NOTES

Hydrogen Exchange Between Water and Epoxy Resin

The change in mechanical properties of epoxy resin–graphite fiber composites upon the absorption of water[1–7] has prompted an IR and NMR study of water absorbed by the neat resin.

Samples of epoxy resin (tetraglycidyl-4,4′-diaminodiphenylmethane; curing agent diaminodiphenyl sulfone) were supplied by NASA Langley. Transmission IR spectra of the samples (thickness < 1 mm) were obtained with a Perkin–Elmer 457 for dry samples, soaked in H_2O, and samples soaked in D_2O. The water-soaked samples had picked up a few percent weight increase due to the water. The spectrum of the dry samples was the same as that obtained for samples that had been soaked in H_2O and allowed to dry in the IR beam (Fig. 1). On the other hand, the spectrum of the D_2O-soaked resin (Fig. 2) showed a shift of a band at about 3300 wave numbers to about 2600 wave numbers. The frequency shift is consistent with what one would expect, since the mass of the deuteron is twice that of the proton, and the frequency is inversely proportional to the square root of the reduced mass. Our hypothesis is that the water absorbed by the resin is involved in an ex-

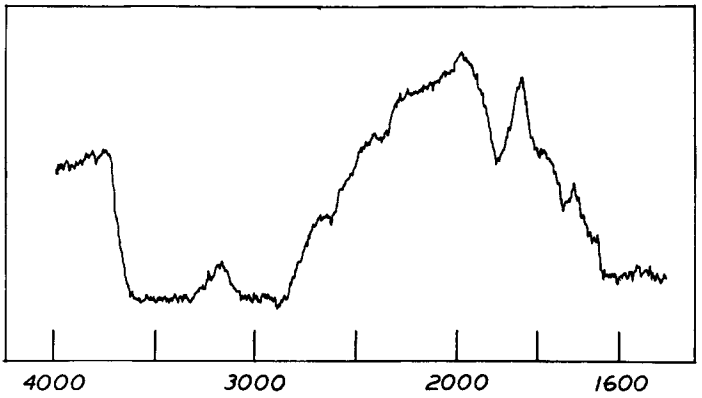

Fig. 1. Transmission IR spectrum of resin after H_2O soak and drying. Transmittance increases vertically, and the horizontal scale is in cm^{-1}.

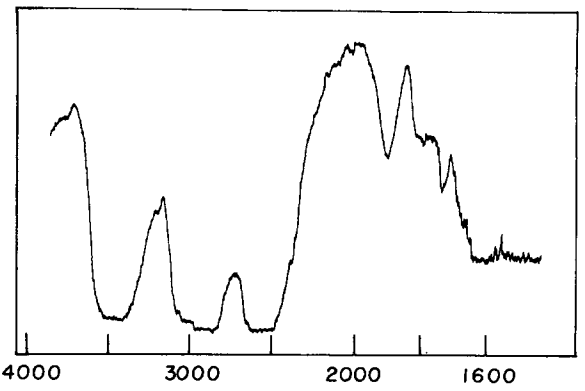

Fig. 2. Transmission IR spectrum of resin after D_2O soak. Transmittance increases vertically, and the horizontal scale is in cm^{-1}.

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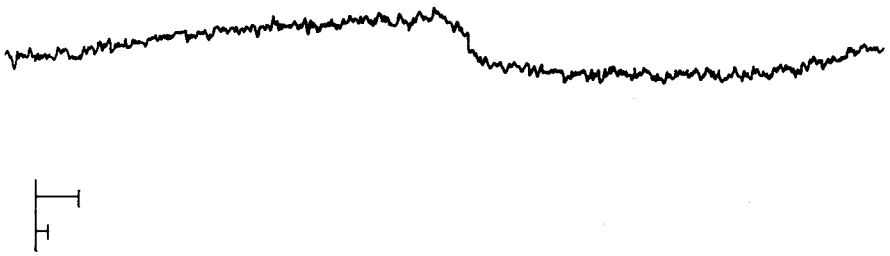

Fig. 3. Broadline PMR spectrum of dry resin. The wider scale indicates 2G. The narrower scale gives the modulation amplitude.

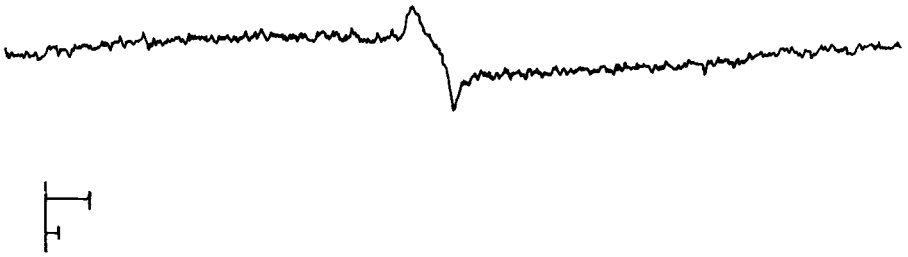

Fig. 4. Broadline PMR spectrum of resin after D_2O soak. The wider scale indicates 2 G. The narrower scale gives the modulation amplitude.

change between the hydrogens of the water and the hydrogens on the polymer. Two pieces of evidence indicate that the line in the IR spectrum is due to a stretching mode involving a hydrogen bonded to the polymer backbone rather than to a stretching mode in a water molecule in the solid. First, the IR spectrum of the H_2O-soaked resin is equivalent to the spectrum of the dry sample. Second, in the D_2O-soaked sample, the new line is accompanied by a *decrease* in intensity in another region of the spectrum. In other words, a line originally present in the dry sample is no longer there, indicating that protons present on the dry polymer backbone have been replaced by deuterons from the D_2O absorbed by the sample.

Additional evidence that hydrogen exchange is taking place comes from broadline NMR measurements that we have made using a Varian DA-60 spectrometer. Dry cylindrical samples of the resin give a line with a width characteristic of the solid state (Fig. 3). When such a sample was soaked in D_2O for several days, we obtained a *proton* NMR sharp line (Fig. 4). The width of the narrow line is characteristic of water absorbed by the resin system.[8] The fact that a *proton* sharp line is present after a D_2O soak indicates that some of the water in the system now contains protons, which come from hydrogen exchange between the D_2O and the protons in the polymer.

We suggest that the exchange occurs at a hydroxyl site in an opened epoxy ring; the frequency of the band in the IR spectrum, around 3300 wave numbers, is consistent with an OH stretching frequency. It is possible, of course, that the exchange occurs with unreacted curing agent.

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