

Behavior of Nonazeotropic Compositions of a Styrene–Unsaturated Polyester Resin Analyzed Through FTIR Spectroscopy and Dynamic Mechanical Thermal Analysis

L. M. Marroyo, X. Ramis, J. M. Salla

Laboratori de Termodinàmica de la E.T.S.E.I.B., Universitat Politècnica de Catalunya, Diagonal 647, Barcelona 08028, Spain

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ABSTRACT: Styrene is one of the comonomers most frequently used in the curing of unsaturated polyester resins. The use of nonazeotropic compositions leads to the formation of networks, in which the styrene–polyester ratio varies significantly during curing, as shown through FTIR spectroscopy. Dynamic mechanical thermal analysis (DMTA) showed how the variation in the styrene content affects the network structure that is formed. The results showed a

decrease in network density in the systems in which the azeotropic composition was not used. The styrene content is therefore a factor that governs the curing process, in addition to the ultimate properties of the cured resins. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3618–3625, 2003

Key words: FT-IR spectroscopy; unsaturated polyester resin; dynamic mechanical thermal analysis

INTRODUCTION

Styrene is the most frequent crosslinking agent in unsaturated polyester resin formulations. The proportion of styrene normally used is that of the azeotrope, that is, the composition for which the polymer formed during the reaction has in its structure the same ratio of comonomers as in the initial system. During the processing and application of the resins, the styrene/polyester content (S/E) variations can influence the curing process and can modify the final properties of the cured resins.

Yang and Lee worked with a high-reactivity resin.^{1,2} They encountered compositions that were near-azeotropic, with S/E ratios (styrene/polyester double bonds' molar ratio) between 1 and 1.5, although none of the compositions studied maintained a constant S/E ratio throughout the curing process. Lucas et al. encountered an S/E azeotropic ratio of 2.5. When they used styrene quantities above or below the azeotropic level, the S/E ratio varied during the resin cure.³ Huang and Leu used an unsaturated polyester resin with an S/E ratio of 2 and observed that this ratio was maintained constant to the 40% conversion mark.⁴ At

that point, the styrene reacted in a higher proportion. In other words, the S/E ratio in the products increased. They attributed this effect to the low mobility of polyester chains in comparison to that of styrene, for moderately high degrees of conversion.

Various authors have analyzed the effect of the styrene concentration and the polyester structure on the kinetics and the change in the rheological properties that takes place during curing.^{1,5–8} They found that the conversion achieved when the system reaches gelation was higher than that predicted based on the classical Flory–Stockmayer theory. One of the reasons proposed to explain this phenomenon is the existence of intramolecular cyclizations in the polyester chains.^{1,9–11} Other interpretations attribute the phenomenon to a diminished reactivity of the polyester unsaturations as the reaction advanced.^{12,13} For vinyl-divinyl systems, the formations of compact microgels that can influence the kinetics of the process were proposed.¹⁴ The work of different authors^{2,11,15–17} further proves the formation of microgels during the curing reaction of unsaturated polyester resins.

Yang and Lee² found that, as the proportion of styrene in the initial mixture (using an equimolar composition as a reference) increased, the behavior during curing deviated from the azeotropic model to a greater degree, toward the formation of a polymer which contains less reacted styrene in its composition. Similar results were attained by Huang and Chen.^{18–20}

Cook and Delatycki used a torsional pendulum to analyze the influence of the styrene content in the

Correspondence to: J. M. Salla (salla@mmt.upc.es).

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TABLE I
Characteristics of the Compositions Used

Characteristics	Compositions					
Styrene (% in weight)	21	25	29	35	50	60
Styrene (% molar)	54.3	59.8	64.7	70.7	81.7	88.2
S/E	1.2	1.5	1.8	2.4	4.5	6.7

^a Molar percentage and the S/E ratio refer to the unsaturation content.

glass transition and the density of polyester resin networks.²¹ They found a maximum in both the temperature of the glass transition, T_g , and the density of the network when the molar styrene fraction was near 0.7. The variation in T_g with the styrene content is attributed to a compromise between the network density and the chemical composition of the system. The results obtained are in accordance with the work of Katz and Tobolsky, although the interpretation of the latter²² is based on the deviation of the materials' behavior from that of an ideal rubber.²³ Other authors^{24,25} encountered a decrease in T_g as the styrene content increased and also attributed the phenomenon partially to the decrease in the crosslinking density and partially to the change in the polyester resins' chemical composition.

Most of the studies carried out on the influence of the styrene content on the evolution of curing and the final properties have been based on proportions close to the azeotropic level. In the present work, an attempt was made to establish the relation between the styrene content and the properties of the cured material in a wide range of compositions. The curing of a polyester resin, with different proportions of styrene, was monitored using FTIR. The influence of the crosslinking agent on the dynamic mechanical properties of the crosslinked materials was examined by dynamic mechanical thermal analysis.

EXPERIMENTAL

Materials

We used a commercial orthophthalic-type unsaturated polyester resin (Estratil A-228, Burgos, Spain) with styrene (35% wt) as a crosslinking agent. The number-average molecular weight of the resin was found to be 1969 g mol⁻¹, during the fabrication process, by end-titration. The resin is composed of phthalic anhydride, maleic anhydride, and propylene glycol with a molar ratio of 3:2:5 determined by nuclear magnetic resonance (¹H-NMR). By comparing the ¹H-NMR peaks (at 100 MHz in CDCl₃ at room temperature) of fumarate ($\delta = 6.7$ ppm) and maleate ($\delta = 6.3$ ppm), the *cis*→*trans* isomerization can be estimated to be close to 100%. The styrene used was supplied by Carlo Erba (Barcelona, Spain).

We used a dispersion of benzoyl peroxide with an approximate peroxide content of 50%, supplied by Akzo Chemie (Barcelona, Spain) under the trade name of Lucidol BW-50T, as an initiator. The promoter used was *N,N*-dimethylaniline, supplied by Merck (Barcelona, Spain). Samples with different styrene contents were prepared by adding or evaporating the comonomer. The main characteristics of the resins used are indicated in Table I.

FTIR spectroscopy

A Bomem Michelson MB100 FTIR spectrometer, with a resolution of 4 cm⁻¹ in the absorbance mode, was used for conversion measurements of styrene and polyester C=C bonds during the curing reaction. All compositions included 2 phr of benzoyl peroxide and 0.1 phr of dimethylaniline. One drop of the sample (10 mg approximately) was placed between two NaCl plates for liquids. The liquid cell was placed in the oven, which was then mounted into the spectrometer. The temperature was maintained at 30°C and FTIR measurements were taken over time.

The consumption of reactive C=C in the polyester chains was evaluated by measuring the changes in absorbance at 1645 cm⁻¹ (stretching modes of the C=C in polyester). The changes in the absorbance peak at 1630 cm⁻¹ (stretching modes of the vinyl group in styrene) were used to follow the styrene conversion. The absorbance at 1730 cm⁻¹ (stretching modes of carbonyl groups) was chosen as an internal standard. The invariant absorbance at 695 cm⁻¹ (C—H out-of-plane bending in benzene ring of styrene) indicates no styrene evaporation. Absorbances were calculated in terms of peak areas and conversions for styrene (α_s) and polyester (α_E) were determined from the change of normalized absorbance as

$$\alpha_s = 1 - \left(\frac{\bar{A}_{1630}^t}{\bar{A}_{1630}^0} \right) \quad (1)$$

$$\alpha_E = 1 - \left(\frac{\bar{A}_{1645}^t}{\bar{A}_{1645}^0} \right) \quad (2)$$

where A^0 and A^t are the normalized absorbance of the functional group before and after the reaction time

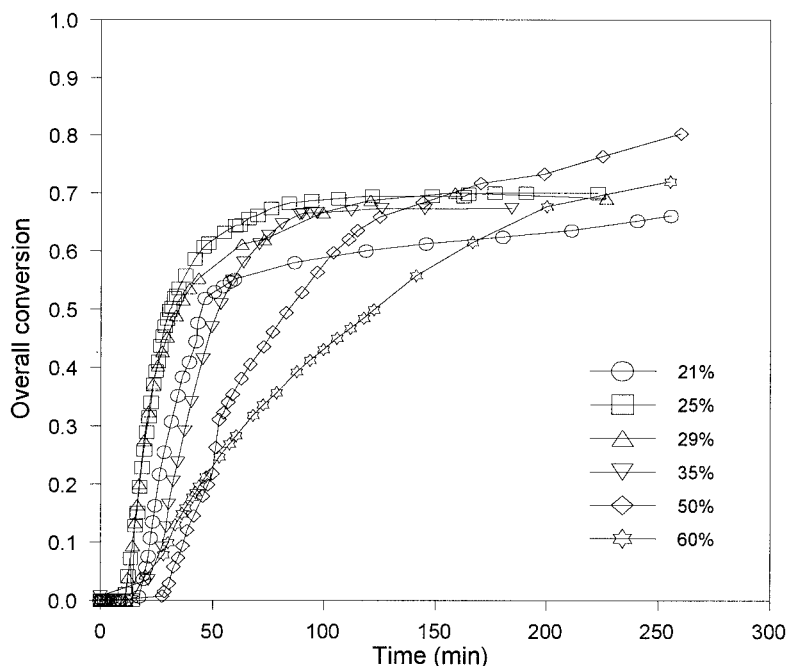


Figure 1 Overall conversion versus time for the various compositions studied.

t ($\bar{A}_{1630}^0 = A_{1630}^0/A_{1730}^0$; $\bar{A}_{1645}^0 = A_{1645}^0/A_{1730}^0$; $\bar{A}_{1630}^t = A_{1630}^t/A_{1730}^t$; and $\bar{A}_{1645}^t = A_{1645}^t/A_{1730}^t$). By using Gaussian and Lorentzian functions, the peaks at 1645 and 1630 cm^{-1} were deconvoluted. We showed that the overlap between the two peaks is small and that it does not have a great affect on the calculation of α_s and α_E using eqs. (1) and (2). The total conversion (α_T) of C=C double bonds in the unsaturated polyester resins was determined as

$$\alpha_T = \frac{(S/E)\alpha_s + \alpha_E}{1 + (S/E)} \quad (3)$$

where (S/E) is the styrene/polyester double bonds' molar ratio.

Dynamic mechanical thermal analysis

To analyze structural changes in the cured materials, the storage modulus (E') and loss factor ($\tan \delta$) were collected on a Rheometrics PL-DMTA MK3 analyzer. Samples with different styrene contents and 2 phr of benzoyl peroxide were cured in an oven at 75°C for 12 h and postcured at 150°C for 4 h. Single-cantilever bending was performed on prismatic rectangular samples ($1.5 \times 5 \times 12.5 \text{ mm}^3$). Tests were done from 0 to 210°C at 2 K/min and 1 Hz.

RESULTS AND DISCUSSION

Figure 1 shows that the evolution of the systems overall conversion differs depending on the quantity of

styrene that the resin contains. It can be seen that certain curves cross and that the degree of curing they achieve is not the same. In general, the overall conversion increases quickly and stabilizes when the material approaches vitrification. Only the compositions richest in styrene (50 and 60% wt) showed a differentiated behavior. In these formulations, the conversion never stabilizes and its evolution is more uniform throughout the curing.

Equation (3) shows that when the S/E ratio is higher than 1 the styrene conversion has the greatest influence on the overall conversion. As is shown in Table I, the S/E ratio is higher than the unit in all of the compositions used. Therefore, it follows that the evolution of the styrene conversion determines the evolution of the systems' overall conversion.

Figure 2 shows the conversion of the unsaturated polyester unsaturations versus time. It can be seen that as the percentage of styrene increases so does the final conversion achieved by the polyester, although in no case is a complete cure reached. With low styrene proportions, the medium is highly viscous. Thus, many polyester unsaturations can remain blocked and unreacted due to the immobility of the chains and the density of the network that is formed. Huang and Chen encountered a similar tendency for cured isothermics at 40°C attributed to the different density and morphology of the microstructures formed during the reaction.¹⁸

Figure 3 shows the consumption of styrene unsaturations versus time. As the initial mixture become richer in styrene, the conversion reached by this type

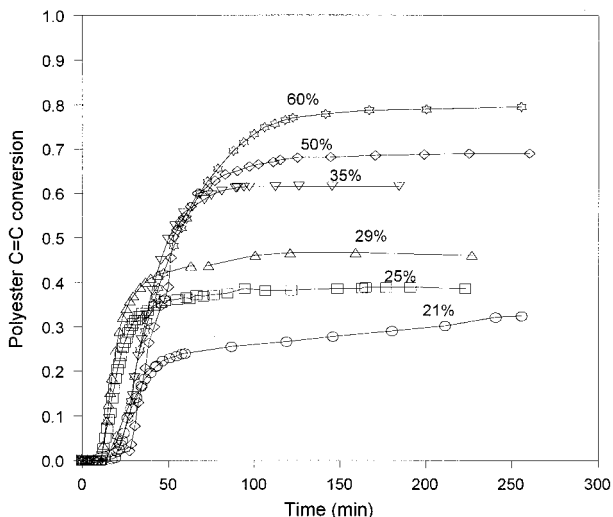


Figure 2 Conversion of the polyester unsaturations versus time for the various styrene percentages studied.

of unsaturation becomes lower. In observation of the behavior of the compositions rich in styrene, it appears that the dilution effect plays a negative role in comparison with the conversion of polyester. As the initial mixture becomes richer in styrene, the conversion of this type of unsaturation becomes lower and the rate reaction is slower. This could be attributable to chemical factors, as the propagation rate constant k_{12} of the copolymerization of styrene (M_1) with fumarate ester units (M_2) of the polyester resin is much higher than is k_{11} of the homopolymerization of the styrene.

Figure 4 shows the conversion of the polyester unsaturations versus the conversion of the double styrene bonds. The 35% composition polymerizes in conditions closest to azeotropic behavior. Taking this

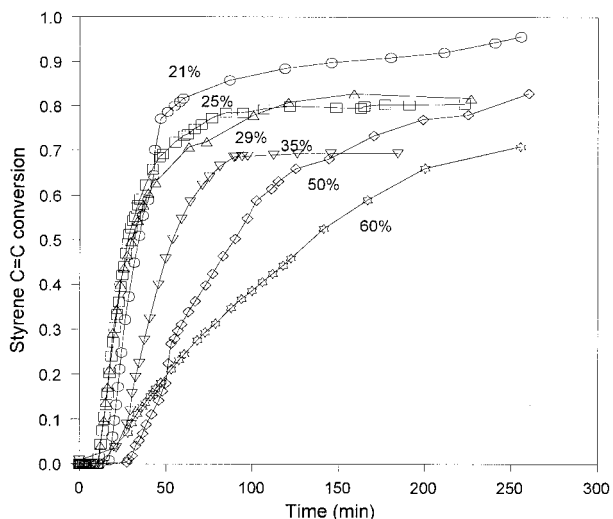


Figure 3 Conversion of the styrene unsaturations versus time for the various compositions.

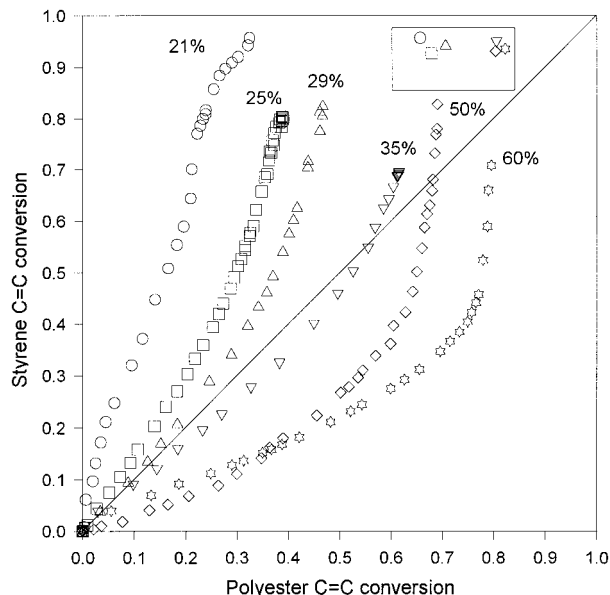


Figure 4 Conversion of the polyester unsaturations versus the conversion of the styrene double bonds.

composition as a reference, it can be observed that the systems richest in styrene show a less azeotropic behavior in the zone of highest polyester conversion, whereas the systems with the lowest styrene content are distanced or deviated toward the zone of highest relative styrene conversion, with an intensification of this tendency as the proportion of the crosslinking agent decreases.

In the composition richest in styrene, two areas are observed in which the evolution of the reaction is very different: In the first zone, the slope is lower than the unit or the copolymer that is formed contains less styrene in its composition than that contained in the initial mixture (see Fig. 4). In the second zone, the polyester conversion practically does not advance, but the styrene conversion does. In this case, the slope is much higher than the unit and the S/E ratio in which the sample is reacting is much higher than the initial ratio. The polymer formed in the latter zone can be expected to contain polystyrene chains that may or may not form part of the network.

The compositions with lower styrene content tend to deviate from the azeotropic line from the beginning of the reaction. In other words, the S/E ratio increases over that of the initial mixture. Thus, the polymer will contain more styrene in its structure than that fixed in the initial composition. This effect is intensified as the percentage of styrene decreases and becomes extreme in the 21% composition, in which the average slope of the curve is much higher than the unit from the outset of the reaction (between 3.5 and 5.7). This may be due to the low tendency of the polyester unsaturations to react in a medium that is less and less fluid. This behavior is quite different from that observed by Yang

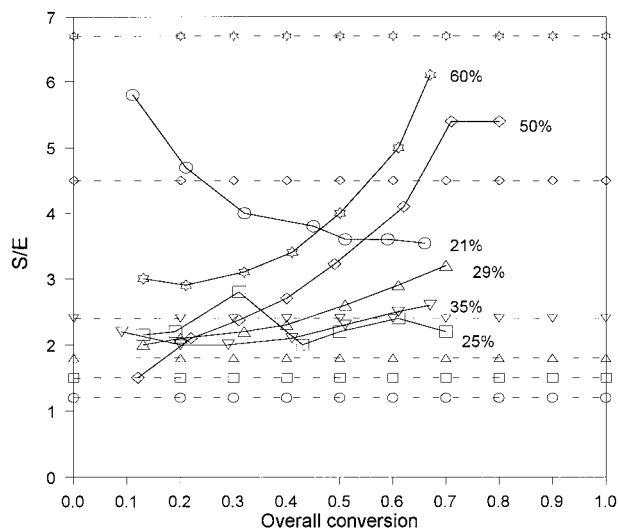


Figure 5 Evolution of the S/E ratio during the course of the reaction. The dashed lines indicate the initial concentration of the various systems $(S/E)_0$.

and Lee² and by Huang and Chen.¹⁸ For systems with $(S/E)_0$ between 1 and 1.5, these authors found that values of the slope of the curve of α_S versus α_E varied between 1 and 2. The differences between their work and ours could be due to variations in the average number of $C=C$ per molecule of the polyester, the initiator and promoter content, the cure temperature, and other factors that influence the competition between intramicrogel and intramacrogel reactions.⁴

The box in the upper-right-hand corner of Figure 4 contains the points corresponding to the postcure of the resins (4 h at 150°C). The final conversion achieved by all the systems is similar, although in no case is the conversion of the unsaturations of both samples complete. This result agrees that observed through FTIR³ by Lucas et al.

The evolution of the S/E ratio throughout the reaction can be calculated using the initial conversions and concentrations. This variation can be observed in Figure 5.

Figure 5 shows two general trends: the compositions which deviate significantly from the initial ratio $(S/E)_0$, which are indicated in the graph as dashed lines with the same symbols for each system, and the compositions that do not deviate as significantly. The first group is made up of extreme compositions (21, 50, and 60% styrene). The 50 and 60% compositions begin the reaction incorporating much less styrene into the polymer structure than that marked by the initial composition of the mixture. As the reaction progresses, the average number of styrene groups incorporated increases, even surpassing the initial ratio, in the case of 50%.

For the 21% composition, this trend is reversed: The reaction begins with the incorporation of much more styrene than that established in the initial ratio, which then diminishes as the reaction progresses, thus indi-

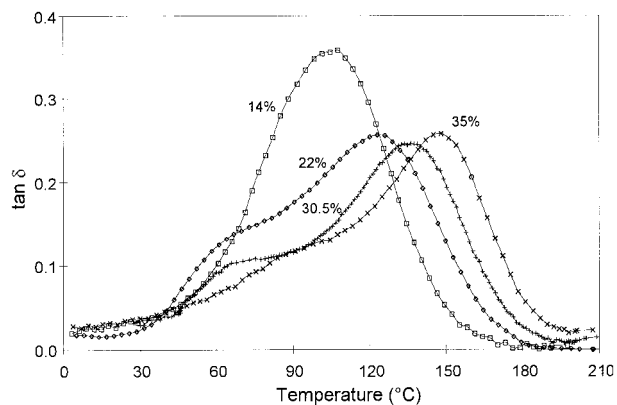


Figure 6 Loss tangent of the cured resins with different styrene content (% in weight).

cating that the control of the reaction is performed mainly by diffusive factors. If this were not the case, the reaction would be controlled chemically and would lead the system toward the formation of styrene-deficient copolymers.²⁶

The 35% composition, which corresponds to an initial ratio $(S/E)_0$ of 2.4, is that which shows a behavior closest to the azeotropic level. In the study of unsaturated polyester resins, one of them aliphatic and the other aromatic, Bermark and Flodin,²⁷ using the styrene and diethyl fumarate copolymerization data,²⁸ found an azeotropic ratio of 1.8. Lucas et al. found an azeotropic ratio of 2.5 using FTIR.³

The compositions of 25 and 29% react by incorporating more styrene than that established by the initial ratio into the polymer. This trend is intensified as the reaction progresses in the case of 29% styrene composition. As shown, the initial composition of the polyester resin is a determinant factor in the evolution of the material curing and presumably also in the structure and properties of the cured material.

Figures 6 and 7 show the relaxation spectrum of

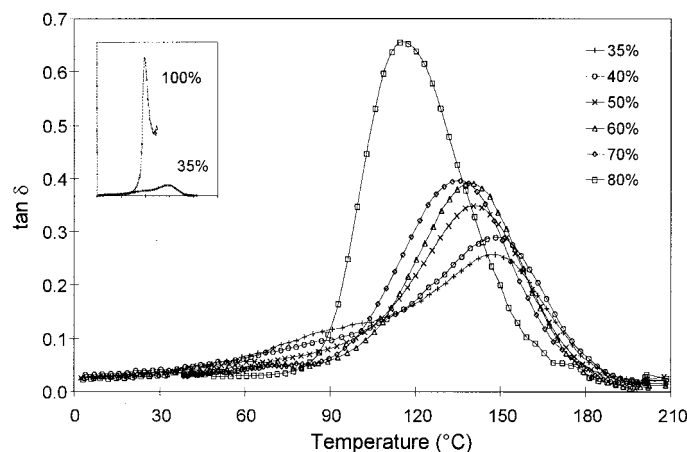


Figure 7 Loss tangent of the cured resins with different styrene content (% in weight). Comparison of the 35 and 100% resins in the upper-left box.

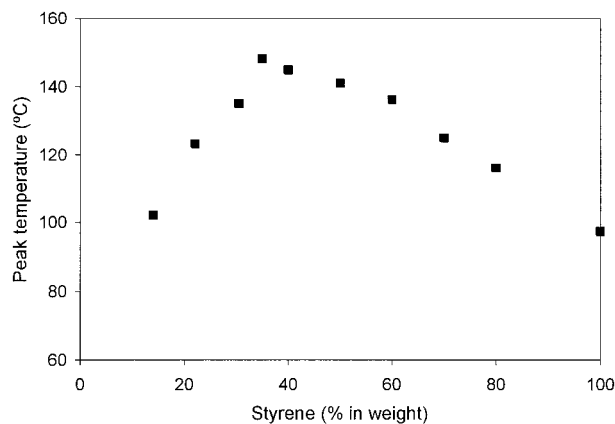


Figure 8 Peak temperature of $\tan \delta$ of the principal relaxation for the various compositions studied.

cured resins with different styrene contents. There is a clear gradation in the temperatures of the peaks of the $\tan \delta$ around 35% of styrene content. As the styrene content increases or decreases from this proportion, the temperature at which the peak appears decreases, as is shown in Figure 8.

Other authors^{21,24,29,30} found similar trends relative to the glass transition temperature in their studies on unsaturated polyester resin using dynamic mechanical testing methods. The decrease of the temperature of the glass transition and the existence of an optimum composition are justified by the ratio between the density of the network structure and the nature of the crosslinking points.

As a general rule, the intensity of the peaks increases as the compositions are distanced from the azeotropic level (35%). The most styrene-deficient compositions are the least crosslinked. Therefore, their structure develops greater mobility during the transition.³¹ In compositions that are more styrene-rich than the azeotropic one, crosslinkings and/or branches are formed with a greater content of styrene groups. Thus, the structure of these formulations is more similar to that of polystyrene (Fig. 7), leading to a greater intensity in relaxation.

Figures 6 and 7 show the existence of a second transition (β) at a lower temperature than the glass transition in some of the compositions studied. The transition β is related to the mobility of localized molecular entities and has been observed by several authors.^{30,32–35} The secondary transition appears in the azeotropic compositions and near-azeotropic compositions. Nevertheless, for compositions that are more distanced, the transition β does not appear or cannot be clearly perceived.

Figures 9 and 10 show the storage modulus versus temperature, for all the compositions used in this study. Using the simplification made in the theory of rubber elasticity,^{36–38} the network density in complex systems can be estimated with the following equation:

$$M_c = \frac{3dRT}{E_r} \quad (4)$$

where M_c is the average molecular mass between crosslinkings; E_r , the modulus of the material in the rubbery segment; d , the density; R , the gas constant; and T , the temperature at which E_r is measured (temperature of the peak of $\tan \delta$ plus 50°C).

As can be seen in Figure 11, the azeotropic composition shows the lowest value for M_c , which corresponds to a network density that is higher than the rest of the compositions studied. The result confirms the evolution presented by the system during curing (Fig. 4), which leads to an optimum network structure, in which the monomer styrene is incorporated into the network structure in a more uniform form. Furthermore, the high network density presented by this system indicates that the two types of unsaturations present in the medium are converted more efficiently. Thus, a higher number of crosslinkings between chains are produced, and there are fewer “defects,” that is, polystyrene branches which hang from the polyester chains or styrene oligomers which can remain blocked in the structure without any connection to the network.

When the styrene content is decreased, taking the azeotropic composition as a reference, the degree of polyester unsaturation conversion becomes increasingly lower, as is shown by the conversion tracked by FTIR. Therefore, it follows that the network density would also be lower and increased values for M_c would be attained. This result is coherent with the decreases of T_g when the network density decreases (lower styrene content).

As the amount of styrene increases, the structure of the system is more similar to that of pure polystyrene. Much longer chains are formed and the crosslinking density of the network structure becomes very small. For example, the 80% styrene composition has an M_c

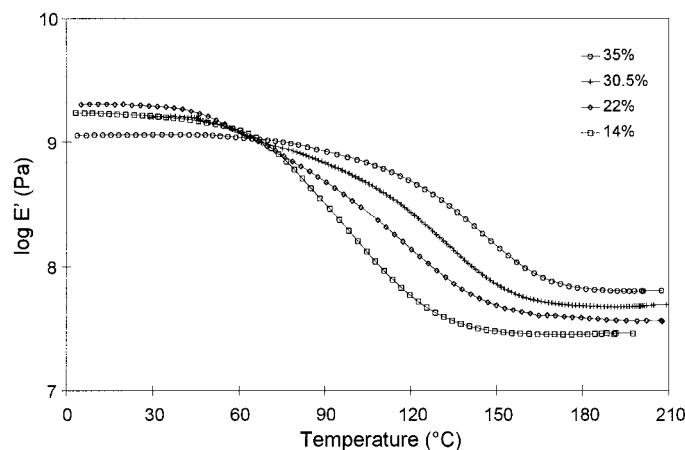


Figure 9 Storage modulus versus temperature for the various styrene weight percentages (low percentages).

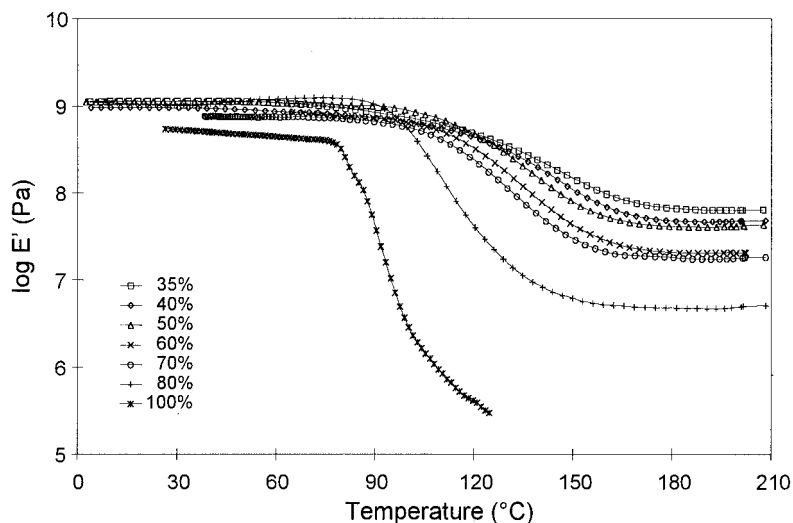


Figure 10 Storage modulus versus temperature for the various styrene weight percentages (high percentages).

that is higher than the average molecular weight of the polyester chains, which indicates that this is a system predominantly made up of very long polystyrene chains bonded by polyester molecules.

CONCLUSIONS

We have found that the styrene–polyester copolymerization has an azeotropic composition of around 35% styrene, which makes for a molar styrene/polyester ratio of 2.4. In the nonazeotropic compositions, the molar *S/E* ratio varies in the course of the curing. Therefore, the network structures that are formed will not be homogeneous on a local level.

When the styrene content increases, the conversion of the polyester unsaturations is governed by diffusive factors and the styrene conversion is chemically controlled. Then, DMTA results show an optimum composition as regards the formation of the network structure that coincides with the 35% styrene contents. This

optimum point depends on the balance between the degree of crosslinking and the copolymer effect.

The evaluation of the network structure density, performed using the rubber elasticity theory and the T_g values, for the systems studied, shows that the composition of 35% styrene possesses the greatest network density. In styrene-poor compositions, the lack of a network structure is shown, as they have relatively low crosslinking density values. In styrene-rich compositions, the crosslinking density tends toward very low values because the structure is increasingly similar to that of polystyrene, which does not feature crosslinks in its structure.

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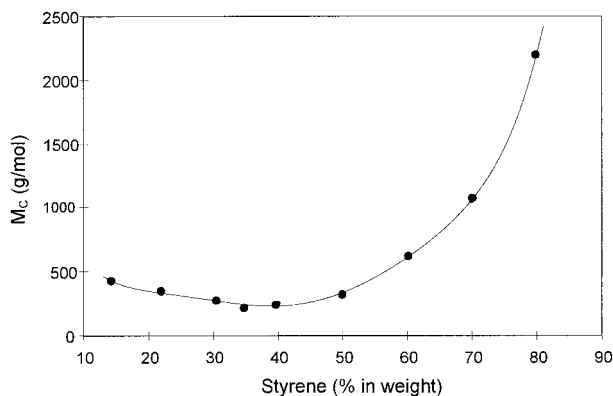


Figure 11 M_c versus styrene content for the various resins. The solid line indicates the tendency followed by the values.

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