Interaction of Epoxy Resins with Water. A Quadrupole Echo Deuterium NMR Study

The detrimental effect of water when absorbed by epoxy resins presents a major problem in the areas of composites and adhesives.[1-3] It is known that sorbed moisture plasticizes epoxy resins, thus lowering T_g[4,5] and leading to a degradation of the mechanical properties of epoxy-based materials.[3] Although the phenomenological aspects of the water–epoxy interaction have been well established, two basic questions remain largely unanswered: (1) what is the nature of the water absorbed by the resin? (2) Are the water molecules associated with specific sites in the epoxy resin? Answers to these questions should lead to an understanding of the mechanism of T_g depression in systems where absorbed water produces large depressions in T_g[6-8] and in the general case of interaction of small molecules with macromolecular matrices.

Conventional thinking, based partly on experimental evidence, has been that the water interacts specifically with the polar groups of the resin, disrupting the hydrogen-bond network in the system and resulting in the large depressions in the observed T_g. However, recent studies[9,10] have shown that the depression of T_g in epoxies caused by water is not particularly unusual and can be accounted for by general equations derived to calculate the compositional dependence of T_g in mixtures. The large effects observed are a consequence of the particular thermal properties of the resin and plasticizer and do not necessarily stem from specific interactions.

We report here preliminary results from a quadrupole echo deuterium NMR study designed to assess the nature of water in the resin. Quadrupole echo deuterium NMR provides an ideal spectroscopic method for the study of water (i.e., D_2O) absorbed by polymers, and we report here the first example of such an investigation.[21] Made possible by the introduction of the quadrupole echo pulse sequence in 1976,[13,14] solid-state deuterium NMR has become the method of choice for studying molecular motions of specifically labeled solids.[15] The quadrupole echo pulse sequence preserves the line shape of the inhomogeneously broadened deuterium NMR signal, thus circumventing the problems normally encountered with broad signals and receiver ringdown.[16] As opposed to its conventional broad-line NMR counterpart, quadrupole echo deuterium NMR spectroscopy lends itself to Fourier transform methods. It is thus practical to observe weak signals, using repeated spectral accumulation. Further, the deuterium line shapes (obtained from Fourier transformation of the free induction decays) can be analyzed in terms of models for molecular motion. Deuterium NMR spectroscopy thus provides highly specific and detailed information on a molecular level.[15]

The samples used in this study are the *m*-phenylenediamine-cured epoxies based on the diglycidyl ether of bisphenol A (see Chart I). The resin samples were exchanged with D_2O in the following manner. An ampule of D_2O was placed into a glass tube containing the epoxy. After evacuation and sealing, the ampule was broken by shaking and the whole assembly placed in an oven at 160 °C. This was repeated five times, each time with a fresh ampule of D_2O, to ensure complete exchange. After the final cycle a given amount of D_2O was introduced into the system and the final weight percent D_2O was determined gravimetrically. The plasticized samples used in this study ranged from ca. 1 to 3 wt % D_2O. A dried reference sample was prepared by heating a deuterium-exchanged resin to 170 °C in vacuo for 2 days in the presence of phosphorus pentoxide. All samples were sealed under dry nitrogen until the NMR experiments were performed. A fresh sample was used for each NMR experiment unless otherwise noted.

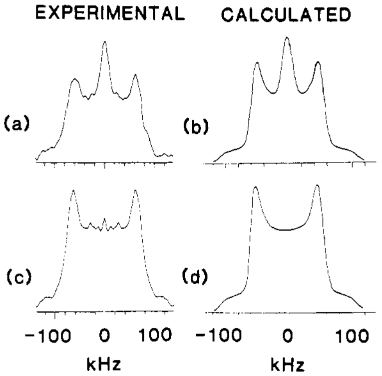
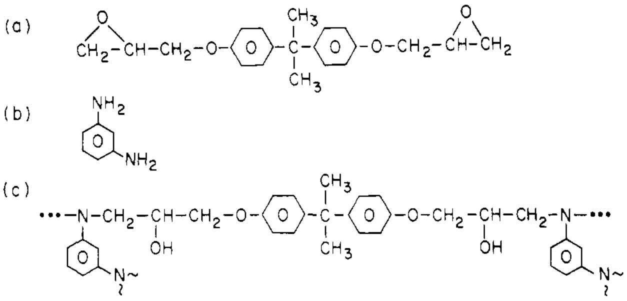


Figure 1. Experimental (left) and calculated (right) solid-state deuterium NMR spectra of epoxy resins at 20 °C: (a) epoxy resin containing 2 wt % D_2O; (b) calculated spectrum corresponding to 75% static and 25% mobile deuterons; (c) deuterium-exchanged and dried epoxy resin corresponding to the sample used in (a); (d) calculated spectrum corresponding to static deutrons only.

Chart I



The quadrupole echo deuterium NMR spectrum of the epoxy sample containing 2 wt % D_2O is shown in Figure 1a. The spectrum consists of a static quadrupolar pattern ($\Delta\nu_q \simeq 125$ kHz) with a relatively sharp line superimposed on it ($\Delta\nu_{1/2} \simeq 20$ kHz). Deconvolution of the NMR spectrum into two components (Figure 1b) indicates that the static (broad) pattern represents 75% of the deuterons and that the sharp peak accounts for the other 25%. (The calculated spectrum was obtained by taking into account pulse power fall-off as a function of frequency.[17,18])

In contrast, the dried epoxy sample yields the deuterium NMR spectrum shown in Figure 1c. Here, the sharp component is missing, and only the static part of the pattern is observed. The spectrum in Figure 1c is again in good agreement with the calculated spectrum shown in Figure 1d, in which only one component has been required for the simulation.

Several conclusions can be drawn from the spectra shown in Figure 1. First, the observed intensity ratio in Figure 1a (75% static: 25% mobile) is in excellent agreement (78:22) with that calculated assuming 2% plasticization and stoichiometric deuterium exchange of the resin as shown in Chart I. We also note that the spectrum of the deuterium-exchanged and dried sample (Figure 1c) is in accord with a structural explanation for the static part of the deuterium pattern. The observation and absolute intensities of the static deuterium NMR spectrum for the dried sample indicate that under the conditions of the deuterium-exchange process the –OH and the residual –NH groups of the resin exchange readily with D_2O. Second, the very appearance of a narrow component using the quadrupole echo pulse sequence (Figure 1a) indicates that the D_2O giving this resonance is not completely

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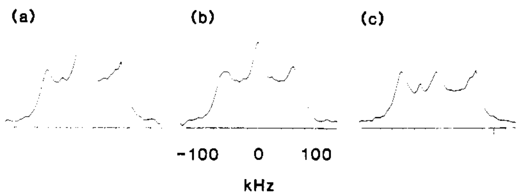

Figure 2. Solid-state deuterium NMR spectra of epoxy resins with differing levels of water: (a) 3 wt %; (b) 2 wt %; (c) the sample in (b) equilibrated in the atmosphere for 3 weeks. All spectra were obtained at 20 °C.

isotropically mobile. Such a "pseudosolid echo" spectrum arises because the electric field gradient tensor at the deuterium nucleus is not completely averaged by motion of the water molecules.[19] For a completely isotropically mobile D_2O, no sharp component would be observed with the particular pulse sequence used. Although the narrow line represents D_2O molecules that are not tumbling isotropically, it is clear that very substantial motional narrowing is occurring. For example, if the only motion of the water molecules were a 180° flip about an axis bisecting the H–O–H bond angle, the expected pattern would be a totally axially asymmetric one with a breadth of ~120 kHz.[20] The observed pattern is 5-fold narrower than this.

The quadrupole echo spectra shown in Figure 2 illustrate the differences observed as water content in the resin is varied. The sample corresponding to the spectrum in Figure 2a contains 3 wt % D_2O, whereas the one for Figure 2b contains approximately 2 wt %. The peak for the mobile water fraction is sharper for the sample that contains the larger amount of water. Moreover, it should be noted that the 3 wt % D_2O containing epoxy sample of Figure 2a also yields a spectrum using a standard $90°-\tau$ pulse sequence (with a 30-μs receiver dead time), whereas the sample containing 2 wt % does not. The inference therefore is that a fraction of the water in the 3 wt % sample comes even closer to displaying total isotropic mobility. When the 2 wt % D_2O sample is allowed to equilibrate with atmospheric water at ambient temperature for a period of 3 weeks, the narrow component of the spectrum decreases in intensity (Figure 2c), showing the back-exchange of the plasticizing molecules with atmospheric water.

For epoxy samples containing 2 wt % D_2O, deuterium NMR results at 20 °C (Figure 1) and at lower temperatures (not shown) together support the conclusion that the water is distributed homogeneously throughout the resin. As noted above, the D_2O is not isotropically mobile at room temperature, and the narrow resonance does not "freeze out" at −20 °C, well below the freezing point (3.8 °C) of D_2O. If plasticized samples contained aggregations of D_2O, the spectrum would reflect frozen water below 3.8 °C. Specifically, one would obtain a Pake doublet with a 144-kHz separation, rather than the modest broadening actually observed.

A series of temperature-dependent spectra is shown in Figure 3 for the epoxy resin containing 3 wt % water. The line width of the component due to mobile water narrows as the temperature is increased, and it approaches a constant value at ~60 °C. At 81 °C the signal from the static deuterium component in the resin begins to broaden, and the intensity of the sharp component decreases concomitantly. From a temperature-cycling experiment we infer that the latter observation merely reflects the desorption of D_2O from the epoxy sample.

The broadening of the static component could have two explanations. Chemical exchange between the mobile D_2O and the resin-bonded deuterium could be occurring at an intermediate rate on the deuterium NMR time scale. Saturation transfer experiments are in progress to determine whether the sharp water component is undergoing dynamical chemical exchange with the –OD and residual –ND groups of the polymer. However, the fact that the dried samples also have a broad spectrum at 81 °C (Figure 4) militates against this explanation.

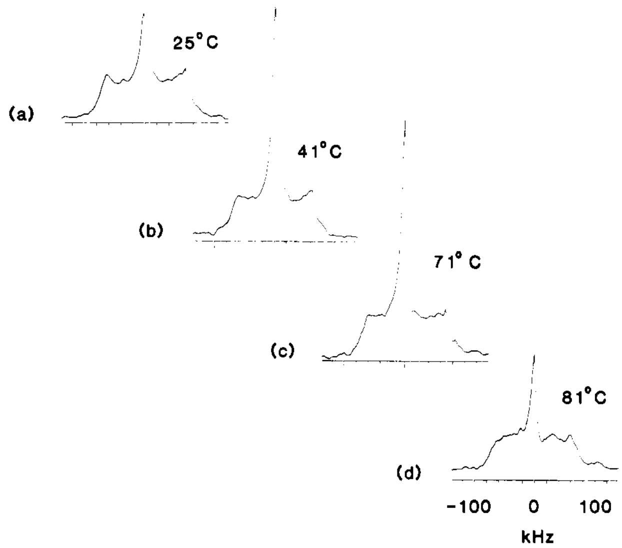

Figure 3. Temperature-dependent quadrupole echo solid-state deuterium NMR spectra of an epoxy resin sample with 3 wt % D_2O. A fresh sample was used for each run. Only 4096 transients were accumulated for each sample in order to minimize the effects of water desorption during accumulation of the spectra.

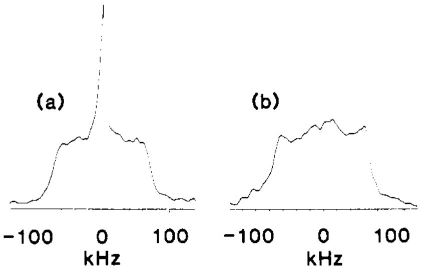

Figure 4. Comparison of the solid-state deuterium NMR spectrum of the epoxy resin containing 3 wt % D_2O (a) with that of the deuterium-exchanged and dried resin (b). Both spectra were obtained at 80–81 °C.

A second and not necessarily mutually exclusive explanation attributes the broadening to the onset of polymer motion at these temperatures. Support of this point of view is provided by the spectra in Figure 4, where it can be seen that the broadening at 81 °C is much greater for the plasticized than for the dried sample. This is to be expected as the onset T_g for the dried sample is 151 °C whereas that of the 3% plasticized sample is of the order of 110 °C, considerably closer to the temperature of these particular measurements.

Taken together, the solid-state deuterium NMR results provide valuable structural and dynamic information on water–epoxy interactions. As such information is not accessible by other physical techniques, the NMR method shows particular promise for the investigation of plasticization phenomena in both thermosetting and thermoplastic materials.

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Registry No. Water, 7732-18-5; poly(bisphenol A diglycidyl ether), 25085-99-8.

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(21) Several broad-line proton NMR studies have been reported on epoxy–water systems.[3,4,11,12] The deuterium NMR approach used here has the advantages that D_2O can be observed selectively, without competing signals from the resin, and that the resultant line shape is straightforward to analyze.

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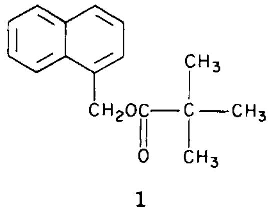
How Dense-Packed Are Collapsed Polymer Chains in Dilute Solution?

Ever since the concept of a Θ solvent was first presented,[1] it was recognized that below the Θ temperature a polymer molecule should suffer an important decrease in its mean dimensions. These decreased dimensions have been notoriously difficult to study. Most experiments fail because polymer molecules are simply not very soluble below $T = \Theta$. This means that appropriate experiments must examine kinetically metastable solutions, in which, because of the enormous dilution of the polymer molecules, the collapse transition would occur much faster than the aggregation and precipitation of macromolecules. Such transitions have been observed by light scattering on very high molecular weight polystyrene polymers,[2] where the high sensitivity of the light scattering technique for polymers of this high molecular weight allows one to carry out experiments in the ppb to ppm concentration range.

Fluorescence and phosphorescence techniques are potentially useful for examining the properties of polymer molecules at high dilution. One needs typically only 1×10^{-6} M concentration of chromophore to detect emission intensity with ease, and one can realistically work with solutions a factor of 10 more dilute. This means that experiments can be carried out at 1 ppm (weight fraction) of polymer, particularly if the polymer contains more than one chromophore per chain.

In this paper we present our observations on the phosphorescence intensity of naphthalene groups attached covalently to a polymer chain. These observations are compared to those on a small molecule containing the same chromophore. In dilute solution, at room temperature or in rigid low-temperature matrices, both show similar luminescence properties. At low temperatures, near the melting point of the solvent, where the solvent is presumably a very poor (sub-Θ) solvent for the polymer, we see indications of collapse of single chains. Our results suggest that these polymer molecules form configurations so compact that the diffusion of oxygen within the coil is retarded by ca. 10 orders of magnitude over its value at room temperature in the same solvent.

Experimental Section. The experiments reported here involve a graft copolymer of poly(methyl methacrylate) (PMMA) and polyisobutylene in which the PMMA blocks contain 10 mol % naphthalene groups distributed randomly along their length. The naphthalene groups were introduced in the form of 1-naphthylmethyl methacrylate during the synthesis of the polymer. This material is reasonably polydisperse. Most of the polymers have apparent molecular weights (by GPC) in the range 20 000–80 000. The isobutylene content by NMR is approximately 10 mol %. These materials were prepared as nonaqueous dispersions of 2-μm particles in isooctane. Their preparation and characterization have been described elsewhere.[3] In these experiments, the polymer was dissolved in ethyl acetate at a weight concentration of ca. 10 ppm, which corresponds to a naphthalene (N) concentration of 7×10^{-6} M. The solutions were placed in 3-mm-i.d. quartz tubes for phosphorescence analysis. The N groups were excited with light at 280 nm. Some of the tubes were outgassed by bubbling argon gas into the solutions for 30 s to 1 min. Emission spectra were compared to that of the model compound 1-naphthylmethyl pivalate (1).



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Results and Discussion. When solutions of the polymer or of 1 in ethyl acetate were immersed in liquid nitrogen, essentially transparent glassy matrices were formed. In these, both fluorescence and phosphoresce from N could be observed. At room temperature, only N fluorescence was observed: the presence of oxygen or other trace impurities at the 10^{-8}–10^{-9} M level effectively quenched the N triplets before they could emit.

In Figure 1a we show what happens to the phosphorescence intensity of the model compound 1 as a frozen

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