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Determination of the Extent of Reaction of Amine Cross-Linked Epoxy Resins by Solid-State ^{13}C and ^{15}N NMR

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ABSTRACT: The chemical substitution of amine nitrogens in cured, ^{15}N-labeled epoxy resins has been determined by a combination of rotational-echo double-resonance ^{13}C NMR and dipolar rotational spin-echo ^{15}N NMR. Amine-nitrogen substitution is at least 90% (that is, no more than 10% of all nitrogens have a directly bonded hydrogen) for resins formed from stoichiometric amounts of epoxide and either hexamethylenediamine or a 1:3 molar mixture of hexamethylenediamine and hexylamine. This direct measure of curing and cross-linking is consistent with indirect Fourier-transform infrared estimates of curing based on the disappearance of the deformation band of the epoxide ring.

Introduction

Epoxy resins are widely used as matrices for high-performance carbon-fiber composites,[1] even though the understanding of the connection between the chemical structure and mechanical properties of the matrix is limited. We are investigating a series of model epoxies to improve this understanding.[2−6] The materials consist of di-epoxides cured with stoichiometric concentrations of diamines or mixtures of monoamines and diamines (Figure 1). The chemical structures of both epoxides and amines are varied from rigid aromatics to flexible aliphatics to alter the local mobilities of backbones and cross-links. An estimate of the cross-link density of the cured resin is usually made by assuming that all reactions are complete: that is, all epoxide rings are opened and all amine nitrogens are fully substituted. Viscoelastic measurements performed on these materials between −100 and +100 °C have shown that the low-temperature onset of the mechanical-loss β transition always occurs at the same temperature, independent of the chemical structure and the cross-link density, but that the width and intensity of the β transition increase with increasing cross-link density.[4−6] In this paper we report the results of ^{13}C and ^{15}N NMR measurements on one of the epoxides of the series cross-linked with ^{15}N-labeled hexamethylenediamine or a mixture of [^{15}N]hexamethylenediamine and [^{15}N]hexylamine (and their unlabeled couterparts) in various combinations. The goal of these experiments is to measure directly the extent of reaction at the amine nitrogen centers and hence improve the determination of the cross-link density.

Experiments

Synthesis of Epoxy Resin. A fully cross-linked epoxy resin was prepared from two parts of the diglycidyl ether of Bisphenol A and one part hexamethylenediamine. A partially cross-linked resin was formed from five parts epoxide, one part hexamethylenediamine, and three parts hexylamine. Labels were introduced by the use of [$^{15}N_2$]hexamethylenediamine and [^{15}N]hexylamine (and their unlabeled counterparts) in various combinations. The labeled amines were 99 atom % ^{15}N and were obtained from Isotec, Miamisburg, OH.

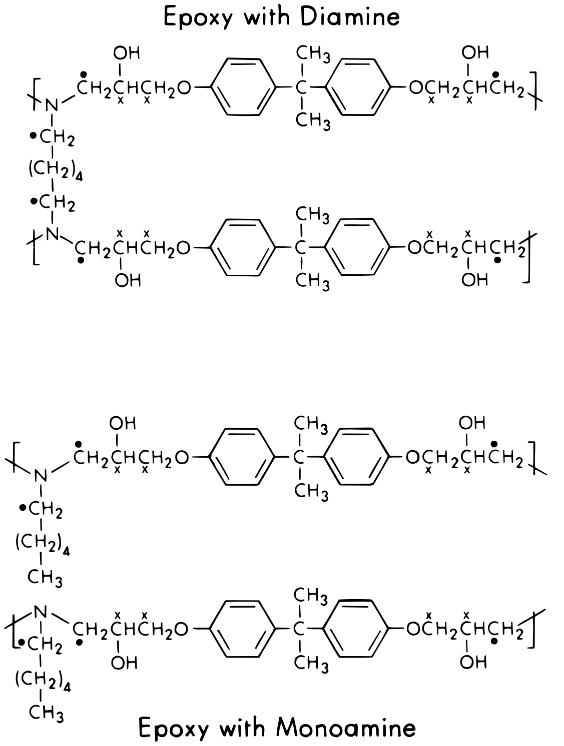

Figure 1. Structure of the resin formed from two parts of the diglycidyl ether of Bisphenol A and either one part hexamethylenediamine (top) or two parts hexylamine (bottom). Carbons directly bonded to nitrogens are marked with circles, and those directly bonded to oxygens with crosses.

A mixture of unreacted epoxide and amine was placed between two KBr windows and the sample thickness adjusted for Beer's law, infrared-absorption behavior. The temperature of the curing was controlled by a Mettler FP80 hot stage. The progress of the curing (Figure 2) was monitored by the disappearance of the deformation band of the epoxide ring at 915 cm^{-1} relative to the stretching band of the phenyl rings at 1580 cm^{-1} (which does not depend on the extent of reaction). These measurements were performed using a Nicolet 205 Fourier-transform infrared spectrometer. This absorbance ratio was independent of changes in sample thickness with curing and was zero for resins cured in the presence of excess amine. The epoxides used in the NMR experiments were cured for 100 min at 100 °C and resulted in approximately 1 g of resin. The fully and partially cross-linked resins were then postcured for 24 h at 150 and 100 °C, respectively, under a N_2

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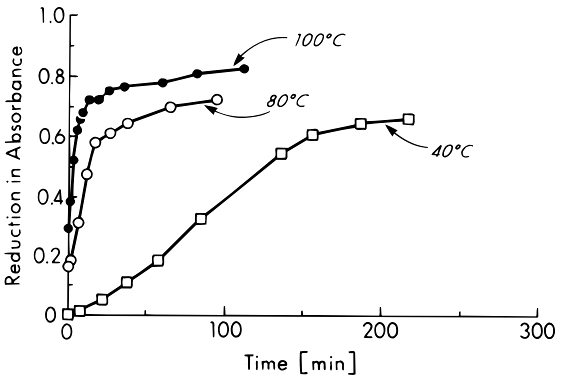

Figure 2. Progress of epoxy resin curing at three different temperatures as monitored by the disappearance of the infrared deformation band of the epoxide ring at 915 cm^{-1} relative to the stretching band of the phenyl rings at 1580 cm^{-1}. The reduction in absorbance is defined as one minus the absorbance ratio, A_{915}/A_{1580}.

atmosphere. A reduction of the absorbance at 915 cm^{-1} of about 95% was observed for the postcured resins. The T_g of the fully cross-linked resin was 114 °C and that of the partially cross-linked material, 63 °C, as determined by differential scanning calorimetry at a heating rate of 10 °C/min. Samples for examination by NMR were powdered by impact at liquid-N_2 temperatures.

NMR Spectrometer. Cross-polarization, magic-angle spinning (CPMAS) Hahn-echo ^{13}C NMR spectra were obtained at room temperature at 50.3 MHz, and the corresponding ^{15}N NMR spectra at 20.3 MHz. The single, 13-mm diameter, radiofrequency coil was connected by a low-loss transmission line to a triple-resonance tuning circuit. One-kilowatt ^{1}H-, ^{13}C-, and ^{15}N-tuned transmitters produced maximum radio-frequency-field amplitudes of 100, 50, and 40 kHz, respectively. Cross-polarization transfers were performed at 38 kHz, and proton dipolar decoupling was done at 100 kHz. Rotors with 1-g sample capacities were made from ceramic (zirconia) barrels fitted with plastic (Kel-F) end caps and supported at both ends by air-pumped journal bearings. In these experiments, 350-mg samples were positioned in the center of the rotor by Kel-F spacers.

REDOR. Rotational-echo, double resonance (REDOR) ^{13}C NMR experiments[7] with ^{15}N dephasing were performed using ^{13}C π pulses at the completion of rotor periods and ^{15}N π pulses in the middle of the rotor periods. The pulses were applied with XY8 phase cycling to suppress the effects of frequency offsets and compensate for pulse imperfections.[8] Two extra rotor cycles (and a Hahn-echo refocusing pulse) were added to the sequence so that the start of data acquisition was not coincident with a pulse. In the absence of ^{15}N pulses, the echo that forms is S_o, the REDOR full-echo spectrum. Application of ^{15}N π pulses at every half rotor cycle causes a net dephasing of the transverse magnetization of those carbons dipolar coupled to ^{15}N. The resulting spectrum, S, is diminished in intensity. The REDOR difference spectrum ($\Delta S = S_o - S$) therefore arises only from those carbons that are dipolar coupled to nitrogen. REDOR dephasing was accumulated for eight rotor cycles with magic-angle spinning at 3205 Hz. For this spinning speed, the eight rotor-cycle REDOR dephasing is 100% for a directly bonded ^{13}C and ^{15}N pair separated by 1.5 Å, 18% for a pair separated by a 2.5-Å two-bond distance, and 1.5% for a pair separated by 4 Å.[7]

DRSE. Nitrogen dipolar line shapes were characterized by a version of dipolar rotational spin-echo (DRSE) ^{15}N NMR extended over two rotor cycles.[9] This is a two-dimensional experiment in which, during the additional time dimension, ^{15}N magnetization is allowed to evolve under the influence of ^{1}H$-$^{15}N coupling, while homogeneous ^{1}H$-$^{1}H coupling is suppressed by homonuclear multiple-pulse semiwindowless MREV-8 decoupling.[10] The ^{15}N magnetization first dephases and then, at the completion of two rotor cycles, refocuses. The rate of dephasing is a direct measure of the strength of the ^{1}H$-$^{15}N coupling. The cycle time for the homonuclear decoupling pulse sequence was 33.6 μs, resulting in decoupling of proton$-$proton interactions as large as 60 kHz. Thirty-two MREV-8 cycles fit exactly into two rotor periods with magic-angle spinning at 1859 Hz.

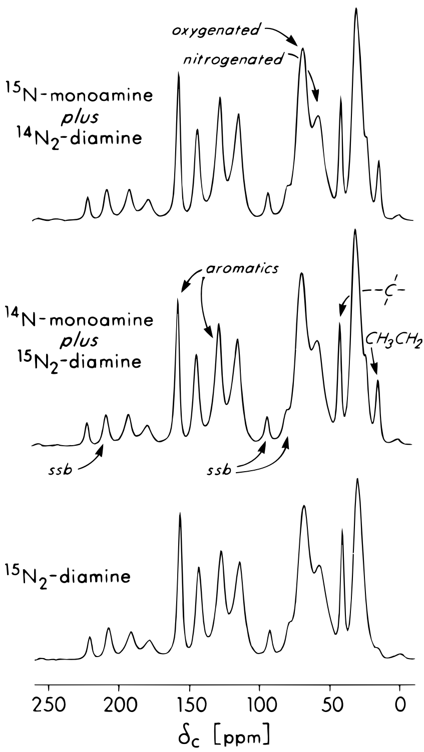

Figure 3. Cross-polarization magic-angle spinning ^{13}C NMR spectra of three ^{15}N-labeled cross-linked epoxy resins. A fully cross-linked epoxy resin (bottom) was prepared from two parts of the diglycidyl ether of Bisphenol A and one part [^{15}N$_2$]-hexamethylenediamine. A partially cross-linked resin was formed from five parts epoxide, one part hexamethylenediamine, and three parts hexylamine, with the ^{15}N label either in the diamine (middle) or the monoamine (top). Magic-angle spinning was at 3205 Hz.

Results and Discussion

Carbon-13 NMR Line Assignments and REDOR-Assisted Deconvolution. The ^{13}C NMR spectrum of the fully cross-linked epoxy resin consists of four aromatic-carbon lines (110$-$155 ppm), an oxygenated-carbon peak (70 ppm), a nitrogen-substituted carbon peak (58 ppm), a quaternary-carbon line (40 ppm), and a combination peak (30 ppm) due to methyl carbons of the epoxy and methylene carbons of the amine (Figure 3, bottom). The minor peaks are aromatic-carbon spinning sidebands. Line assignments for similar spectra have been reported earlier.[11,12] The partially cross-linked resin has a resolved methyl-carbon peak (20 ppm) from the monoamine end group (Figure 3, top and middle). Variation in positions of the ^{15}N labels in the partially cross-linked resins has no effect on the ^{13}C spectra.

No more than 5% of unreacted epoxide rings were detected by infrared in any postcured resin. If all reactions were indeed complete, the chemical substitution around the amine nitrogens would be the same for both diamine and monoamine curing agents (Figure 1). The ratio of oxygenated to nitrogenated sp^3 carbons is 4/3. This ratio increases if some of the nitrogen centers are not fully substituted, which would occur at either a non-cross-linked diamine site or a chain-termination monoamine site. Thus, the experimentally observed ratio of carbon intensities, $r_{obs} = I^{C}_{oxygenated}/I^{C}_{nitrogenated}$,

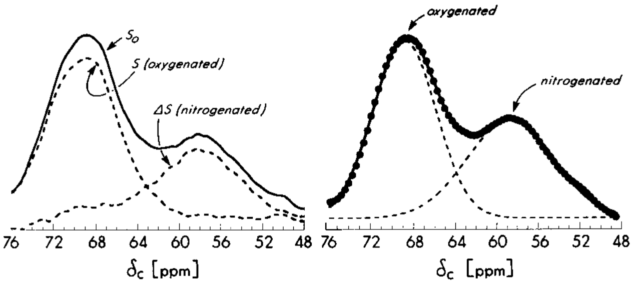

Figure 4. (Left) carbon-13 rotational-echo double-resonance NMR spectra of the cross-linked resin of Figure 3 (bottom) after eight rotor cycles of ^{15}N dephasing with magic-angle spinning at 3205 Hz. The full-echo spectrum is S_o, the dephased spectrum is S, and the REDOR difference is ΔS. Only the region of the spectra between 48 and 76 ppm is shown. For a directly bonded ^{13}C and ^{15}N pair separated by 1.5 Å, the expected REDOR dephasing for this experiment is 100%, so the dephased S spectrum has no contributions from nitrogenated carbons. (Right) carbon-13 cross-polarization magic-angle spinning NMR spectrum of the same labeled resin whose REDOR spectra are shown on the left. The spectrum has been deconvoluted using two Gaussian line shapes with widths and centers determined by the REDOR spectra. The nitrogenated-carbon peak (58 ppm) is bigger than in the corresponding REDOR spectrum because the data were acquired immediately after the cross-polarization proton-carbon transfer, which avoids the homogeneous decay of the methylene-carbon magnetization present in the REDOR experiment.

is a measure of amine nitrogen substitution. However, this determination is complicated by two factors: (i) overlap of aromatic-carbon spinning sidebands and (ii) deconvolution of the 60−80 ppm region into two peaks. These complications are also present for spectra obtained at higher field than 4.7 T with proportionally faster spinning speeds.[13] Faster spinning at 4.7 T eliminates sideband overlap but raises a new set of problems for quantitation.[14] Although sidebands are not a problem for spectra obtained at lower field, such spectra are not as well resolved as those in Figure 3, especially in the 48−76 ppm region.[13] Finally, pulse methods to suppress or phase-alter residual spinning sidebands[15] are not viable options for quantitation because magnetization from oxygenated and nitrogenated carbons refocuses differently due to considerable differences in residual homogeneous coupling to protons (*cf.* caption to Figure 4).

We approached the quantitation problem in the following way. Because upper and lower first spinning sidebands were almost equal in intensity (Figure 3), we removed all aromatic-carbon sideband contributions from the 48−76 ppm region by subtracting a replica of the well-resolved sidebands centered around 200 ppm. Next, we used REDOR dephasing of the [$^{15}N_2$]diamine fully cross-linked resin to establish that the width of the nitrogenated carbon line is 10% greater than that of the oxygenated carbon line (Figure 4, left). We then matched the CPMAS ^{13}C NMR spectrum in the 48−76 ppm region by two overlapping Gaussian peaks of variable heights but fixed centers and widths (Figure 4, right). The resulting relative integrated intensities for three different resins are reported in Table 1 as r_{obs}. These values were independent of choice of cross-polarization contact time[16] between 1 and 5 ms. Based on reproducibility for the same resin in five separate cross-polarization magic-angle spinning experiments, we estimate the accuracy of r_{obs} as ±5%. This degree of accuracy would have been difficult to achieve if we had allowed the linewidths to vary in the fitting procedure. All values of r_{obs} in Table 1 are greater than 4/3, which indicates incomplete reaction of the amines, although two of the entries do not differ from 4/3 by much more than the estimated error.

Table 1. Carbon-Count and Proton-Count Estimates of Amine-Nitrogen Substitution for the Three Cured Epoxy resins of Figure 3

resin	r_{obs}[a]	x[b]	DRSE dephasing[c]	x[d]
^{15}N-monoamine plus $^{14}N_2$-diamine	1.40	0.07	0.24	0.04
^{14}N-monoamine plus $^{15}N_2$-diamine	1.46	0.15	0.25	0.05
$^{15}N_2$-diamine	1.40	0.07	0.26	0.06

[a] From $r_{obs} = I^C_{oxygenated}/I^C_{nitrogenated}$ (Figure 4, right). [b] From $r_{obs} = (4 + x)/(3 - x)$, where x is the fraction of amine nitrogens (monoamine and diamine) with a single, directly attached hydrogen. [c] From Figure 5. [d] From DRSE dephasing assuming that 20% total dephasing is due to the nonbonded proton background.

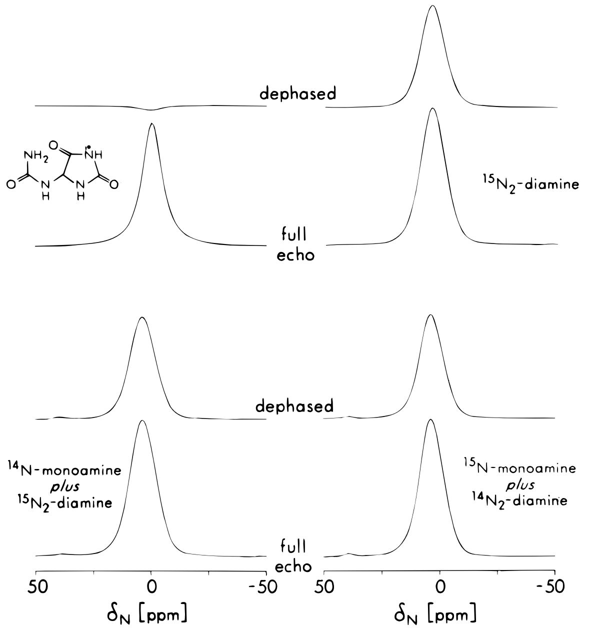

Figure 5. Dipolar rotational spin-echo ^{15}N NMR spectra of the three ^{15}N-labeled resins of Figure 3 and of the singly protonated nitrogen of an ^{15}N-labeled allantoin (upper left). Full-echo spectra (no dipolar evolution) and dephased spectra (dipolar evolution for eight semiwindowless MREV-8 cycles per two rotor cycles) are shown, bottom and top, respectively. Magic-angle spinning was at 1859 Hz.

Nitrogen-15 Dipolar Coupling. A second estimate of chemical substitution of the amine nitrogens is possible by a DRSE determination of the average ^{1}H−^{15}N dipolar coupling. The CPMAS ^{15}N NMR spectra of the cured resins arise exclusively from the ^{15}N label. A single, broad line is observed for both fully and partially cross-linked materials (Figure 5). These amine ^{15}N's are situated in regions of unusually high proton density. At least six protons (and possibly as many as eight protons when *inter*molecular nearest neighbors are counted) are, on average, within two or three bond lengths of each amine nitrogen (Figure 1). We calculated[17] that for the DRSE conditions that produce full dephasing for a secondary nitrogen (Figure 5, top left), a 20% dephasing of ^{15}N magnetization is expected from a double square-pyramidal array of eight independent protons, each 2.2 Å from the centrally located nitrogen. This is an upper limit to the dephasing expected from nonbonded protons undergoing no large-amplitude motions. Dipolar coupling with nonbonded protons therefore accounts for most but not all of the observed 25% amine-nitrogen

DRSE dephasing (Figure 5 and Table 1). We estimate that about 5% of all amine nitrogens have directly bonded hydrogens. With so few hydrogens bonded to nitrogens, the assumption that all primary amines have disappeared seems reasonable.

Amine-Nitrogen Substitution from Carbon Counts. The REDOR-dephased S spectrum of Figure 4 (left) reveals the 48−62 ppm region of the resin spectrum without interference from nitrogen-substituted carbon peaks. This part of the spectrum is a blank. No peak with intensity of more than 1% of the major 70-ppm line is observed. (The minor peak at 50 ppm is an aromatic-carbon spinning sideband, which was not subtracted from the REDOR spectrum.) Because the methine carbon of the epoxide ring has a chemical shift at 51 ppm, the absence of oxygenated-carbon peaks in this region of the S spectrum means that all epoxide rings must have reacted. Nevertheless, both the ^{13}C REDOR and ^{15}N DRSE measurements indicate that some nitrogens (5%) still have hydrogens attached. This means that some epoxide rings must have been opened by reactions not involving amines. Ring opening by water absorbed after the postcuring would produce primary alcohols with oxygenated carbons having chemical shifts near 62 ppm,[18] and so this reaction is unlikely. An amine-catalyzed ring opening by an epoxy-unit hydroxyl to produce an ether linkage and a secondary alcohol is a possibility consistent with the observed chemical shifts.[19] On the basis of this reaction and the assumption that all epoxide rings have reacted but not all amine nitrogens are fully substituted, each residual secondary amine nitrogen removes one spin from the count of nitrogenated carbons and adds one spin to the count of oxygenated carbons. Thus, $r_{\mathrm{obs}} = (4 + x)/(3 - x)$, where x is the fraction of amine nitrogens (monoamine and diamine) with a single, directly attached hydrogen. Values of x of about 10% for fully and partially cross-linked resins are reported in Table 1.

REDOR Constraints on Ring-Opening Chemistry. The experimental values of r_{obs} are all greater than the 4/3 of a perfectly cross-linked lattice. If we had assumed that these values reflect a change in count of the nitrogen-substituted carbons for the experimental lattice but no change in the count of oxygen-substituted carbons contributing to the 70-ppm peak, then a value of r_{obs} equal to 1.4 would mean that 20% of all nitrogens were only disubstituted and still bore a hydrogen. This concentration of NH groups would result in twice as much DRSE dephasing of ^{15}N magnetization as observed (Figure 5). Thus, whatever chemistry is invoked to explain the disappearance of the epoxide rings, the REDOR results require that all resulting oxygenated carbons have chemical shifts between about 62 and 76 ppm (see *S* spectrum, Figure 4, left) and so remain in the count of oxygen-substituted carbons used to determine r_{obs}.

Cross-Link Index. The 5% DRSE proton-count, lower-limit estimate of chemical substitution of amine nitrogens is consistent with the 10% REDOR carbon count, and also with the 5% Fourier-transform infrared count, for the postcured samples. We conclude that the cross-link index (the fraction of possible cross-links that have been converted) for both resins is 0.90 ± 0.05. We believe that this is a conservative estimate; the index may be larger. The cross-link density for the fully cross-linked resin is therefore approximately 2.5 times that of the partially cross-linked resin because, in the latter, the molar ratio of diamine to monoamine curing agents was 1:3. Based on the observation that only 80% of the epoxide rings had reacted during the initial curing process (Figure 2), the high degree of cross-linking in the final resins is the direct result of the extended postcuring at $T > T_g$. The efficiency of cross-linking during this postcuring process may be related to local ordering of epoxide, amine, and antiplasticizer during curing, a possibility discussed in more detail elsewhere.[13]

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