

¹³C Solid-State NMR Analysis of the DGEBA/TETA Epoxy System

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ABSTRACT: Mechanical properties measurements, like Charpy impact tests, provided evidence that the macromolecular network of the epoxy system formed by the hexa-functional triethylene tetramine hardener, TETA, with the diglycidyl ether of bisphenol A monomer, DGEBA, can be modified by changing the hardener content. The previously analyzed monomer-to-hardener ratios were here studied by ¹³C-NMR solid state techniques. The results from crosspolarization/magic angle spinning (CPMAS) ¹³C-NMR spectra, together with the evaluation of proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$), display the behavior of these epoxy/hardener mixtures considering the mobility and interaction of molecular segments present at the macromolecular structure. The results also show that the epoxy-rich mixtures form tight, and therefore brittle, structures as previously observed by mechanical tests. The stoichiometric monomer-to-hardener ratio is a transition point where an increase in the mobility was found. For the amine-rich mixtures the obtained results suggest the presence of domains with different segmental mobilities. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2358–2362, 2000

Key words: epoxy resins; NMR; macromolecular structure

INTRODUCTION

The many applications of epoxy resins have focused attention to these materials since the beginning of their commercial use by the end of the 1930s. The versatility of these resins is due to the instability of the epoxy group that can react with different compounds like polysulfides, polyamides, aromatic, and aliphatic amines and an-

hydrides.^{1,2} Therefore, by selecting a proper hardener distinct epoxy systems with different mechanical, chemical, and physical properties can be obtained. These different macroscopic properties reflect different macromolecular networks.^{3,4} The crosslinked network obtained is also dependent on processing variables such as the time and the temperature of cure because these parameters will sensibly affect the degree of cure.^{5–8} Dealing with a specific hardener, variations from the stoichiometric hardener to resin mixture can also bring important changes on the final properties of epoxy systems.^{9–12} A change on macroscopic mechanical properties as a function of the hardener-

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Table I $T_1^H\rho$ Values for the Different Hardener Amounts. DGEBA/TETA Epoxy System

Hardener Content (phr)	$T_1^H\rho$ (ms)			
	($\delta^{13}\text{C}$) 157.7	144.4	128.5	42.2
7	2.7	2.3	2.3	2.5
9	2.0	1.4	2.3	2.2
11	2.0	2.9	2.0	2.5
13	2.7	3.4	4.5	3.7
15	2.8	1.7	1.3	2.4
17	1.0	1.6	2.0	2.3
19	2.1	2.8	1.8	2.4
21	2.5	2.3	2.9	2.1

to-resin ratio was particularly observed for the epoxy system formed by the diglycidyl ether of bisphenol A, DGEBA, epoxy resin, and the triethylene tetramine, TETA, hardener.^{11,13} Particularly important was the increase on fracture toughness and impact resistance of the amine rich formulations. However, a clear picture of the changes induced by varying the hardener-to-resin ratio upon the macromolecular network was not yet done.

Solid-state nuclear magnetic resonance spectroscopy is being used as a source of information on molecular dynamics of the blends.^{14–22} Therefore, in this work a study was undertaken using CPMAS ^{13}C , variable contact-time experiment, and $T_1^H\rho$ techniques to evaluate the changes taking place on the macromolecular network of the DGEBA/TETA system as a function of the hardener to resin ratio.

EXPERIMENTAL PROCEDURES AND MATERIAL

The epoxy system investigated was obtained by mixing the difunctional diglycidyl ether of bisphenol A resin with different amounts of the triethylene tetramine hardener. The weight fractions of the hardener varied from 7 to 21 parts of hardener per hundred parts of resin, phr. The complete set of mixtures prepared is shown in Table I. Hereafter, these different mixtures will be called as 7 phr, 9 phr, and so on. The theoretical stoichiometric ratio for this epoxy system corresponds to 13 phr. Therefore, as shown in Table I, besides the stoichiometric mixture, epoxy-rich and amine-rich formulations were also analyzed. The

proper quantities of resin and hardener were weighted within 0.0002 g and stirred for at least 5 min before casting into bar-shaped open silicone rubber molds. The setting of all mixtures was done at $25 \pm 2^\circ\text{C}$, that is the cure temperature recommended by the resin manufacturer for the stoichiometric ratio.²³ The extent of the epoxy conversion was measured by FTIR,¹¹ and shows that as the hardener content increases, the conversion also increases, but only for 19 and 21 phr a complete consumption of the epoxy rings was observed.

For the NMR analysis the bars were ground to obtain a fine powder of each of the eight epoxy hardener formulations. All NMR spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 MHz and 75.4 MHz for ^1H and ^{13}C , respectively. The experiments were done at probe ambient temperature, and were performed using a gated high-power decoupling. A zirconium oxide rotor with a diameter of 7 mm and with Kel-F caps was used to acquire the NMR spectra at rates of 6 kHz. ^{13}C spectra are referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C analyses were carried out in the crosspolarization mode with a 90° pulse and a delay of 2 s, a variable contact time experiment. A range of contact time was established between 100 to 4000 μs . $T_1^H\rho$, was determined from the attenuation of the intensity of ^{13}C peaks with increasing contact times.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the assignments of the CPMAS ^{13}C signals for the 7, 9, 15, and 17 phr blends. These spectra were taking as examples of all hardener to epoxy monomer analyzed, because the information obtained from them is common to the other mixtures. The CPMAS ^{13}C resonance frequencies in the NMR spectra can be changed by the chemical environment; thus, the assignments shown in Figure 1 are based on the expected macromolecular structure (Fig. 2) that could evolve from the reaction of the TETA hardener and the DGEBA monomer. Nine wide NMR signals were detected at: 156–158 ppm (C_4), 143–144 ppm ($\text{C}_1\text{—O}$), 127–129 ppm ($\text{C}_{3,5}$), 114–115 ppm ($\text{C}_{2,6}$), 69–70 ppm (CH—O and $\text{CH}_2\text{—O}$), 56.1 ppm ($\text{CH}_2\text{—N}$), 50.4 ppm (CH—N), 41–42 ppm (unreacted epoxy rings), and 31–32 ppm (CH_3).

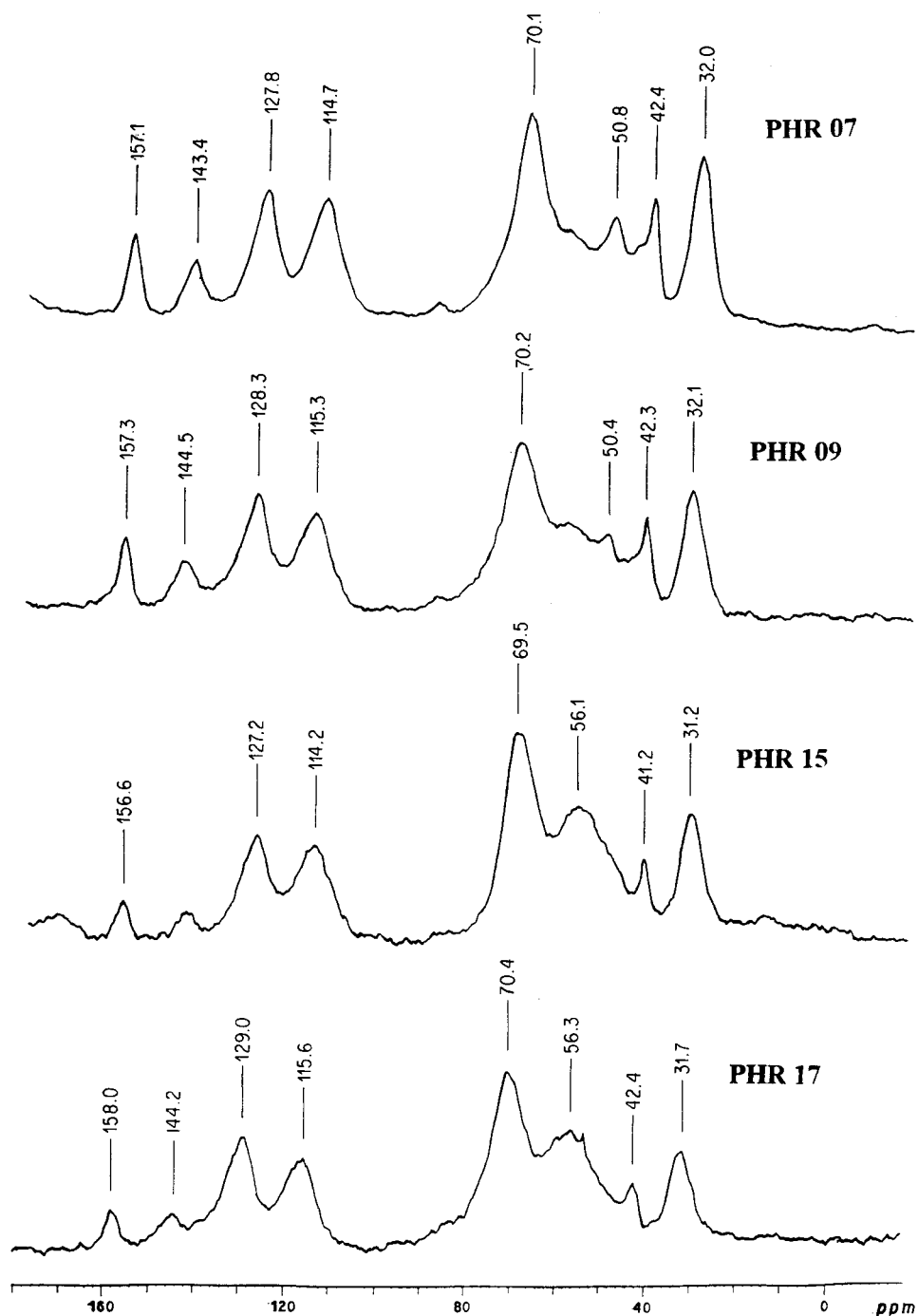


Figure 1 CPMAS ^{13}C -NMR spectra of the 7, 9, 15, and 17 phr blends.

In the present work, the CPMAS ^{13}C results could be associated with modifications due to the addition of amine hardener to the DGEBA monomer. From Figure 1 it can be seen that a wide signal is located at 56.1 ppm. This signal comes from amine and, as expected, it increases as the amount of hardener component increases, due to

the interaction process between epoxy monomer and the hardener. The NMR signal located at 42.4 ppm, which was assigned as unreacted epoxy rings, shows that the amount of epoxy rings decreases with the increase in the phr values. In other words, a more complete reaction takes place as the hardener-to-epoxy monomer ratio in-

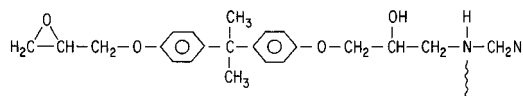
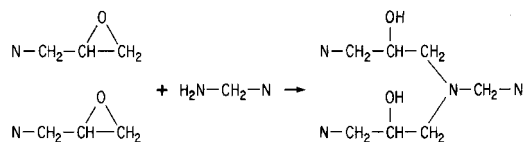


Figure 2 Basic structure of the DGEBA/TETA epoxy system.

creases. The presence of more unreacted amine sites on the hardener molecule was postulated as a major source for the deformability of formulations with excess of hardener.¹¹

The results obtained from the CPMAS ¹³C NMR spectra together with the evaluation of the $T_{1\rho}^H$ for each of the epoxy formulations are shown in Table I. These values can be correlated with the mobility and interaction of molecular groups or segments.¹⁷⁻²²

For samples with 7–11 phr, rich in the epoxy monomer, the $T_{1\rho}^H$ values indicate that the molecular chains present a good interaction. This behavior could come from the total reaction of the reactive groups in the amine molecule tightening together the epoxy molecules, and a rigid macromolecular structure is developed. This result is in close agreement with the mechanical properties (impact strength and fracture toughness) obtained for these epoxy-rich formulations, that can be characterized as brittle materials.^{12,13} The sample with 13 phr shows a change in the chemical shift for a low frequency and at the same time an increase in the $T_{1\rho}^H$ values. Both changes indicate that this ratio presents higher mobility than the epoxy monomer-rich formulations. In fact, the 13 phr formulation is an inflection point where it is shown that a brittle to ductile transition occurs.¹³

For the amine-rich mixtures, the $T_{1\rho}^H$ values suggest that two phenomena could be occurring: one related to phase separation, which could be a consequence of the formation of domains with different molecular mobility, and the other one referred to a better interaction between molecular chains. Although not conclusive, the possible existence of a two-phase system was found by thermogravimetric

analysis for the 15, 19, and 21 phr formulations.²⁴ On the other hand, it is expected that a tight network is developed as the phr ratio is increased, because the extent of epoxy rings consumption is also increased, as shown by infrared analysis.¹¹ Therefore, the values shown in Table I could represent the contribution of these two aspects to the overall mobility of the macromolecular structure of these amine rich formulations. In fact, from the distribution form of the decay intensities it was observed that there was a limit point indicating the presence of two regions with distinct mobilities, which corroborated with the information obtained by the relaxation parameter. One group is formed by epoxy-rich mixtures and the other one by the amine-rich mixtures.

CONCLUSIONS

From the NMR data it was shown that the chemical structure of the DGEBA/TETA epoxy system is strongly affected by the changes in the hardener content. The data show that the epoxy-rich mixtures presented good interaction between the molecular chains. Rigid structures are therefore obtained. These results are in good agreement with the mechanical properties measured for these systems. However, for the amine-rich systems, two phenomena could be occurring: phase separation, or better interaction between molecular chains.

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