*NMR Study of Water Absorbed by Epoxy Resin**

Degradation of the mechanical properties of epoxy resin–graphite fiber composites upon the absorption of water[1–3] prompted an NMR study of moisture absorbed by the neat resin.

Samples of epoxy resin (tetraglycidyl-4,4′-diaminodiphenyl methane; curing agent: diaminodiphenyl sulfone) were supplied for these experiments by NASA Langley. Sample A was soaked in a solution of distilled water until its mass had increased by 1.5%. Sample B was dried out at 45°C in an oven containing a desiccant for a period of four weeks. Sample C was used in the experiments without either drying or impregnation with water. First-derivative proton NMR spectra were obtained, using a Varian DA-60 spectrometer, with a time averaging computer used to enhance the signal-to-noise ratio. At room temperature both samples B and C (the dry samples) showed a single broad NMR absorption line whose width, approximately 10 G, is characteristic of protons in the solid state[4] (Figs. 1 and 2). Sample A (the wet sample) showed a sharper line in addition to the broad line seen in the other two samples (Fig. 3). The conclusion that this extra line arose from the absorbed water is straightforward. The linewidth of the sharper line, about 1 G, is intermediate between the width of the broad singlet from the protons in the solid state,[4] and the linewidth for protons in free water, which is of the order of 1 mG or less,[4] and is somewhat greater than that observed in this laboratory from water bound to cellulosic fibers.[5] Since the linewidth is inversely related to molecular mobility,[4] one would conclude that the water absorbed by the resin is in a less mobile state than free water. The experiments were repeated at a temperature of 68°C. The narrow line in the wet sample sharpened more, and increased slightly in amplitude (Fig. 4). For the two dry samples, a small narrow line appeared at the elevated temperature (Figs. 5 and 6). We suggest that this line is due to residual

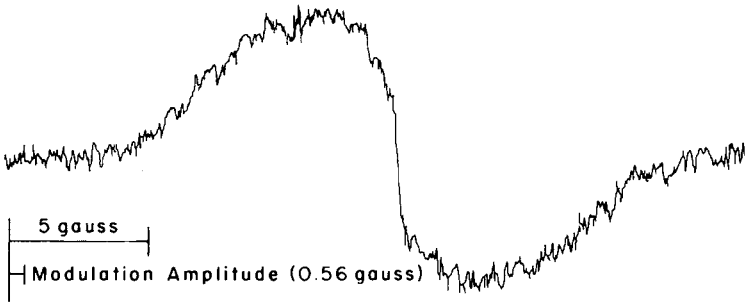

Fig. 1. NMR spectrum of sample C at 26°C.

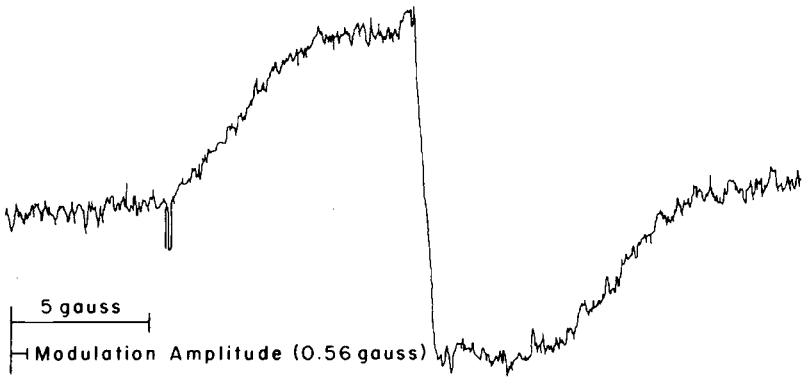

Fig. 2. NMR spectrum of sample B at 26°C.

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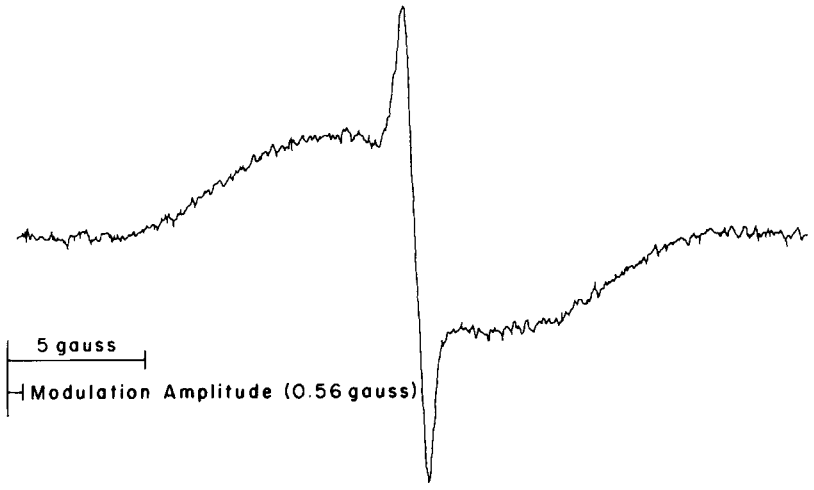

Fig. 3. NMR spectrum of sample A at 26°C.

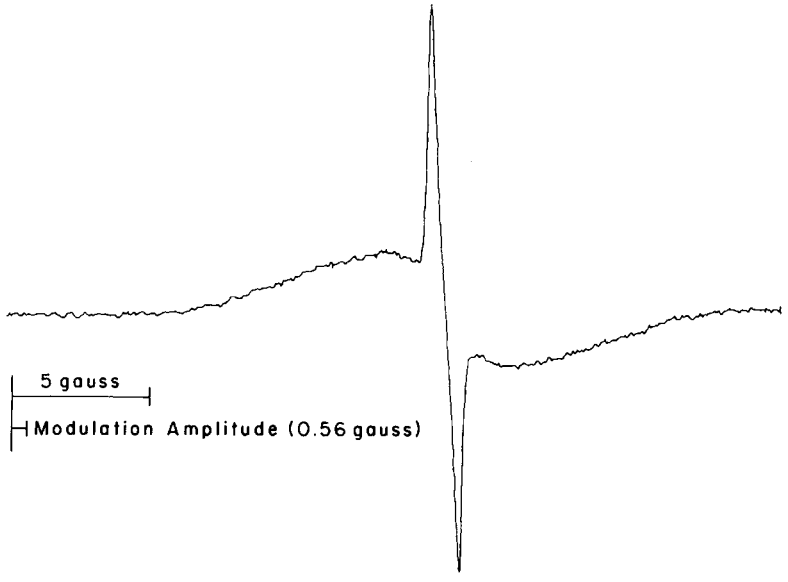

Fig. 4. NMR spectrum of sample A at 68°C.

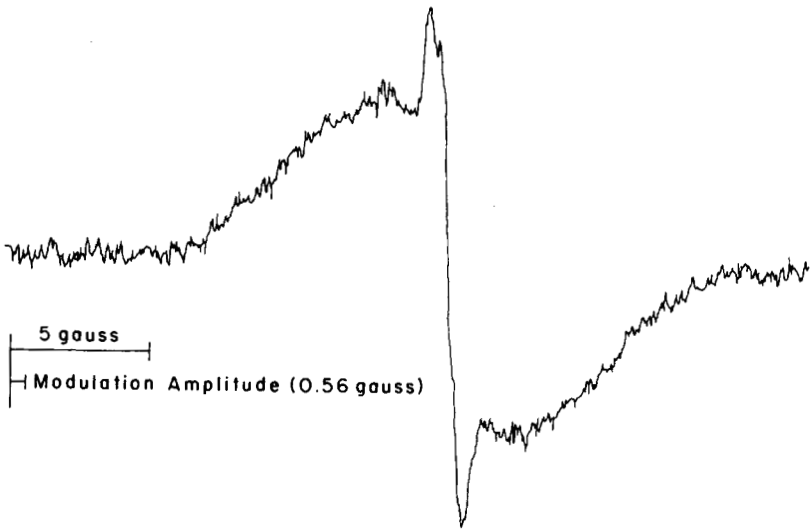

Fig. 5. NMR spectrum of sample B at 68°C.

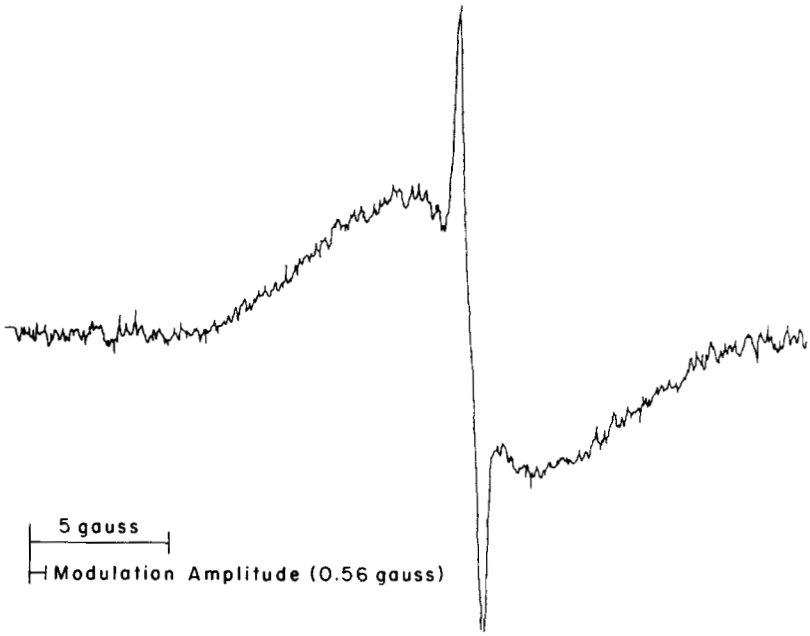

Fig. 6. NMR spectrum of sample C at 68°C.

water in the dry samples. When the temperature of these samples was elevated, the lines sharpened with a concurrent increase in amplitude so that they became observable.

In conclusion, it is suggested that the NMR evidence indicates that water absorbed by this epoxy resin is in a state less mobile than that of free water, but more mobile than that of a crystalline state.

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