

Dependence of Dynamic Mechanical Behavior of DGEBA/DDM Stoichiometric Epoxy Systems on the Conditions of Curing Process

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SYNOPSIS

Dynamic viscoelastic properties of diglycidyl ether of bisphenol A (DGEBA) cured with diaminodiphenylmethane (DDM) have been studied. The relaxation spectra of stoichiometric mixtures have been investigated as a function of the casting procedure and the thermal history during curing. Variations on the temperatures of the loss peaks and also on their magnitude have been observed when a solvent was employed to cast the mixtures. These variations have been attributed to the existence of high crosslinked regions formed at the earlier stage of curing inside the overall matrix. The results obtained from mixtures cured with different thermal histories underline the importance of adequate selection of curing conditions in order to obtain the optimum properties for these materials. Differences in crosslink density amongst the mixtures cured at different conditions have been correlated to the extent of reaction obtained by infrared measurements. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Numerous dynamic mechanical studies of epoxy resins correlating changes into relaxations in the glassy region with their chemical structures have been reported in the literature survey.¹⁻¹⁵ Many investigations have been conducted into variations in the low temperature transitions as a function of cure conditions and/or chemistry and concentration of resin and curing agent. These relaxation processes at temperatures far below the glass transition temperature have been denoted as β , between -30° and -60°C , and γ , occurring near -140°C ; relaxations which result from the motion of glyceryl amine groups and other parts of the network structure^{3,5-9,12-17} and the movement of methylene units, respectively. Another relaxation, denoted as ω , γ or β' , at 50° to 90°C (called ω -transition in this study) has been also reported,^{2,6,10-12,16,17} although its mean is not very clear; in a recent paper, it has been shown to change and/or even disappear on physical an-

nealing at temperatures around which this relaxation is observed.¹⁸ The mechanisms of the relaxations below the α -transition, however, are still not fully accepted, particularly due to the contribution of several molecular processes for the β -transition and to discrepancies upon contribution or not of the network morphology to the ω -relaxation.

On the other hand, it is now well known that the crosslink density of the formed network has a pronounced effect on the glass transition temperature^{2-10,19} and also on the lower temperature processes, especially at low crosslink extents,^{3-6,10,13,17} although the influence of other factors—such as free volume at high crosslink densities—remains to be clearly evidenced.

Usually these transitions have not been related to thermoset morphology, although some works about the existence of inhomogeneities in the morphology of highly crosslinked epoxy resins have been published.^{7,17,20-22} These inhomogeneities should be highly crosslinked nodules immersed in an inter-nodular matrix of lower crosslink density; indeed, the intranodular crosslink density should be responsible for the onset of molecular motion corresponding to the glass transition and also for some

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variations in low temperature relaxations, the last one especially at stoichiometric compositions.²² The existence of these high crosslink density regions responsible for the ω -relaxation would be produced by a heterogeneous crosslinking reaction.¹⁶ In this way Grof et al. have recently suggested that the growth of polymers near the gelation threshold is a connectivity phenomenon rather than a statistical process.²³

Industrial-scale production of certain composites based upon an epoxy matrix involves the employing of a solvent and it is often assumed that the solvent, after being removed, does not influence the behavior of the final products. Nevertheless, as some investigations have shown, solvent employing can affect the physico-chemical behavior of epoxy resins^{12,24} as well as that of their composites.²⁵ The properties of thermoset networks depend upon the conditions under which the cure reactions occur, because the viscosity, the crosslink density, and the number of accessible conformations all change with time. Therefore, variations on the physical properties of crosslinked epoxy resins have been attributed to a lower crosslink density of the formed network structure because of solvent employing.^{12,26} It has also been shown, however, that for a complete cure schedule the epoxy conversion remains similar for mixtures cast with or without solvent,²⁴ and therefore the crosslink density could also be similar. These contradictory observations could be related to differences in the method of solvent removal employed to make these investigations.

The purpose of the present work is to investigate the changes in the dynamic mechanical properties of epoxy resins, caused by variations in cure schedules used to cure diglycidyl ether of bisphenol-A (DGEBA) with diaminodiphenyl methane (DDM) mixtures at stoichiometric compositions. This study also examines the influence of the solvent employed in the mixing process prior to the cure schedule on the viscoelastic transitions which appear in this epoxy system. The investigation has been made at a frequency of 10 Hz in the temperature range of -80° to 250°C . For explanation of differences in the three relaxations, the existence of a nodular morphology is suggested.

In order to know the crosslink densities of mixtures cured with different thermal histories throughout curing, the molecular weights between crosslinks have also been studied by means of the rubber modulus behavior of the networks above their glass transition temperature.

Fourier-transform infrared spectroscopy studies have been carried out to compare the extent of re-

action of the mixtures corresponding to the several cure conditions employed. Band absorption values were normalized to that corresponding to the uncured mixture.

EXPERIMENTAL

The DGEBA epoxy resin, DER 332, was supplied by Dow Chemical. 4,4'-diaminodiphenyl methane (DDM) from Ciba-Geigy was used as the hardener in stoichiometric epoxide/amine ratios.

Stoichiometric mixtures of DGEBA and DDM were generated by dissolving the curing agent in the pre-heated epoxy resin in an oil bath to 80°C for 10 min. Samples were also prepared by first dissolving DGEBA in dichloromethane in a 10% weight concentration at room temperature. The solvent was removed from the solution by slow evaporation at 80°C with continuous stirring and further overnight vacuum pumping at 80°C ; stoichiometric mixtures were then prepared according to the previous method. The mixture was then cast into $300 \times 100 \times 6$ mm plaques using a preheated parallel glass plate mold coated with Frekote 44 release agent. Temperatures and times employed in the cure-schedules were as follows: 80°C for 2 h 30 min, including degassing for 50 min under vacuum; 110°C for 1 h 30 min; 140°C for 50 min; and 200°C for 2 h. The standard cure schedule included all cycles and the other cure-schedules are defined below by the temperatures employed. In order to avoid internal stresses, all mixtures were slowly oven-cooled after the corresponding last cure-cycle was finished. Epoxy N and S mixtures were also prepared by using 90 min vacuum at the early stage of the cure schedule. Formulations cast without or with solvent are named below as epoxy N or epoxy S, respectively.

Dynamic mechanical analysis of cured mixtures was performed at 10 Hz using a Polymer Laboratories DMTA machine between -80°C and 250°C ; the specimen cross-section used was 11×1.7 mm with a 14-mm span. The influence of cure conditions on the crosslink density of samples cast with different cure schedules was investigated by means of a viscoanalyser Metravib testing samples of $60 \times 12 \times 6$ mm by a three points bending device with a 44-mm span. Runs were made from room temperature up to 250°C at a heating rate of $3^{\circ}\text{C}/\text{min}$ and a 10-Hz frequency.

FTIR studies were performed using a Perkin-Elmer infrared spectrophotometer, 16 PC model. The analysis of the plaques prepared with different cure-schedules was performed by making KBr-pellets with a small amount of the samples; the scans were

collected at a 4 cm^{-1} resolution from 4000 to 400 cm^{-1} , and the resulting spectra have been plotted in the transmittance mode. The 1510 cm^{-1} band associated with the phenyl group was taken as an internal reference.

RESULTS AND DISCUSSION

The mechanical loss tangent measured at a 10-Hz frequency of stoichiometric DGEBA/DDM mixtures cast without and with dichloromethane are plotted against temperature in Figure 1. At high temperatures, the big peak in $\tan \delta$ indicates the α -relaxation process corresponding to the glass-to-rubber transition of the epoxy system. From the smaller $\tan \delta$ peak, below 0°C and centered at about -35°C , the β -relaxation temperature may be identified. For epoxy-diamine networks, the most authors^{1,3-8,10,12-15,27,28} associate this broad low-temperature secondary transition to the crankshaft motion of the glycidyl amine linkage after reaction of the epoxide ring and the amine group. An intermediate ω -relaxation, denoted as ω , γ , or β' in the

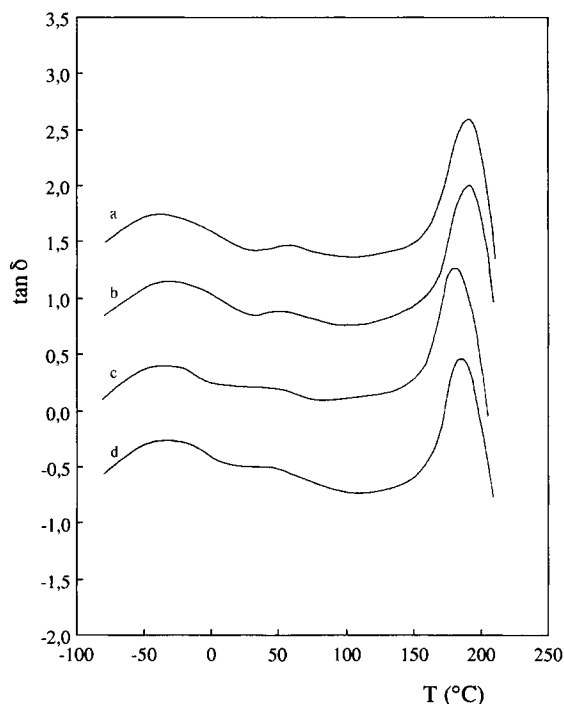


Figure 1 Dynamic mechanical behavior of stoichiometric compositions prepared with the standard cure schedule. Samples cast without a solvent: (a) 50 min in vacuum; (b) 90 min in vacuum. Samples cast with solvent: (c) 50 min in vacuum. (d) 90 min in vacuum. The log ($\tan \delta$) scale indicates only the range of variation of $\tan \delta$ values.

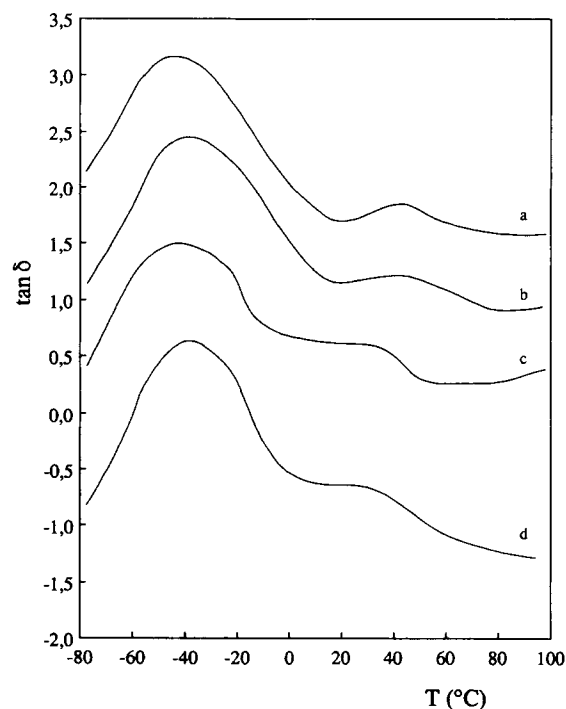


Figure 2 β and ω relaxations of the stoichiometric composition cast with the standard cure schedule. Symbols as in Figure 1. The $\tan \delta$ scale indicates only the range of variation of $\tan \delta$ values.

literature survey, appeared at temperatures between 20°C and 70°C in the same way shown in other works.^{2,6,10-12,16,17} This transition has usually been assigned to the unreacted molecular segments and/or inhomogeneities in the sample arising from dissimilar crosslinking sites.^{6,12,17}

As Figures 1 and 2 show, mixtures prepared using the solvent showed the low temperature β -relaxation with no significant change in temperature when compared to the ones cast without the solvent, but the peak disappeared at lower temperatures than in mixtures cast without the solvent because of overlapping with the ω -relaxation; this difference was more clear as vacuum time employed in the cure schedule was shortened. This variation could be related to the modification in the kinetics upon residual solvent in the earlier stages of the cure schedule^{24,26} which could modify the ulterior network structure. The ω peak was broader and appeared at lower temperatures in the solvent-cast specimens, showing in its low-temperature region certain connection with the β -relaxation. The position of the ω peak depends upon the analyzed epoxy system. For instance, it appears at the frequency of 10 Hz at about 100°C in DGEBA/diaminodiphenylsulfone (DDS)²⁹ and tetraglycidyl-diaminodiphenyl-

methane (TGDDM)/DDS⁶ systems, or around 60°C in DGEBA/4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM),³⁰ and it is centered at about 60°C in DGEBA or TGDDM/DDM mixtures.¹⁶ The position of the ω -relaxation together with the different shape on the right side of the β -transition could indicate a lower epoxy conversion in the solvent-cast mixtures,^{6,28} though as shown below by IR measurements, this is not evident. The higher temperature of the ω -transition in epoxy N samples could also correspond to regions of higher crosslink density or nodules embedded in a lower crosslink density matrix,^{7,17,22} and/or to the unreacted molecular segments; although, as shown below, the nonexistence of important differences in the crosslink density in samples cast prior to the cure-schedule without or with the solvent does not confirm the last possibility, which agrees with that suggested by other authors.^{12,16}

The most important difference between the mixtures cast with or without the solvent becomes evident in the α -relaxation region. This peak appeared at 187°C for the samples prepared without the solvent, decreasing to 178°C in the solvent-cast mixture when vacuum time at 80°C in the cure schedule was 50 min; this evidence could be a consequence of some trapped solvent exerting a plasticization effect and/or because of a less complete network formation in the solvent-cast mixtures although, as shown below, it is not evident from dynamic mechanical analysis of the rubber modulus above the glass transition. The presence of residual solvent in the early steps of the curing process can also decrease the probability of complete chemical bonding of DGEBA with DDM.²⁶ However, as has been stated above, the existence of residual solvent could modify the crosslink density of the reacting material formed at the earlier stages of the cure schedule, thus changing the viscoelastic behavior of these epoxy systems.

In order to analyze the influence of solvent removal on the dynamic mechanical behavior, another solvent-cast stoichiometric mixture was prepared and kept at 80°C in vacuum for 90 min at the early stage of the cure schedule, instead 50 min in the other epoxy S sample. As shown in Figure 2, the temperatures and shapes of the β - and ω -relaxations do not suffer any important variation, although the β -relaxation peak was higher in the 90-min vacuum-cast mixture, indicating that more hydroxyether groups were moving in this temperature region. In the same way, the α -relaxation temperature increased (Fig. 1), becoming closer to that of the samples cast in the absence of solvent. This increase could be related to a further removing of residual

solvent because of the longer vacuum period employed²⁴ and/or to an increase in the extent of reaction during the earlier stages of cure.²⁶ Although the use of solvent in the preparation of these epoxy mixtures can decrease the number of crosslinks in the epoxy network,¹² as shown below by FTIR measurements, the ultimate conversion of epoxy groups was similar in epoxy S and N mixtures; thus these variations on the relaxational behavior should be connected with morphological differences produced at the earlier stages of curing.

The storage modulus, E' , for these DGEBA/DDM mixtures is plotted against temperature in Figure 3. E' conducted in a relatively similar way for mixtures prepared by both casting methods. Its value had a relatively rapid decrease at the temperatures where β peak appeared, though the variation was lower in the solvent-cast systems, followed by a not-so-quick decrease up to the temperature range corresponding to the α -relaxation where it dropped for two orders of magnitude. The variation of the storage modulus at the ω -relaxation was apparent for all mixtures but it was not so important, and as it happened on the β -transition, it was lower for the solvent-cast mixtures.

Plots of $\tan \delta$ corresponding to various cure conditions against temperature are shown in Figures 4–

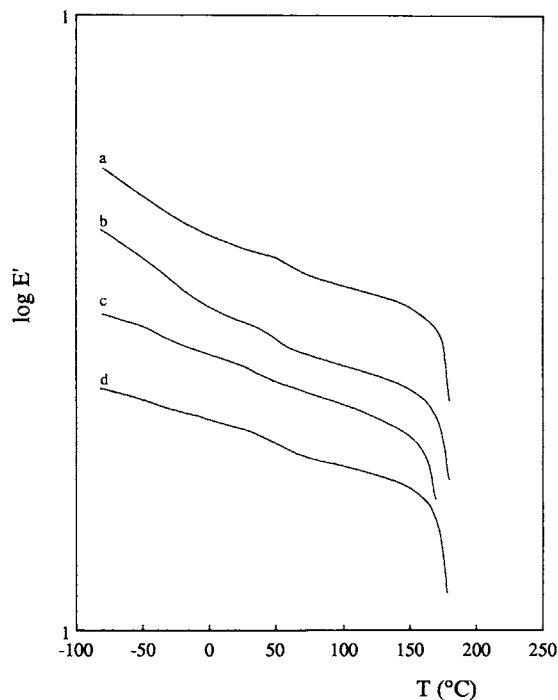


Figure 3 Storage modulus versus temperature for samples cast with and without a solvent. Symbols as in Figure 1.

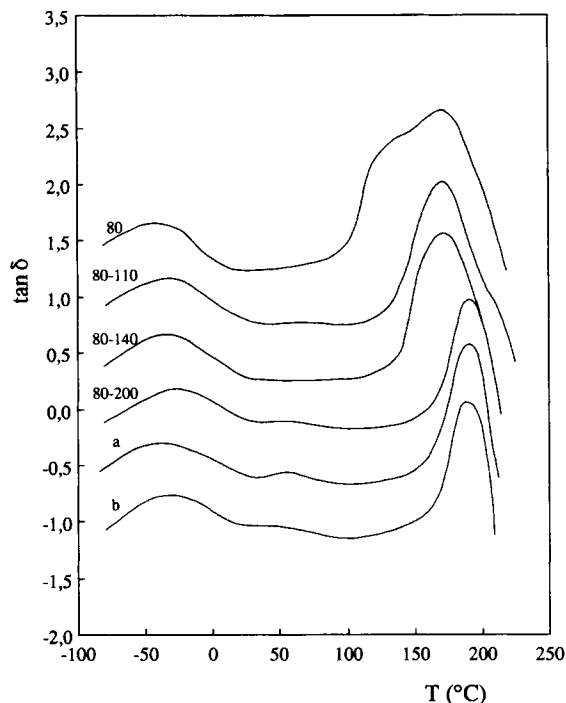


Figure 4 Loss tangent for stoichiometric compositions cured at different conditions. All cure schedules include the curing at 80°C. The $\tan \delta$ scale is as in Figure 1.

6. As illustrated from these figures, the conditions employed in the cure schedule influenced not only the temperatures of the relaxations but also the shape of these transitions. For mixtures prepared with cure schedules which had as a common feature a temperature of 80°C (Fig. 4), the $\tan \delta$ peak corresponding to the α -relaxation increased in temperature and decreased in broadness with increasing post-cure temperature, apparently reaching a maximum value around 188°C for the 80°–200°C and standard schedules. A similar behavior has been reported by differential scanning calorimetry studies with epoxy systems based on DGEBA and catalysts by increasing post-cure temperature.¹⁵ In the sample cured at 80°C for 3 h, a really broad peak with a well defined shoulder was obtained. The shoulder observed around 125°C was due to the α -transition of the sample, and the higher temperature peak at 167°C appeared as a consequence of further crosslinking because of the temperature increasing throughout the scan. Results obtained on mixtures prepared with 80°–110°C or 80°–140°C schedules were very similar; indeed, in both cases only a broad α -transition around 169°C was observed (Fig. 5), indicating that the employed cure treatment to 140°C produced a similar crosslink density to that obtained at 110°C. For both samples a small should-

der appeared at about 200°C which could correspond to high crosslink density zones included inside the epoxy matrix. Similar shoulders have also been observed in non-stoichiometric mixtures.²⁴

Curves shown in Figure 5 correspond to mixtures cured with several cure schedules, including the 200°C post-cure stage. The α -relaxation peak appeared in all mixtures at higher temperatures and it was sharper than those shown by mixtures cured without the 200°C stage (Fig. 4), indicating a higher crosslink density in the post-cured mixtures. The higher the α -relaxation peak temperature was, the lower the earlier temperature in the cure schedule was, thus indicating the importance of the control of temperature in the first stages of the crosslinking process. As stated by Pangrle et al.,¹⁷ lower temperature curings suppose that linear propagation of the epoxy chain is preferred relative to further reaction (crosslinking) at an already reacted monomer end, leading primarily to a low crosslink density matrix. When the first cure-schedule stage is carried out at higher temperatures, high local crosslink densities materials are obtained. It results in variations in the local environments of the molecular segments contributing to the low temperature relaxations on the matrix.

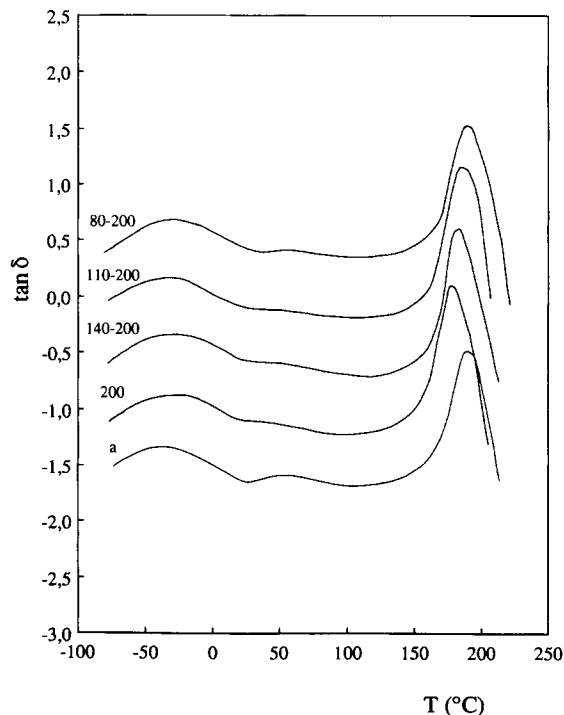


Figure 5 Loss tangent for stoichiometric compositions cured at different conditions. All cure schedules include the curing at 200°C. The $\tan \delta$ scale is as in Figure 1.

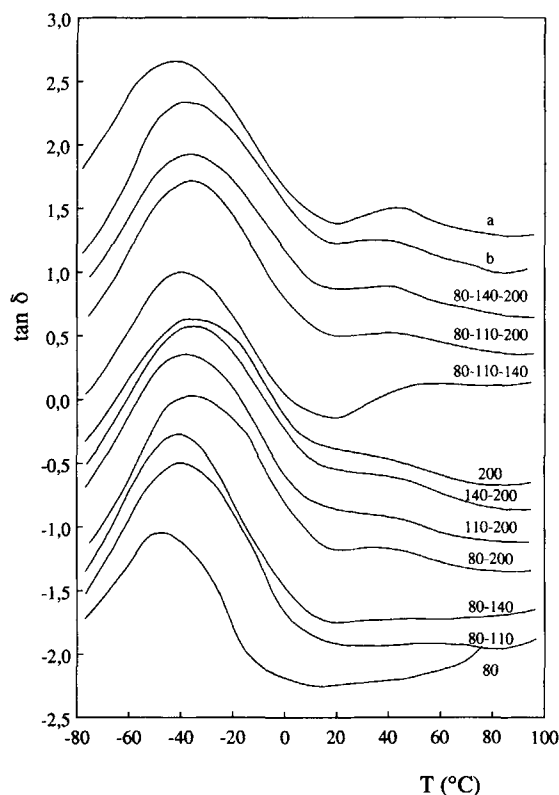


Figure 6 Temperature dependence of $\tan \delta$ in the low temperature range for stoichiometric systems cured in different conditions. The $\tan \delta$ scale is as in Figure 2.

Plottings obtained on the low temperature relaxations for mixtures cured with the various cure schedules employed are shown in Figure 7. No large differences among the temperatures at the maximum $\tan \delta$ in the β -transition or in the breadth of this relaxation were observed. However, in the system prepared with only the 80°C cure-step the β -relaxation temperature appeared at a slightly lower value, as though this decrease would correspond to a lower crosslink density network containing a lower amount of glycidyl amine groups,¹⁴ thus showing that the β -relaxation is affected by the progress of the cure reaction or network formation.^{22,25,28} Furthermore, samples cured upon the 80°–110°C, 80°–140°C, and 80°–110°–140°C cure schedules showed a breadth of the β damping peak slightly lower than that of other cure schedules. This indicates a lower number of hydroxy ether groups formed^{17,22} despite, as shown below by FTIR measurements, the insignificant differences in the extent of reaction of the epoxy group.

To complete the above observations the DGEBA/DDM mixture has been analyzed with three different cure schedules, using 80% curing agent with re-

spect to that employed in the stoichiometric composition. As inferred from Figure 8, it is evident that the crosslink density obtained in these systems with the only 80°C cure stage was lower than that obtained with other cure schedules, because the α -relaxation temperature was clearly lower than that corresponding to the stoichiometric mixtures cured under the same conditions. The β -relaxation was small and appeared at low temperatures rather than those of the stoichiometric mixtures. It must be noted that the magnitude of the β -relaxation for the sample corresponding to the standard cure schedule was similar to that obtained for the stoichiometric system solely cured upon the 80°C stage and, as shown in Tables I and II, this fact agrees with the extent of reaction of the epoxy group in both mixtures, and consequently with the amount of hydroxyether groups formed. Otherwise, the ω -relaxation was not evident for these epoxy-rich mixtures non-post-cured, although a shoulder in the α -relaxation at high temperatures as well as a small ω -relaxation in the mixture cured with the standard cure schedule were observed.

On the other hand, the variation on α - and β -relaxations can also be explained considering the existence of high crosslink density inhomogeneities, or nodules, in the morphology of the resins prepared with different cure schedules.^{7,16,17,22} These inhomogeneities should be immersed in an internodular matrix of lower crosslink density. As has been suggested,³¹ the incipient formation of these high-density zones should take place prior to gelation. Otherwise, as has been pointed out,³² the size of these zones should not change on post-cure above the maximum glass transition temperature, $T_{g\infty}$. Since for the stoichiometric mixture the gelation time was reached before the cure time employed in the 80°C cure stage, the size of the high-density zones should not vary in the stoichiometric mixtures cured with the 80°C stage. High crosslink density nodules could act as supporting sites of a framework which hold the thermosetting network together.²² As the post-cure time is increased, additional crosslinking takes place, in both the nodules and the internodular matrix. The further increase of nodular crosslink density, which leads to the formation of a more rigid framework, will be of utmost importance to the change in glass transition temperature,²² explaining the variations shown above for epoxy N and epoxy S mixtures by the kinetics variation at the earlier curing stage when the solvent was employed.²⁴ Instead, both nodules and internodular matrix are responsible for the β -relaxation because hydroxyether groups appear in both. However, their contribution

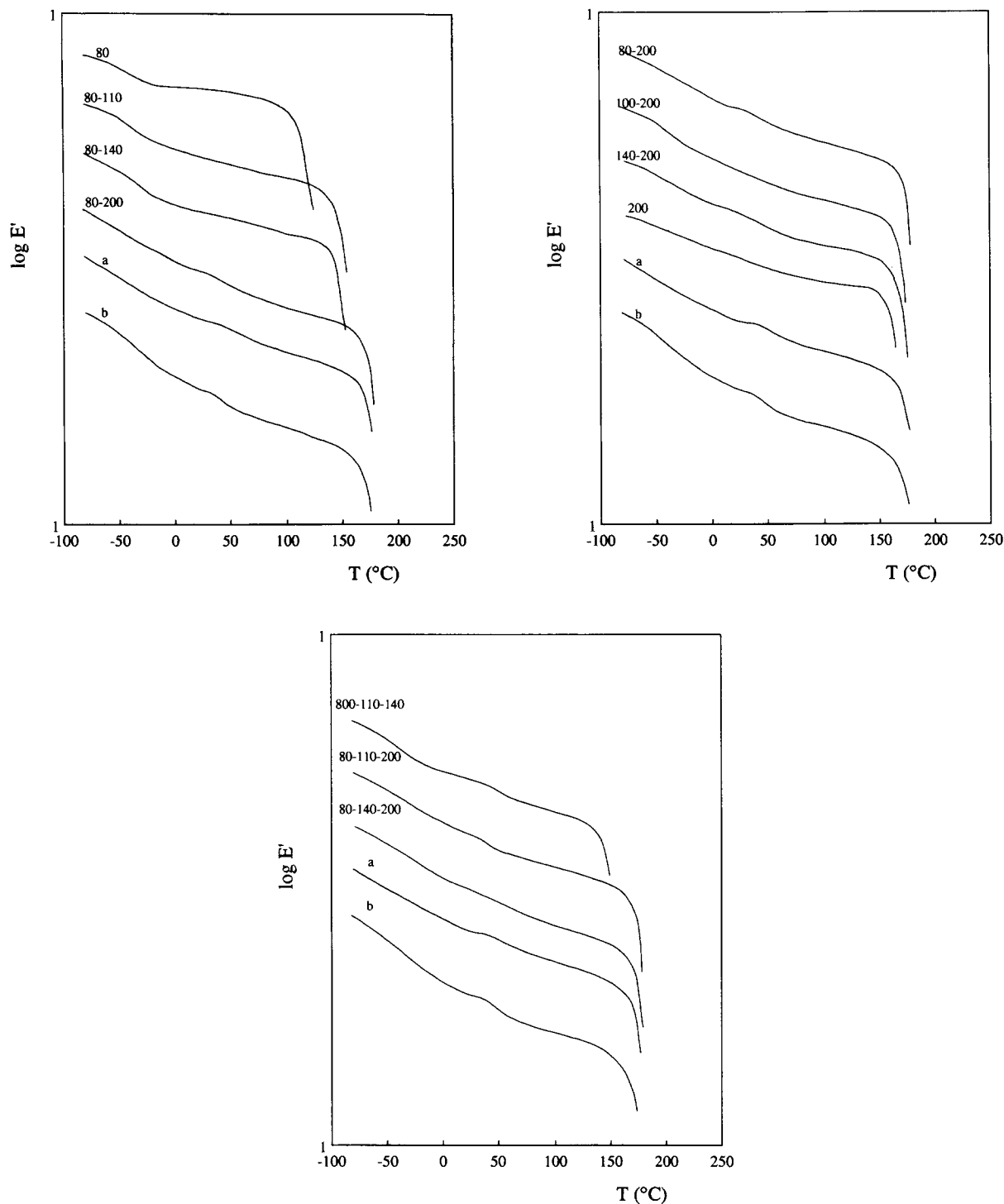


Figure 7 Plots of $\log E'$ versus temperature for the stoichiometric mixture cured with different cure schedules.

is not similar since the hydroxyether groups and other related parts of the network will be more hindered in the highly crosslinked zones and so will display more difficulty in initiating the crankshaft

motion than in the internodular matrix.²² Because of the network hindering, the β -relaxation would appear at higher temperatures and become broader as post-cure temperatures and times increase.²² This

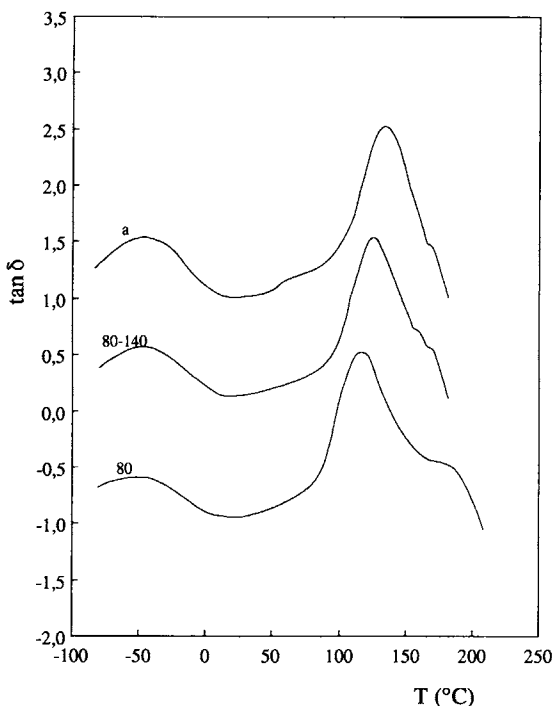


Figure 8 Loss tangent values of the epoxy-rich mixture cured with different cure schedules.

explanation could also be valid in interpreting the variations shown in the ω -relaxation.

As can be observed from Figure 6, the ω -relaxation peak appeared at temperatures between 20°C and 70°C but was not evident on all cure schedules employed. Indeed, when the 200°C step was not employed in the cure schedule, it did not have the same shape. It is also worth noting that when the temperature employed at the early stage of the cure schedules was not 80°C, this relaxation appeared as a shoulder of the β -relaxation, indicating that the ultimate morphology of the mixtures is a function of the cure conditions employed. The ω -relaxation (and T_{α} value) of samples cast with a first cure stage of 110° or 140°C had a similar shape to that of epoxy S mixtures, indicating that residual solvent could decrease the viscosity of the mixture and thus possibly change the cure kinetics modifying the

structure of the network formed. On the other hand, all samples performed with the standard or with cure schedules using the 80°C and 200°C steps instead showed a well-defined ω -relaxation. These observations, along with the higher α -relaxation temperatures for these samples, could indicate a higher crosslink density in the mixtures cured upon schedules using the lowest and highest temperatures of the cure schedule because their α -relaxation temperature was the highest reached for the stoichiometric mixture. Moreover, these results agree with the nodular morphology considered above. According to that interpretation, high-density regions would be formed solely prior to gelation increasing their crosslink density in further cure stages. Thereupon, when the first stage of the crosslinking process was not at 80°C, gelation took place quickly and so the time for nodule formation was lower, and thus their size would change.²² Because of this, the variations observed in the ω -relaxation zone should be a consequence of the existence of dissimilar crosslinking sites in the cured epoxy. Thus, the ω -transition should correspond to the motion of glycidyl amine groups in regions highly crosslinked inside an internodular matrix of lower crosslink density. The absence of this relaxation in mixtures prepared without using the 200°C cure stage could be due to the higher flexibility of the surroundings at those cure conditions. That explanation dismisses the possibility that this relaxation can be attributed to the regions of low crosslink densities, as suggested in the bibliography.^{10,58} Besides, it seems reasonable to suppose that this relaxation probably does not correspond to the motion of parts of the overall network structure other than the hydroxyether groups as has been proposed,^{6,25} because the number of these parts was constant in all the cure schedules employed.

The storage moduli of samples cured with different cure-schedules are shown in Figures 7(a)–(c). The modulus decreased sharply at the glass–rubber transition region for all networks. The variation of that property was also evident at low temperatures for all samples. A clear decreasing of modulus at the

Table I Glass Transition Temperatures, Rubber Moduli, and IR Absorptions of Residual Epoxy Group for Epoxy-Rich, $r = 0.8$, Mixtures

Cure (°C) Schedule	80	80–110	80–140	80–110– 140	80–200	110–200	140–200	200	80–110– 200	80–140– 200	Standard Schedule
T_{α} (°C)	110.5	127.5	130.5	129.5	134.0	135.0	134.0	134.0	134.0	—	132.5
E_r (MPa)	17	21	23	23	27	24	31	29	26	—	26
A916/A1510	0.23	0.20	0.21	0.22	0.19	0.19	0.19	0.19	0.18	0.19	0.19

Table II Glass Transition Temperatures, Rubber Moduli, and IR Absorptions of Residual Epoxy Group for Stoichiometric Mixtures

Cure (°C) Schedule	80	80-110	80-140	80-110-		110-200	140-200	200	80-110-	80-140-	Standard	Standard
				140	80-200				200	200	Schedule	(Solvent)
T _α (°C)	124.5 (164.5)	163.5	167.5	164.5	187.5	187.0	184.5	185.0	186.0	186.5	189.5	185.5
E _r (MPa)	62	73	70	79	86	89	95	80	88	102	91	100
A916/A1510	0.17	0.14	0.12	0.12	0.12	0.12	0.11	0.13	0.12	0.12	0.12	0.11

β -relaxation zone happened for all schedules, indicating the usefulness of that relaxation in explaining variations of the stiffness of epoxy networks at temperatures higher than those of the β -relaxation peak.^{3,8,9,33} Indeed, as has been shown for non-stoichiometric epoxy systems,^{9,27} higher values of elastic modulus for low crosslinked systems can be expected at room temperature as a consequence of a lower magnitude of the β -relaxation. Instead, in the ω -transition region solely, the networks which showed this relaxation had an evident decreasing of the modulus throughout the transition, also indicating the significance of ω -relaxation on viscoelastic properties.

In order to know the variation of dynamic mechanical behavior upon crosslink density, dynamic mechanical studies have also been made by using a viscoanalyseur Metravib. Results for 0.8, 1.0, and 1.2 stoichiometric amine/epoxy ratios are shown in Tables I-III. The stoichiometric mixtures showed α -relaxation values similar to those obtained in the previous way for epoxy N and epoxy S systems and for those cured with different cure schedules. Rubber modulus, E_r, taken as the elastic modulus value at T_α + 30°C, for the stoichiometric mixture increased as cure schedule was more complete (Table II). As the theory of elasticity shows, E_r can be considered in a first approximation as inversely dependent upon the molecular weight between fixed crosslinks, M_c. It follows that, in spite of experimental error, the higher crosslink density was, the higher the post-cure temperature employed was. However, there were not very important differences between the

stoichiometric mixture cured only at 80°C for 3 h and the mixture cured at all. Besides, samples cured by using a 110° or 140°C cure-temperature after the 80°C stage showed similar α -relaxations and rubber modulus values. Changes on α -transition temperatures were more remarkable when the cure schedule was more complete. These results indicate that small variations in crosslink density produce great modifications in the glass transitions when the crosslinking reactions have taken place in a high extent. On the other hand, the slight decrease in the α -relaxation temperature as the temperature of the first stage of the cure schedule increased (similar to that shown in Figure 5) should correspond to variations in the morphology of these mixtures since the crosslink density (the lower value of E_r for the mixture cured only at 200°C could correspond to kinetic variations during the earlier stage of curing) was similar for these mixtures. (See Table II.)

Results from mixtures with a 0.8 stoichiometric ratio (Table I) showed the same trends since α -relaxation values increased as rubber modulus was higher, although the variation was lower than for stoichiometric mixtures because the α -relaxation temperature for the r = 0.8 mixtures was close to the intermediate cure temperatures used in the cure schedule. As shown in Table III, the variations observed in formulations with a 1.2 stoichiometric ratio were lower, possibly as a consequence of the amine excess enabling a more complete reaction before vitrification occurred.

From Tables II and III it is worth noting that, similar to the stoichiometric mixtures, for the r = 1.2

Table III Glass Transition Temperatures, Rubber Moduli, and IR Absorptions of Residual Epoxy Group for Amine-Rich, r = 1.2, Mixtures

Cure (°C) Schedule	80	80-110	80-140	80-110-		110-200	140-200	200	80-110-	80-140-	Standard
				140	80-200				200	200	Schedule
T _α (°C)	170.5	167.0	171.0	170.0	175.0	171.0	168.5	165.5	176.0	174.5	174.5
E _r (MPa)	43	—	—	—	—	—	—	—	—	—	61
A916/A1510	0.14	—	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.10	0.10

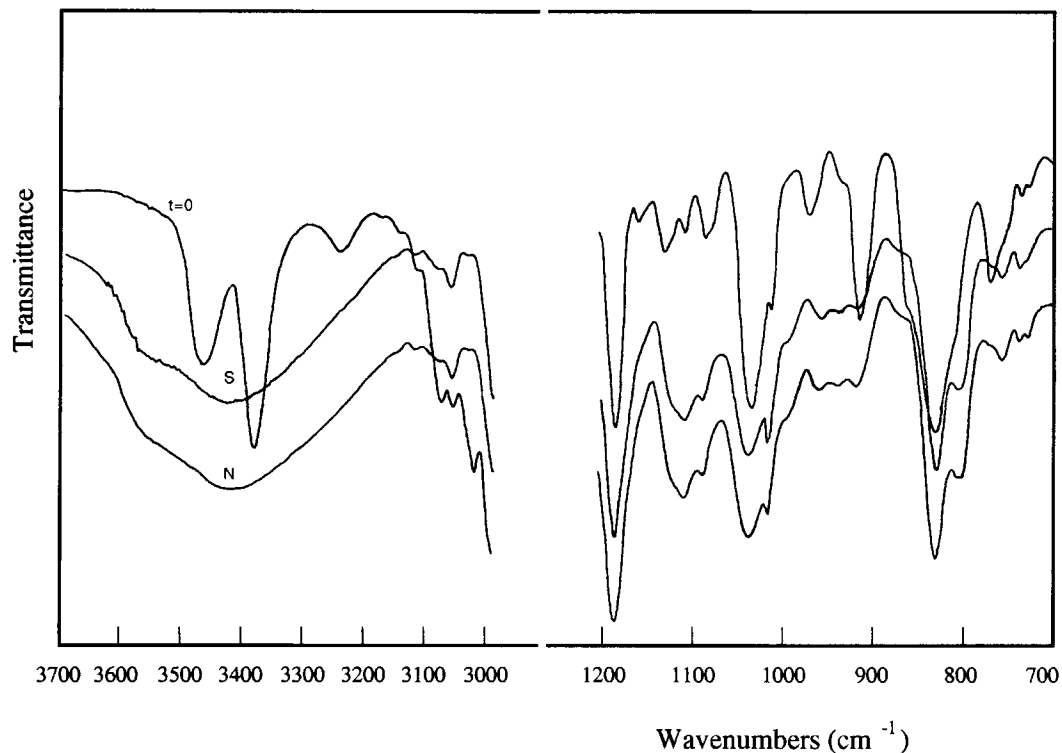


Figure 9 Infrared spectra of different samples: DER/DDM at $t = 0$; epoxy N and epoxy S mixtures at the end of the cure schedule.

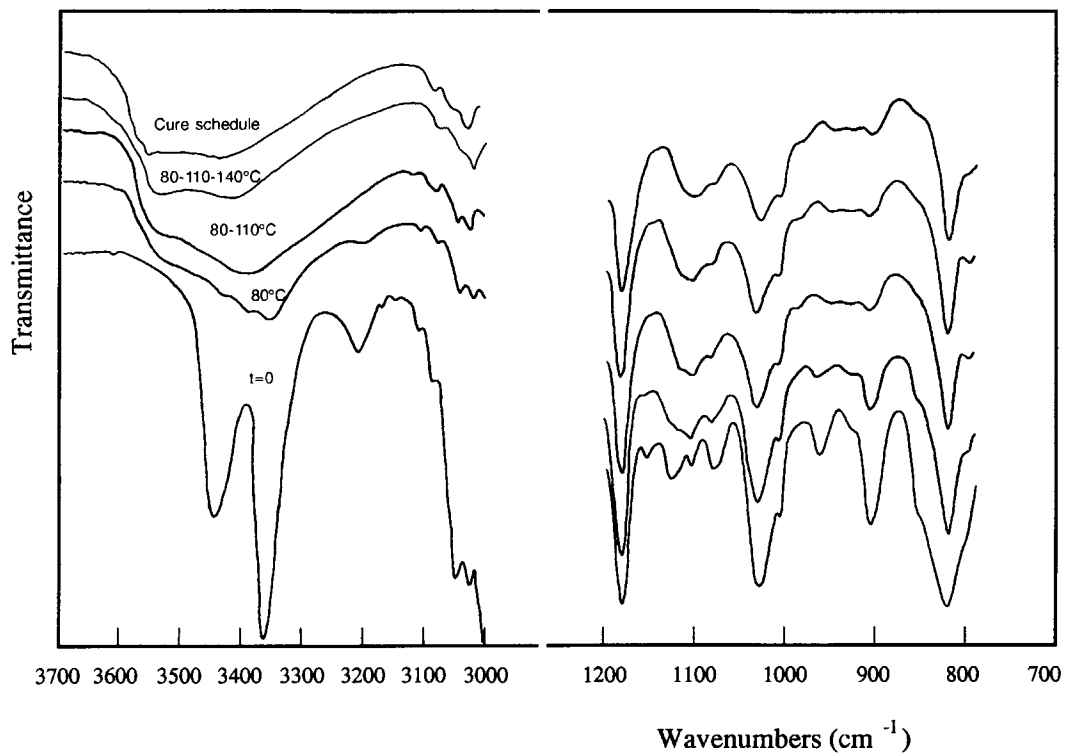


Figure 10 Infrared spectra of samples cured in the sample holder of the spectrophotometer at the same conditions as the cure schedule.

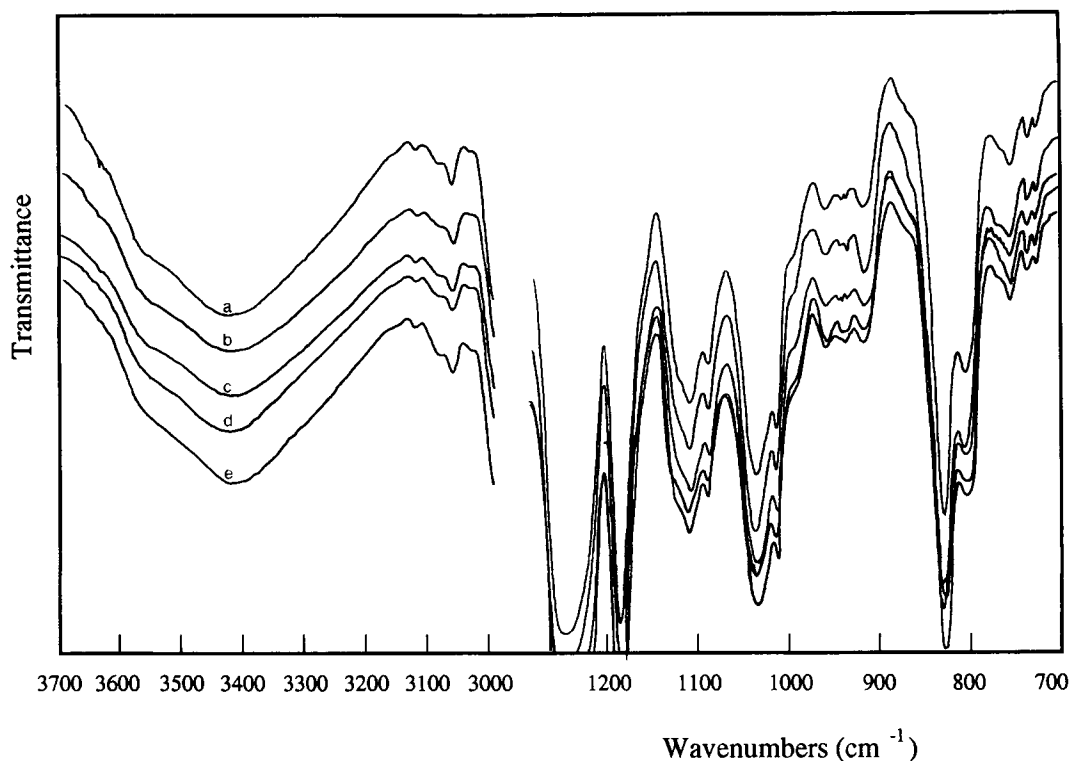


Figure 11 Some infrared spectra of plaques prepared with different cure schedules: (a) 80–110°C; (b) 80°C; (c) 80–110–140°C; (d) 200°C; (e) cure-schedule.

mixtures the α -relaxation temperatures in mixtures post-cured at 200°C were lower as a lower temperature was employed at the early stage of the cure schedule, indicating differences in the internal structure of the formed networks despite the similarity of the overall crosslink density. These differences could be related to the modifications shown in the ω -relaxation (Fig. 6) and could indicate the existence of more highly crosslinked regions inside the matrix in mixtures prepared at a lower cure temperature at the earlier stage of the cure schedule.

In order to relate the influence of cure extent on the crosslink density, and also on the dynamic mechanical behavior, infrared studies have been carried out. Figure 9 illustrates how the intensity of the 916 cm^{-1} band, corresponding to the epoxide groups, decreased as the cure schedule was completed in the same way shown by other authors.^{34,35} Moreover, as curing progressed the amine hydrogens were depleted and the bands corresponding to the stretching of the N—H bonds within the DDM became in a broad O—H stretch between 3100 and 3600 cm^{-1} . No important variations were observed between systems cast with and without the solvent, indicating that the cure extent was similar in these samples.

These observations, along with those shown in Table II for epoxy N and epoxy S mixtures (1 h 30

min in vacuum), seem to indicate that the extent of reaction and the crosslink density were similar for these systems, which is corroborated when rubber moduli of these samples, taken at $T_\alpha + 30^\circ\text{C}$ from Metravib results, are compared.

As a previous publication has shown,²⁴ the epoxy group conversion after the end of the first step on the cure schedule was slightly lower for the epoxy S mixture. These results emphasize the importance of the conditions employed at the early stage of the crosslink process and could explain the differences observed in the relaxations obtained by dynamic mechanical techniques. Although the ultimate average crosslink density was similar for both mixtures, possibly the morphology of the cured material changed when solvent was employed because of the existence of regions of different crosslink density inside these matrices.

Simulation of cure schedule conditions was carried out by maintaining the uncured mixture in the sample cell of the sample holder of the infrared spectrophotometer at temperatures and times employed in the standard cure-schedule. Results corresponding to the finishing of each cure step are shown in Figure 10. As can be seen, the first 80°C cure step of the standard cure schedule implied a clear lowering in the bands corresponding to the ep-

oxide rings. After the 110°C cure step, the intensity of the 916 cm^{-1} band smoothed in each following heat-step, indicating further crosslinking in the latest cure steps. This fact corroborates the observations made when the α -relaxation was analyzed, therefore higher glass transition was reached as a higher cure temperature was employed. Anyway, as inferred from Table II, not-so-important differences in absorption were obtained with the 200°C post-cure step, thus showing that a small increase in the extent of reaction for the stoichiometric mixture at this last cure schedule stage supposed a higher glass transition because the crosslink density clearly was higher, as shown by the rubber modulus data in Table II.

Furthermore, spectra of plaques prepared for DMTA measurements have also been analyzed in order to check the crosslink density obtained. Although all stoichiometric plaques have been studied (results are shown in Table II), Figure 11 shows the spectra of only some. Conclusions are the same as those obtained above: the absorption at 916 cm^{-1} slows down as the 80°C step of the cure-schedule is overcome. Therefore, and taking into account the rubber modulus results, it can be concluded that a direct correlation exists between the glass transition of these stoichiometric DGEBA/DDM systems and the crosslink density reached. On the contrary, at high epoxy conversions, small variations in the extent of reaction produced important changes in the network structure. The high glass transition obtained for the mixture cured at 200°C for 2 h can be also interpreted in this way because the absorption of the 916 cm^{-1} band was very low—although slightly higher than that obtained for the fully cured sample. On the other hand, as deduced from the 1100–1200 cm^{-1} region in Figure 11, the formation of ether linkages does not become important in any sample, in spite of employing the highest temperature of the cure schedule.

Results on transmittance for systems with 0.8 and 1.2 ratios, shown in Tables I and III, agreed with those obtained from rubber modulus for these systems, indicating that at these compositions the crosslink density increased as epoxy conversion was higher.

When the infrared results shown above are compared with the relaxations and rubber moduli obtained from dynamic mechanical tests (Tables I–III), it can be inferred that dynamic techniques are adequate to analyze the internal structure of these crosslinked systems, although a quantification of the relaxation variations still becomes necessary.

CONCLUSIONS

The influence of residual solvent and that of thermal history during curing on the dynamic mechanical properties of DGEBA/DDM epoxy resins are summarized as follows:

- The existence of residual solvent at the earlier stages of curing clearly affects the relaxational behavior of these mixtures, since the glass transition temperature of the cured networks decreases and the shape of the relaxations appearing at lower temperatures (and even their position) is modified. These variations seem to be related to differences in local density inside the cured networks.
- The variations in the ω -relaxation would be connected to local motion of chains in high crosslink density regions located inside the overall matrix.
- Changes in cure temperature at the earlier curing stages can modify the dynamic mechanical behavior of epoxy systems. Similarly, the significance of post-curing to complete the network formation has also been shown.
- Dynamic-mechanical measurements seem to be excellent for detecting any significant variation in the cured networks of thermoset resins.
- Crosslink densities of fully cured networks, and so the glass transition temperatures, are higher for the stoichiometric mixtures than for any other composition, but amine-rich systems can have higher crosslink densities than those for stoichiometric systems when post-curing is not done.
- Despite the optimum cure-schedule employed, a few epoxy groups remain unreacted.

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