similar. However, resin M was tougher than resin D, and this may have been due to the closer structure in the fully cured state. Atomic force microscopy was performed for each cured resin and confirmed the difference in the nanostructures. The main reason for the differences in the developed structures was the use of an accelerator, which influenced the final morphology. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3895–3903, 2006

Key words: mechanical properties; atomic force microscopy (AFM); vinyl ester; FTIR; microstructure

INTRODUCTION

The thermosetting resins that are most used in resin transfer molding are unsaturated polyester and vinyl ester. These resins have good mechanical properties and have low viscosity for injection at low pressure.¹

Vinyl ester resins as prepolymers can be obtained by the reaction of epoxy and carboxylic acids, generally acrylic or methacrylic acids. The vinyl ester crosslinking reaction is the result of different kinds of reactions between the unsaturated bonds: (1) the reaction of the vinyl ester prepolymer with styrene, (2) the homopolymerization of styrene monomer giving polystyrene, and (3) the homopolymerization of the resins.² Several authors^{3–7} have reported that at the very beginning of polymerization, there is a very small concentration of macromolecules dissolved in the monomers, and most of the pendant double bonds participate in intramolecular reactions. These macro-

molecules form the microgel as crosslinked microparticles. Microgels are domains of high crosslinking density dispersed in a pool of noncrosslinked material. Some authors^{8,9} have shown that initially copolymerization is favored over styrene homopolymerization. After the formation of the microgels, the polymer becomes more compact, the reaction probability of double bonds located inside a large branched macromolecule decreases, and intermolecular reactions start to increase, reaching the gel point or macrogelation. The network structure is schematized in Figure 1, and styrene acts as an agent of crosslinking.

Vinyl ester and styrene compounds form a homogeneous mixture in the entire composition range. However, the commercial product is formulated with 40–45 wt % styrene because of the viscosity that the material should have for the injection process. There are two main reasons for the variation of the styrene content in the industrial use of the resins: (1) the evaporation of styrene and (2) the addition of styrene to reduce the viscosity value. As a result, it is very important to know how the mechanical properties change as a function of the styrene content.

The relationships between the structure of vinyl ester and its properties have been investigated in several studies.^{4,9,10} Auad et al.¹¹ found that the glass-transition temperature (T_g) and storage modulus in the rubbery state (E') of vinyl ester decreased when

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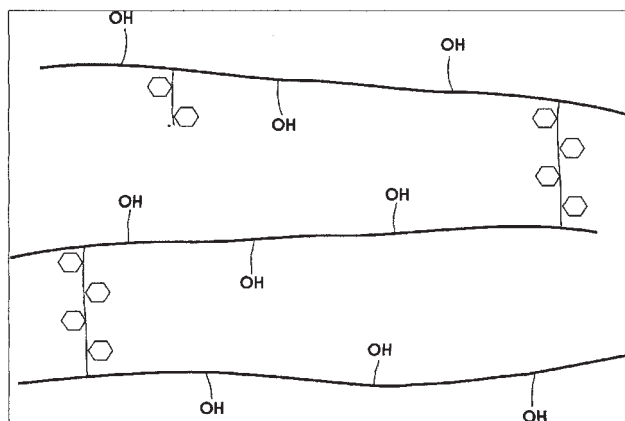


Figure 1 Scheme of the crosslinking reaction.

the styrene concentration increased because of a drop in the crosslink density. The volumetric contraction during curing also increased when the styrene concentration was raised. Scott et al.¹² showed that the decrease in T_g when the styrene content increased was not consistent, and a small maximum was observed in T_g between 30 and 40 wt %. These differences found by different authors were due to the effects of competing factors on T_g . Loshak and Fox¹³ and Nielsen¹⁴ proposed that as the concentration of the crosslinking monomer varies in a network, the change in T_g depends on the additive effects of crosslinking and copolymer reactions. As the styrene content rises in a vinyl ester formulation, the rubbery modulus tends to drop as expected for a reduction in the crosslink density, but a small maximum in the storage modulus can be observed near 30 wt %. The different behaviors found in a literature survey with the styrene content can also be related to the molecular weights of the monomers. Li et al.¹⁵ found that T_g decreased with increasing styrene concentration for vinyl ester resins with a low molecular weight based on a dimethacrylate oligomer, whereas it was almost invariant with the styrene concentration for vinyl ester resins with a high-molecular-weight dimethacrylate oligomer.

Several authors^{10,16,17} have discussed the width of the relaxation time distribution, finding that the width of the loss factor changes with an increase in the crosslink density. More recently, Rey et al.¹⁰ observed by atomic force microscopy the network structure as a function of the double-bond conversion. They found a nodular structure that was assigned to microgels. The presence of microgels strongly affected the polymerization kinetics and controlled the mechanical properties. The results showed that the more densely crosslinked the network was, the more heterogeneous its structure was. They observed a nodular morphology and attributed it to the growth of the network through the formation of microgels, their agglomeration into clusters, and the linking between them. Ziaee

TABLE I
Cure Formulations (%) Employed in This Study

Compounds	Resin D	Resin M
Resin	100	100
MEKP	2	1.5
DMA (10% in styrene)	0.5	—
Cobalt naphthenate	0.5	0.6

and Palmese⁵ observed a similar morphology in vinyl ester networks. This observation was in agreement with the description of the network buildup proposed by Dusek,¹⁸ and it was adopted by many other researchers.

The toughening of vinyl ester resins changes with the formulation and cure temperature^{5,9,10} because of the buildup of the network structure. Rey et al.¹⁰ proposed a mechanism of crack propagation in a network formed by microgel agglomeration. They found that the regions with a low crosslink density between the microgels are the regions in which crack propagation occurs.

The aim of this study is the characterization of two commercial vinyl ester resins, relating their morphology to the styrene content and its effect on mechanical properties. This work is a part of a study of the resin transfer molding process for manufacturing composites for car parts.

EXPERIMENTAL

Materials

The epoxy vinyl ester resins Derakane 411-350 (resin D) and Derakane 411-350 Momentum (resin M) from Dow Chemical were kindly supplied by Poliresinas San Luis (Buenos Aires, Argentina). Vinyl ester resins containing 45 wt % styrene were used as purchased without the removal of inhibitors present in the resin. The initiating system consisted of methyl ethyl ketone peroxide (MEKP) together with dimethylaniline (DMA) and cobalt naphthenate. The tested formulations are given in Table I. The cure schedules for the mixture are shown in Table II. The styrene content in the commercial vinyl ester was determined gravimetrically by the evaporation of the styrene from the resin. The resin was dissolved in acetone and placed under

TABLE II
Cure and Postcure Schedules

Temperature (°C)	Time (min)
50	120
80	90
160	120

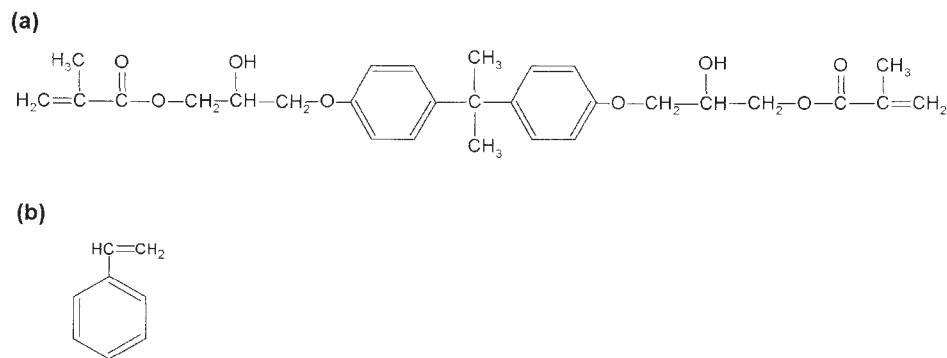


Figure 2 Scheme of the compounds: (a) vinyl ester resin and (b) styrene.

reduced pressure at 60°C for 2 h. The process was repeated until a constant weight was achieved.

Methods

Fourier transform infrared (FTIR) spectroscopy was performed with a Matson Genesis II spectrometer (Mattson Instruments, Madison, WI) with a spectral width of 4000–400 cm^{-1} , 32 accumulations, and 2- cm^{-1} resolution. Uncured samples were spread on NaCl windows. For fully cured samples, the spectra were recorded in the solid state from windows made of KBr and resin powder.

The resins were analyzed in a Waters 510 gel permeation chromatography (GPC) instrument (Milford, MA) with a refractive-index detector and Ultrastay-gel 100–100–500 and 100 A columns. The injection volume was 10 μL , and the flow rate was 1 mL/min.

A PerkinElmer DMA-7 dynamical mechanical analyzer (Boston, MA) was used in these experiments. The tests were carried out in the temperature scan mode from 30 to 175°C with a three-point-bending measuring system. The test conditions were 1 Hz, a heating rate of 10°C/min, a dynamic stress of 300 kPa, and a static stress of 500 kPa. The specimens were rectangular (20 mm \times 3.5 mm \times 1.5 mm). The span was 15 mm. Ares equipment (TA Instruments, New Castle, DE) in the torsion mode was used at 1 Hz and at a heating rate of 10°C/min for a low-temperature determination from –100 to 175°C. The height of the loss factor ($\tan \delta$) was measured from the base to the maximum height value.

The density of the cured specimens was determined at 20°C by the floating method with two solvents with different densities. The solvent mixture was put in a 500-mL vessel, and the specimens were immersed in the liquid. The pure solvent and mixture density was determined by pycnometry. The density of the mixture was considered the density of the samples when they floated in the middle of the solution. The technical-grade solvents were carbon tetrachloride (CCl_4) from Ciccarelli (Buenos Aires, Argentina) with a mea-

sured density of 1580 kg/m^3 , and toluene ($\text{CH}_3\text{C}_6\text{H}_5$) from Tensol (Buenos Aires, Argentina), with a solvent density of 867 kg/m^3 .

Compression tests were performed with an Instron 4467 dynamometer (Norwood, MA) at a crosshead speed of 2 mm/min (ASTM D 695-00). An average value of at least five cylindrical specimens was determined. The specimens were 6 mm in diameter and 11 mm high.

The impact test (ASTM D 256-84) was performed with a Fractovis Ceast falling weight (Pianezza, Italy). The speed of the test was set at 1 m/s, and the striker minimum mass (3.6 kg) was used. The specimens were 64 mm \times 12 mm \times 6 mm.

RESULTS AND DISCUSSION

To determine if the chemical structure corresponded to the structure shown in Figure 2, infrared spectroscopy of each sample before cure was performed. Figure 3 shows the spectrum for unreacted resin D and resin M. The absorption from 3200 to 3400 cm^{-1} is related to hydroxyl groups on the dimethylacrylate

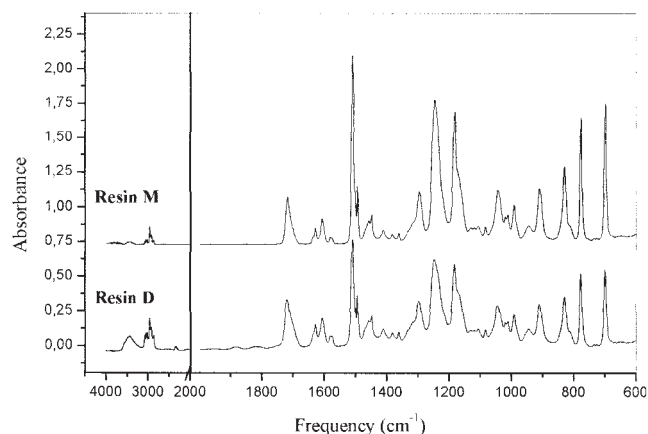


Figure 3 FTIR spectra of unreacted resin D and resin M with 40 wt % styrene.

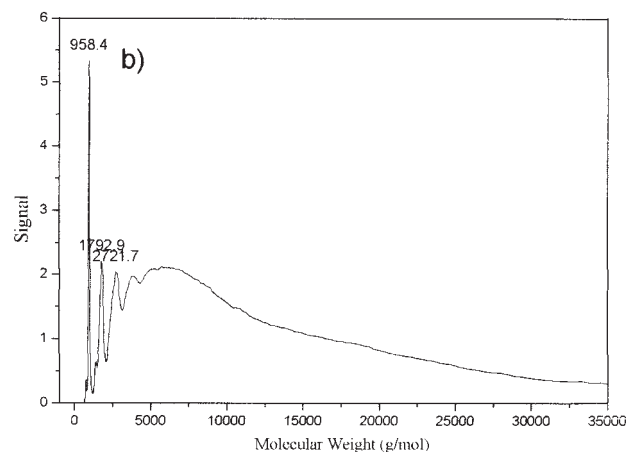
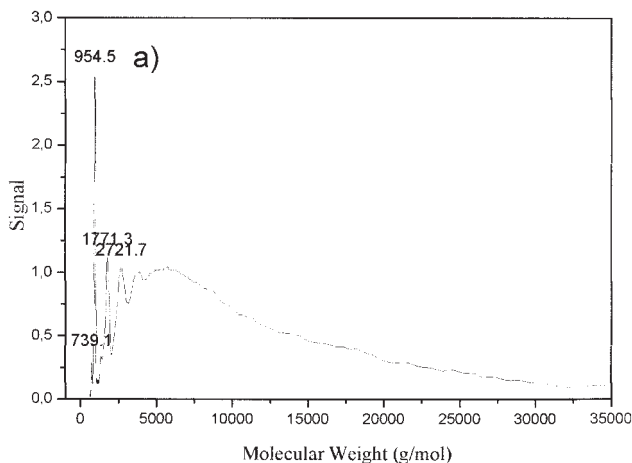


Figure 4 Elution volume measured by GPC runs: (a) resin D and (b) resin M.

backbone. The absorption intensity of 915 and 856 cm^{-1} corresponds to the epoxy groups. The absorptions due to carbonyl groups in methacrylate can be observed at 1718 and 1180 cm^{-1} . The stretching and wagging vibration of $\text{C}=\text{C}$ and methacrylate correspond to the absorption peaks at 1636 and 945 cm^{-1} , respectively. The methacrylate absorption peak at 1636 cm^{-1} is overlapped by a styrene double-bond absorption peak at 1630 cm^{-1} .^{12,19} Both resins have the same chemical structure. Figure 4 shows the elution volumes measured from GPC runs. The average molecular weights of the resins were calculated from these runs (Table III). Resin D presents a slightly

TABLE III
Molecular Weights of Each Resin

Resin	M_w (g/mol)	M_n (g/mol)	Polydispersity index
D	5609	2100	2.67
M	5277	1977	2.67

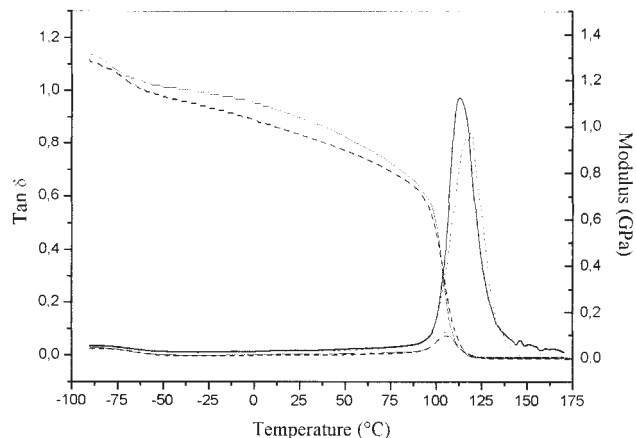


Figure 5 Storage modulus and $\tan \delta$ in the torsion mode for each resin with 40 wt % styrene: (—) resin M and (---) resin D.

higher average weight-average molecular weight (M_w) and number-average molecular weight (M_n) than resin M. However, such differences could be within the experimental error. The polydispersity is the same for M and D. Figure 5 shows the results of the dynamic mechanical analysis of fully cured resins with 40 wt % styrene, showing that both resins have one main transition temperature in the same temperature range and that no additives with a low transition temperature value are added to resin M. The cure reaction of vinyl ester resins goes through the microgels that are formed in the first step of the reaction, and a nodular structure is obtained.^{2,5,10} The existence of such microdomains in the final structure could result in two main transition temperatures. However, because of the nanosize of the heterogeneities, the different transitions cannot be detected, and they are probably very close. In a comparison of both fully cured resins, T_g for resin D is slightly higher than that for resin M, and this may be due to their final morphology.

Figure 6 shows atomic force micrographs for both resins with different styrene contents. The final morphology of the vinyl ester resins presents heterogeneity on the network due to the formation of microgels. The nodules can be attributed to agglomerated microgels formed by vinyl ester/styrene molecules. The zones around the nodules are mainly formed by styrene-styrene molecules. The nodules formed in resin M are bigger than the nodules formed in resin D. These differences could be the results of the reaction produced in the early stage. Resin M has no accelerator (DMA) in the formulation, and as a result, the vinyl ester has less reactivity and produces macromolecules with higher molecular weights and fewer cyclization reactions (which are responsible for the formation of microgels). For resin D, the higher reactivity of the resin produces cyclization in the early stage of the reaction, and the formed nodules are small. Resin M

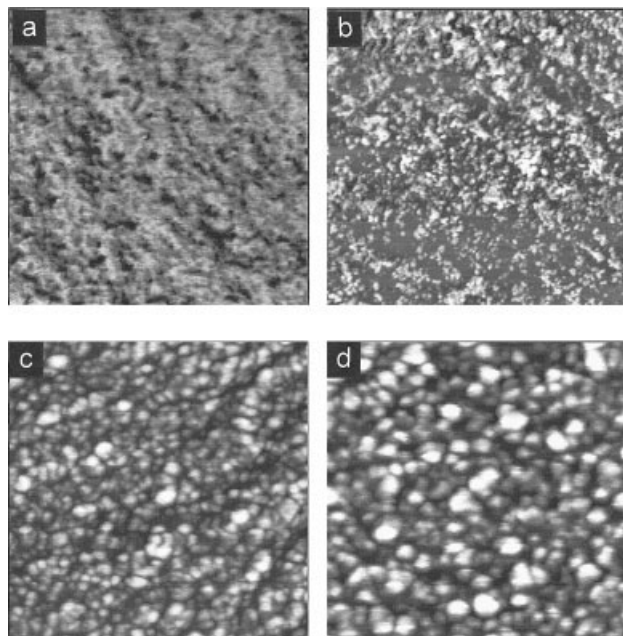


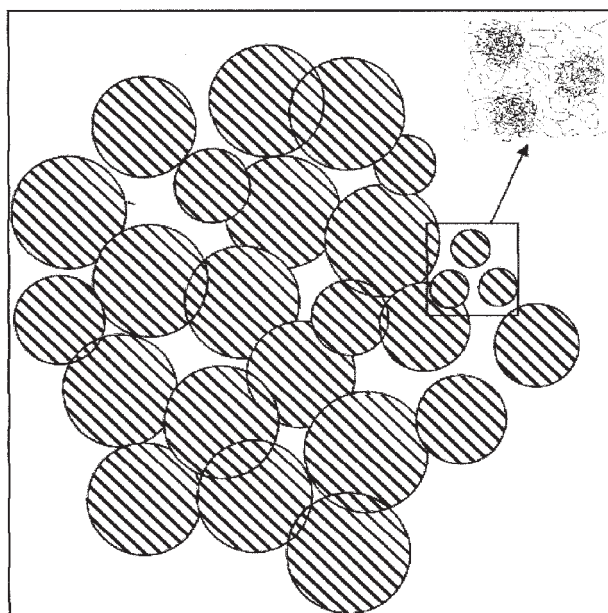
Figure 6 Atomic force micrographs ($1\ \mu\text{m}$ at full scale) for fully cured vinyl ester resins with different percentages of styrene: (a) 30 and (b) 60 wt % for resin D and (c) 30 and (d) 60 wt % for resin M.

appears to have a closer microstructure than resin D, which presents a coralline structure. The proposed morphological structure is shown in Figure 7. As the styrene content is raised, the size of the nodules in resin M increases, and the crosslinking density in the nodules decreases because of the reactions between styrene and styrene inside the nodules. For the case of resin D, the styrene–styrene chain length grows in the matrix of the coralline structure, giving a more open structure between nodules.

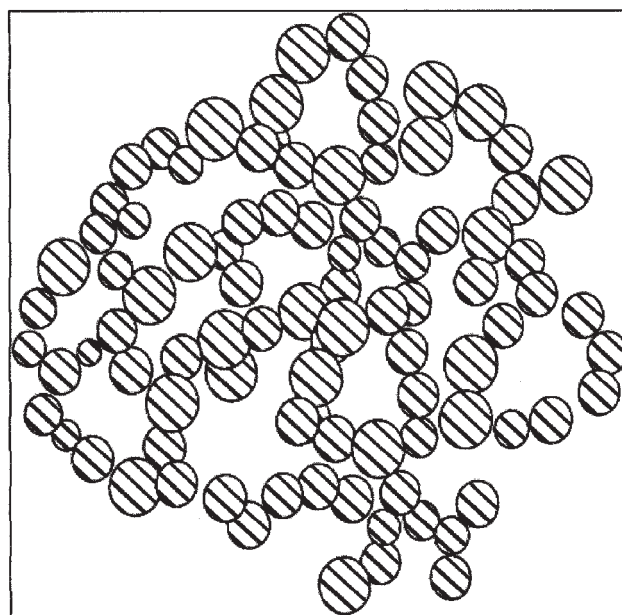
FTIR measurements were performed for both resins (Fig. 8). The absorbance at $945\ \text{cm}^{-1}$ corresponds to out-of-plane bending of carbon–hydrogen bonds in the vinyl group of the vinyl ester monomer, whereas the peak at $910\ \text{cm}^{-1}$ results from wagging of CH_2 in the vinyl group of the styrene monomer. The absorption intensities corresponding to the bending of aromatic carbon–hydrogen bonds at $830\ \text{cm}^{-1}$ in vinyl ester and at $700\ \text{cm}^{-1}$ in styrene^{2,5,8} were used to correct the effects associated with evaporation and dimensional changes. The absorbance peaks at 945 and $910\ \text{cm}^{-1}$ shifted to 930 and $898\ \text{cm}^{-1}$ in the fully cured specimens. Brill and Palmese² attributed such results to the coupled vibration modes in the compounds. A second peak at $955\ \text{cm}^{-1}$ appears as a result of the backbone mode of the vinyl ester resin.

Figure 9 shows the values of the absorbance ratio of vinyl ester/styrene double bonds when the styrene content is increased in the initial mixture. This ratio indicates the relative quantity of double bonds that exist after the full cure of the resins. For resin D, when

the styrene content is raised, the absorbance ratio decreases, and the relative styrene–styrene double bonds without reaction increase. As a result, some pools of monomers or chains of polystyrenes with low molecular weight appear between the nodules. For resin M, when the styrene content in the initial mixture increases, the relative styrene–styrene bonds without reaction decrease. This means that the reacted styrene has produced nodules with lower crosslinking density.



(a)



(b)

Figure 7 Morphological structures of the vinyl ester resins: (a) resin M and (b) resin D.

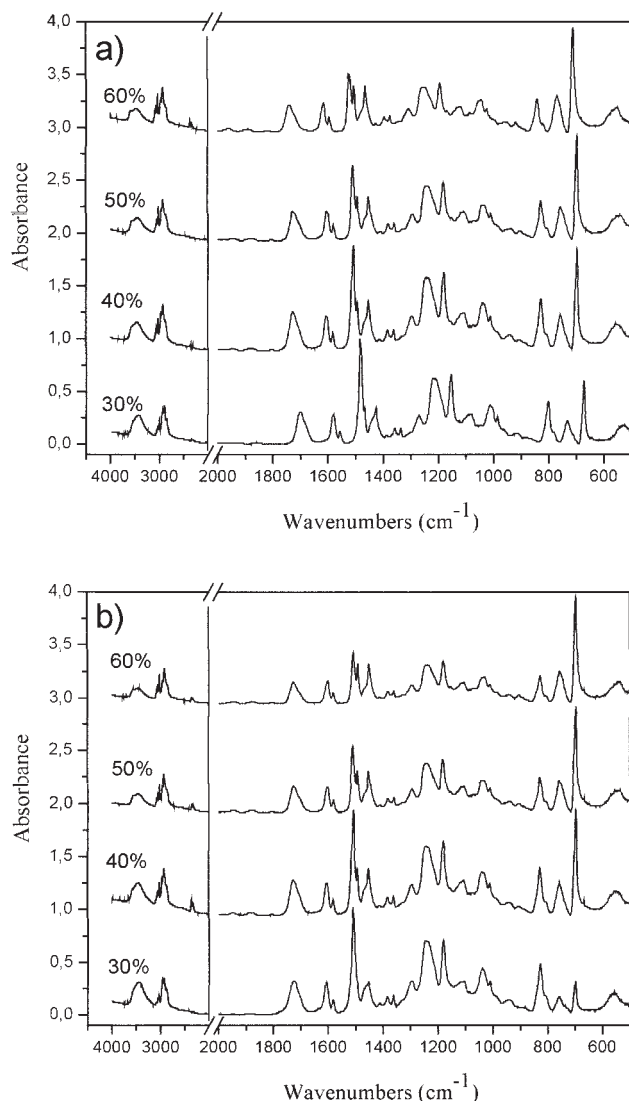


Figure 8 FTIR measurements of fully cured resins with different percentages of styrene (30–60 wt %): (a) resin D and (b) resin M.

Figure 10 shows the dependence of the resin density on the styrene percentage. The density slightly decreases with the styrene content, in agreement with previous results.^{11,20} This parameter is related to the packing density and chemical interaction.²¹ The density of resin M depends more on the styrene content than the density of resin D. At low styrene percentages, resin M has higher density than resin D, but close to 40 wt %, there is an inversion of the relative values. During the network formation, the vinyl ester/styrene reaction provides crosslinking capacity and branch points to the network, whereas styrene–styrene provides linear chain extension. As a result, for resin M, when the styrene content increases, the styrene monomers diffuse into the nodules, swelling them. Then, the styrene–styrene reactions inside the nodules increase, giving nodules with less crosslink-

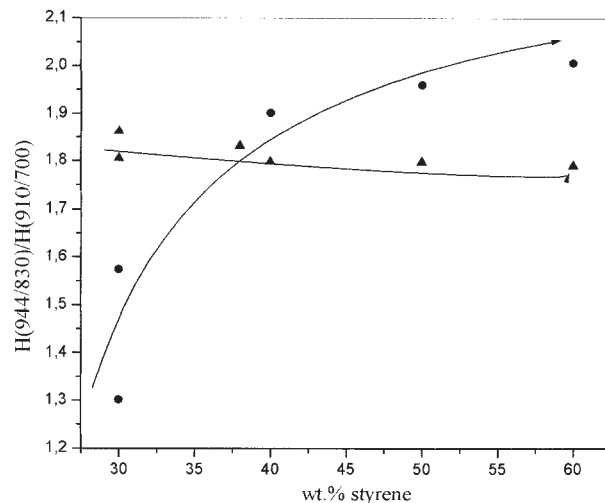


Figure 9 Relative peak heights [$H(944/830)/H(910/700)$] for (▲) resin D and (●) resin M.

ing density. For resin D, the pathway of the reaction goes through internodule reactions because the nodules have very high crosslinking density, and the increase in styrene produces higher styrene–styrene chain lengths in the zone around the nodules. In both cases, the reaction in the nodules and the reaction in the matrix around the nodules, the crosslinking density decreases. However, the crosslinking density inside the nodules appears to decrease more in the nodules (resin M) than around them (resin D). The measured density depends on the consumption of styrene, in agreement with Figure 9.

Another important practical result from the density values is the volumetric shrinkage of the resin during curing. Resin M has a higher difference in the shrinkage with the styrene content than resin D (close to 5% from 30 to 60 wt % styrene).¹¹

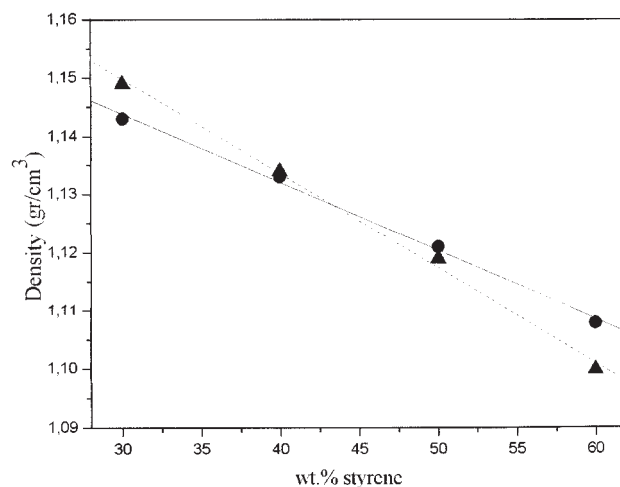


Figure 10 Densities of fully cured resins versus the styrene content for (▲) resin M and (●) resin D.

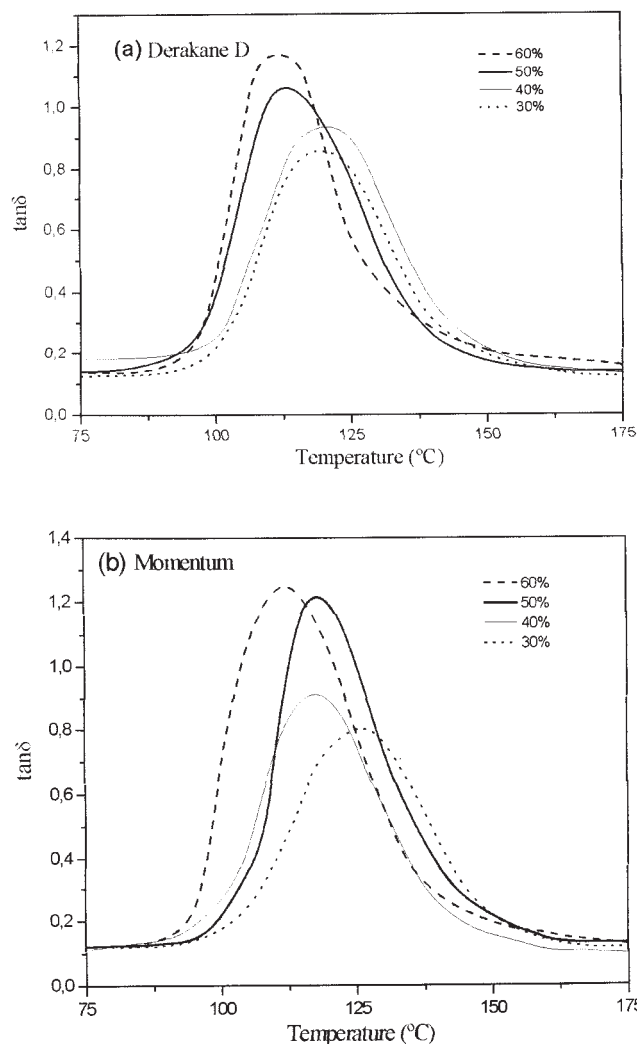


Figure 11 Tan δ from dynamic mechanical analysis for different percentages of styrene: (a) resin D and (b) resin M.

The effect of the styrene content on the structure was also studied by means of the viscoelastic properties (Fig. 11). The width of the peak of tan δ can be related to the heterogeneity of the network.¹⁰ Resin D

TABLE V
 $T_{g\text{lcop}}$ and M_c Results

Resin	Styrene (wt, %)	$T_{g\text{lcop}}$ (K)	M_c (kg/mol)
D	30	339.6	0.2679
	40	343.9	0.3387
	50	348.5	0.3836
	60	353.1	0.4403
M	30	339.6	0.2544
	40	343.9	0.2899
	50	348.5	0.3659
	60	353.1	0.4125

has a slightly higher width of the peak, possibly because the coralline nanostructure of this resin is more heterogeneous than the closed nodular one (Table IV).

Table IV shows the height of the peak of tan δ (damping) for both resins and different styrene contents. Resin D presents slightly higher damping than resin M, and it can be related to the greater flexibility of the microstructure network. Damping increases with the styrene content because of the increases in the styrene–styrene reaction and free volume, which produce high chain mobility.

E' can be related in an homogeneous polymer with the molar mass of the network chains by the theory of rubber elasticity:²²

$$E' = \frac{3RT\rho}{M_c} \quad (1)$$

where R is the gas universal constant, ρ is the density, and M_c is the molar mass of the network chains (i.e., the molar mass between crosslinks). Although this theory cannot be applied to a nonhomogeneous system, we have used M_c as an indication of the apparent crosslinking density^{10,11} or restriction of the movement of the chains (Table V). The M_c value is slightly higher for resin D than for resin M.

TABLE IV
Dynamic Mechanical Analysis Results for Resins D and M and Different Styrene Contents

Parameter	Resin	Styrene (wt %)			
		30	40	50	60
E' at $T_g + 50^\circ\text{C}$ (MPa)	M	16.9	14.4	11.2	9.7
	D	15.7	12.3	10.6	9.1
Height of tan δ	M	0.79	0.90	1.21	1.24
	D	0.85	0.93	1.06	1.17
T_g (tan δ)	M	126.2	120.3 ^a	117.9	112.1
	D	119.6	117.4 ^a	113.3	111.9
E' at 25°C (GPa)	M	2.29	2.06	2.68	2.47
	D	2.28	2.97	2.32	2.64
Width of tan δ	M	27.5	28.0	22.0	28.0
	D	26.0	27.0	25.0	21.0

^a T_g values were taken from torsion results.

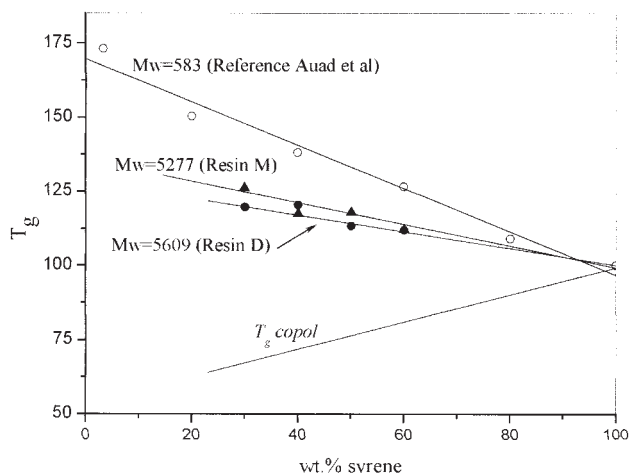


Figure 12 T_g values versus the weight percentage of styrene for (▲) resin D, (●) resin M, and (C) vinyl ester from ref. 11.

An increase in the styrene content in a sample produces a decrease in the T_g values, and it can be related to the decrease in the crosslink density.¹¹ The decrease in T_g with the styrene content is slightly more pronounced for resin D than for resin M.

The variation of T_g with the styrene content can be explained by the use of the Fox model,²³ which was applied before by Auad et al.¹¹ The contribution to T_g of the hypothetically linear copolymerization between vinyl ester and styrene and the effect of crosslinking on that copolymer are taken into account by the Nielsen equation:¹⁴

$$T_g = T_{g\text{lcop}} + \frac{k}{M_c} \quad (2)$$

where $T_{g\text{lcop}}$ is the glass transition of the linear copolymer and k is an experimental constant.

The first value is calculated by the rule of mixture or Fox equation:²²

$$\frac{1}{T_{g\text{lcop}}} = \frac{W_{VE}}{T_{gVE}} + \frac{W_s}{T_{gS}} \quad (3)$$

where W_{VE} is the weight fraction of vinyl ester, W_s is the weight fraction of styrene, T_{gVE} is the glass transition of the hypothetical linear vinyl ester (taken as 54°C for a polyphenoxy homopolymer as a model compound),¹¹ and T_{gS} is the glass transition of the polystyrene (taken as 100°C).¹¹ The results obtained for our samples are shown in Figure 12.

The obtained k values are 14.4 mol/kg for resin M and 16.23 mol/kg for resin D. A value of 19.8 mol/kg was obtained for resins with low molecular weights,¹¹ and these resins had lower molecular weights between crosslinking points. The crosslink functionalities of the

TABLE VI
Compression Test Results at 25°C

Resin	Styrene (%)	Yield stress (MPa)	Modulus (GPa)
D	30	105.8 ± 2.4	2.54 ± 0.12
	40	103.8 ± 2.5	2.42 ± 0.04
	50	103.2 ± 4.4	2.38 ± 0.15
	60	99.3 ± 2.6	2.25 ± 0.12
M	30	110.5 ± 1.4	2.61 ± 0.05
	40	108.1 ± 1.5	2.48 ± 0.13
	50	105.7 ± 1.5	2.35 ± 0.07
	60	104.7 ± 1.3	2.31 ± 0.01

resins are as follows: $\phi_M \approx \phi_D < \phi_{VE \text{ reference}}$. As the resins have functionality in the extreme of the chain, the higher the molecular weight is, the lower the functionality value is, and the less apparent the average crosslink density is.

A compression test was performed for the fully cured resins with different styrene contents. All the specimens showed softening by deformation and after a step of hardening by chain orientation. Table VI shows the obtained results. The yield stress was taken as the maximum of the stress-strain curve, and we found that it decreased with increasing styrene content. This fact can be related to the development of a network with a higher length of styrene-styrene copolymer chains and less free volume as the styrene fraction is increased. This molecular-scale structure is responsible for the slight decrease in the modulus too.

An impact test also was performed for a sample with 30 wt % styrene (Table VII). Resin M shows higher impact energy than resin D. The distribution and size of the microgels influence the mechanical behavior, especially the toughness. The crack propagates through a weak zone and is located between the microgels.¹⁰ Resin M appears to have a closer structure and higher toughness than resin D at the studied styrene content. However, this property is the only one that shows an important difference when the two resins are compared. The main cause of the difference in toughening is the use of DMA, which produces higher driving forces for radical creation. Similar results for toughening and morphology were found for vinyl ester with a different cure temperature.⁵ At low cure temperatures, the network formed is tougher because the incorporation of vinyl ester chains is faster

TABLE VII
Izod Impact Tests of Vinyl Ester Resins with 40 wt % Styrene

Resin	Energy (kJ/m ²)
D	0.25 ± 0.04
M	0.45 ± 0.05

than that of styrene chains. That also happens when the accelerator is avoided.

CONCLUSIONS

Commercial resins have been characterized by different methods (FTIR, GPC, and DMA) and have not shown large differences; differences have been found only in impact tests with 30 wt % styrene.

Dynamical mechanical analysis has been performed for the resins, and the T_g value of resin D is slightly higher than that of resin M. The damping is also slightly higher for resin D than for resin M, and this can be related to the more open morphological structure of the microgels. We have evaluated the morphological structure of the vinyl ester resins by atomic force microscopy. The toughening and yield stress of resin D are lower than those of resin M, and this could be due to the crack propagation facilitated through the weak zone between nodular structures. All the results show that resin D forms a more open structure than resin M and that the addition of an activator of radicals is an important factor that influences the morphology of the network.

The effects of the styrene content on the properties have been determined for both resins. An increase in the styrene content produces a decrease in T_g . Damping increases with the styrene content and can be related to the higher molecular weight for the crosslinking points. The influence on the damping is more pronounced in the case of resin D. From the compression test at room temperature, we can conclude that the higher the styrene content is, the lower the yield stress is for both resins.

FTIR has been performed for resin D with different styrene contents. The effect of the initial styrene content in both resins has been determined. When styrene increases, the ratio of the height of the peak of vinyl ester and styrene changes in different ways for the two resins. For resin M, when the styrene content increases, the relative content of double bonds from vinyl ester increases, or the styrene double bonds de-

crease; this is an indication that more reactions between styrene can be expected inside the nodules. For resin D, when the styrene content increases, the relative content of double bonds from vinyl ester decreases, or the styrene double bonds increase; this indicates that the addition of styrene leads to a zone with less crosslinking density and more styrene without reaction between nodules.

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