The Glass Transition Temperature of an Epoxy Resin and the Effect of Absorbed Water

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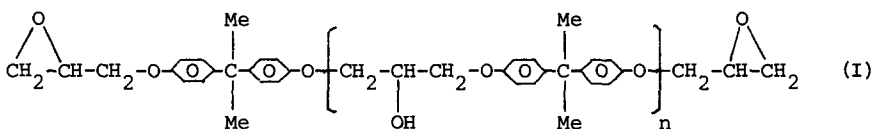
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Summary

The glass transition temperature, T_g, of a diamino-dipenyl methane (DDM, II) cured diglycidyl ether of bispenol-A epoxy resin (I, n = 0) has been determined by proton NMR line width studies to be $410^{\circ}K$. In the presence of 2.5 ± 0.1 w/o absorbed water T_g is reduced to $378^{\circ}K$. Such a large reduction of Tg by such a small amount of water requires specific interactions. It is postulated that segmental motion is increased as a result of the disruption of hydroxyl group hydrogen bonds by the absorbed water molecules.
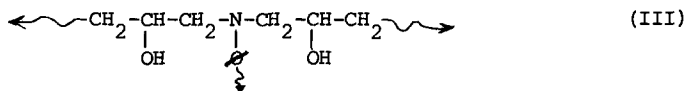
Introduction

Because of the central importance of the glass transition behaviour of polymers there is a very voluminous literature on this subject (SHEN and EISENBERG 1970). However, the attention given to the study of highly crosslinked resins is small compared with the very many studies of thermoplastics. NIELSEN (1969) has reviewed studies of the effect of crosslink concentration, and KAEBLE (1973) has reported on epoxy resins, comparing results obtained using dynamic, mechanical and broad-line proton NMR methods. Broad-line NMR spectra are obtained when solids or viscous liquids are studied, and a narrowed line is obtained when molecular motion occurs. The theory of motional narrowing is discussed by ANDREW (1958); the condition for a narrowed line is that isotropic reorientation of the protons occurs at a rate greater than about 10^4 Hz. The effect of resin molecular weight on the glass transition temperature of bisphenol-A type epoxy resins (I, n = 0 to n = 10) has been measured (ELLIS 1972) using proton broad-line NMR line width measurements.

$$CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}\langle O \rangle\text{-}\overset{\text{Me}}{\underset{\text{Me}}{C}}\text{-}\langle O \rangle\text{-}O\text{-}\left[CH_2\text{-}\underset{\text{OH}}{CH}\text{-}CH_2\text{-}O\text{-}\langle O \rangle\text{-}\overset{\text{Me}}{\underset{\text{Me}}{C}}\text{-}\langle O \rangle\text{-}O\right]_n CH_2\text{-}CH\text{-}CH_2 \quad \text{(I)}$$

The purpose of the present study was to use broad-line NMR to measure the effect of absorbed water on the glass transition temperature of an epoxy resin with n = 0, cured with diamino-diphenyl methane (DDM, II).

$$H_2N\text{-}\langle O \rangle\text{-}CH_2\text{-}\langle O \rangle\text{-}NH_2 \qquad \text{(II)}$$

With complete cure all the epoxy groups will be reacted, and the junction points will have the structure III. The crosslinks can

$$\longleftarrow\sim\!\!-CH_2-CH-CH_2-N-CH_2-CH-CH_2\sim\!\!\longrightarrow \qquad (III)$$
$$\quad\quad\quad\quad |\quad\quad\quad\quad |\quad\quad\quad |$$
$$\quad\quad\quad\quad OH\quad\quad\quad\quad\quad OH$$

be considered as tetrafunctional because of the rigidity of II.

Experimental

Broad-line proton NMR spectra were obtained using a JOEL (JNM-3H.60) spectrometer operating at 60 MHz. Resin I with n = O ($\overline{M}_n$ = 355.17, epoxy value = 5.15) was mixed at 100°C with the stoichiometric amount (27g/100g resin) of DDM (II), and given a standard cure of 1 hour at 110°C followed by 1 hour at 140°C. A portion of the cured resin was powdered and stored in a vacuum dessicator.

A sample of the powdered resin was exposed to water vapour at 70°C for 7 hours, followed by 15 hours at room temperature. It was then sealed in a glass NMR sample tube, precautions being taken to reduce the unfilled space to a minimum: calculation showed that the amount of water lost to the unfilled space could not exceed 0.1g/100g of resin, and that the pressure in the tube would not rise above 6.2 atmosphere. WARFIELD (1966) has shown that a pressure of this magnitude has no measurable effect on T_g.

NMR measurements were made on the "wet" sample, and also on dry solid and powdered samples, where it was found that powdering did not affect the spectra. The line widths plotted in Figure 2 are derived from the average of six spectra at each temperature, the error bars showing the spread obtained.

After the NMR measurements the tube containing the "wet" sample was broken open and the water content of the resin was determined by weight loss on heating to be 2.5 $\pm$ 0.1 w/o.

Results and Discussion

Broad-line NMR spectra are obtained as the first derivative of the absorption; typical spectra are given in Figure 1 for both "wet" and dry resins, above and below T_g. The line width, δH, is measured as the separation between maximum and minimum, as shown in Figure 1(a). The change in line width with temperature is shown in Figure 2, for the uncured resin and for the "wet" and dry samples of the cured resin. Glass transition temperatures were derived from these curves by the linear extrapolation method described by ELLIS (1972).

With full cure Tg of the resin is raised from 250°K to 410°K. Tg would be expected to increase with cure, since the crosslinks formed would restrict the segmental motion of the polymer molecules; however, it is remarkable that above Tg the line width for the cured resin is only about 0.2 gauss, which is as narrow as that for the uncured resin. Uncured resins above Tg are viscous liquids, and hence have narrowed broad-line NMR spectra. For the highly cross-
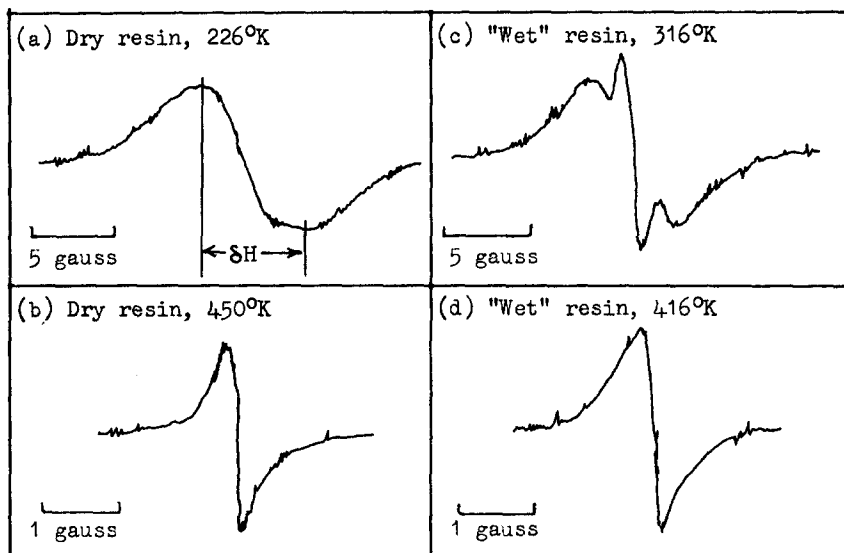
(a) Dry resin, 226°K

5 gauss ←δH→

(b) Dry resin, 450°K

1 gauss

(c) "Wet" resin, 316°K

5 gauss

(d) "Wet" resin, 416°K

1 gauss

Figure 1. Typical 1st derivative plots of NMR absorption spectra.

······ Uncured resin

● Cured resin

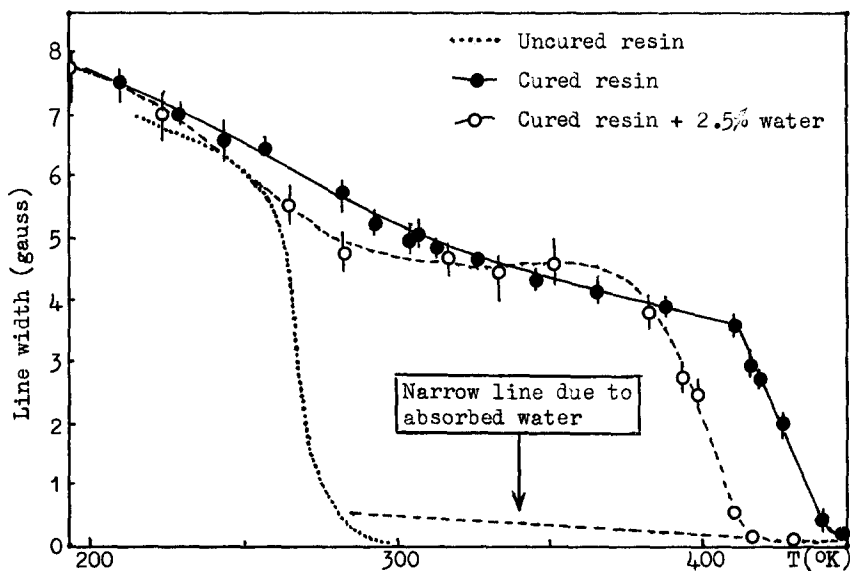─○─ Cured resin + 2.5% water

Narrow line due to absorbed water

Line width (gauss)

T(°K)

Figure 2. NMR line width vs. temperature.

linked cured resin it is surprising that essentially all the protons must be isotropically reorientating at a rate greater than 10^4 Hz, the condition for a motionally narrowed NMR spectrum to have a line width as low as 0.2 gauss: it must be concluded that the junction points, III, are also mobile above T_g. The frequency of the motion of these junction points must be somewhat greater than 10^4 Hz, which can be compared with the "tumbling" of small molecules in liquids, with a frequency of about 10^8 Hz.

From Figure 2 it can be seen that 2.5% absorbed water (i.e. an average of 0.6 water molecules to each junction point III) reduces T_g by about 32°. Clearly, segments of the resin must be able to reorientate isotropically at temperatures 30° lower than when dry. There is a set of relationships for the effect of a diluent on the glass transition temperature, with the general form

$$T_g = f(T_{g.p}, T_{g.d}, \text{composition}) \qquad \ldots\ldots (1)$$

particulary that of MILLER (1966)

$$\frac{1}{T_g} = \frac{w_p}{T_{g.p}} + \frac{w_d}{T_{g.d.}} \qquad \ldots\ldots (2)$$

where T_g, $T_{g.p}$ and $T_{g.d}$ are the glass transition temperatures of the mixture, pure polymer and diluent respectively in $^{\circ}$K, and w_p and w_d are the weight fractions of polymer and diluent.

For the hygroscopic polymers poly(n-vinyl pyrrolidone)(PVP) and poly(2-hydroxy ethyl methacrylate)(PHEMA) the glass transition temperature could be related to the amount of absorbed water using equation 2, with up to 16 w/o water for PVP (TAN and CHALLA 1976), and up to 50 w/o water for PHEMA (SUNG et al 1978). Using the same value (128°K) for the glass transition temperature of water, equation 2 predicts a fall in T_g for the present resin with 2.5 w/o absorbed water of 22° only, compared with the observed fall of 32°. However, relationships such as these, which are based on the additivity of some property such as free volume, are inappropriate when there are specific interactions between the polymer and the absorbed species. In the case of atactic PMMA MIYAYI and TANAKA (1975) showed, using DSC, that 0.5 w/o absorbed water depressed T_g by over 40°. With effects of this magnitude it is imperative to measure T_g of polymers on samples which have been carefully dried, an effect noted for PVP and PHEMA, and discussed by ALLEN and co-workers (1972) for the low temperature relaxation process in poly-sulphones.

ELLIS and RASHID (1978) have concluded from Infra Red studies that absorbed water is hydrogen bonded to the hydroxyl groups in III at room temperature. In the NMR spectra of the "wet" resin a narrow line due to water persists down to about 270°K, showing that water molecules are able to reorientate at T_g-100: if they are hydrogen bonded such reorientation requires that the water molecules migrate from one site to another, since a simple rotation would not be sufficient to remove all dipolar broadening.

Crankshaft models for molecular motion have been proposed for the polymethylene chain in which bonds 1 and 7 (Schatski), 1 and 6 (Wunderlich), and 1 and 5 (Boyer) are colinear with rotation about the common axis (ROBERTS and WHITE 1973). For the segment of the present crosslinked epoxy resin only a modified Boyer model is possible, IV, with bond 1 from the phenylene ring to oxygen, and with a high energy eclipsed conformation about the central bond 3.

(IV)
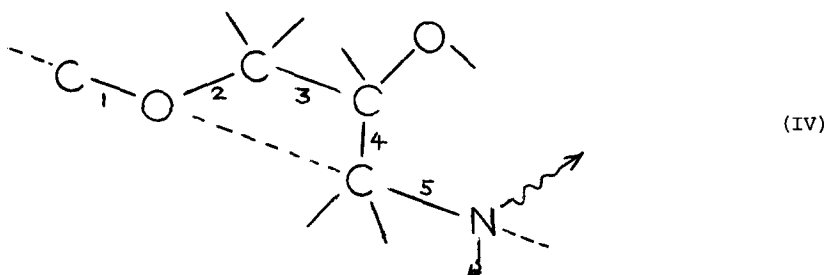
Rotation of chain segment IV will be inhibited, not only by adjacent groups, but also by the formation of a hydrogen bond by or to the hydroxyl group. The hydrogen bond may be formed with either a hydroxyl group on a nearby chain, or with the hydroxyl group on the adjacent chain segment in III, in which case a seven-membered ring is formed, as for example in V.

(V)

- ○ C
- ● N
- ▨ O
- ○ H
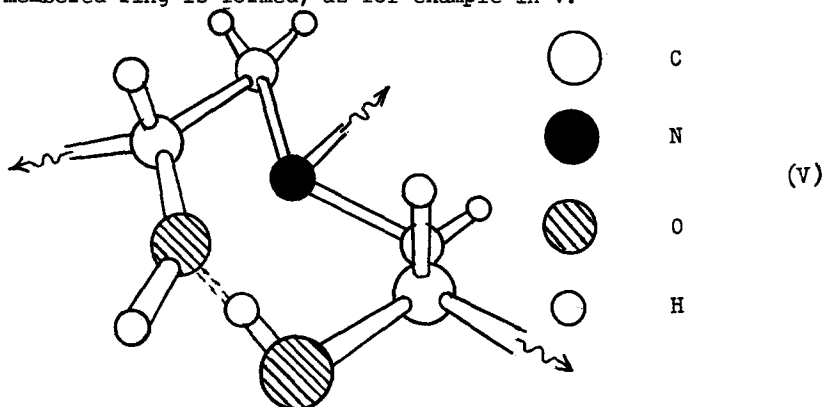
When water is absorbed the hydrogen bonds, either between nearby chains or in the ring V, are readily broken, as shown by the rapid deuterium exchange at room temperature (ELLIS and RASHID 1978). With the breaking of such hydrogen bonds rotation of chain segment IV is made possible. Thus, the role of absorbed water is to "catalyse" the breaking of hydrogen bonds; small amounts of water have a large effect because water molecules migrate from one group to another. This may be concluded both from water diffusion studies, where the calculated jump frequency is at least 10^5 Hz (ELLIS and RASHID 1978); and also from the presence of a narrow NMR line due to water at up to 100° below T_g. However, the critical factor which determines T_g is not the average residence time of the water molecules, but the average persistence time of the inter-hydroxyl hydrogen bonds.

Obviously, the explanation offered here for the anomolously large reduction of T_g with water absorption in epoxy resin cannot be applied to the effects reported by MIYAYI and TANAKA (1975) of water absorption in PMMA.

A complete description of the modes of segmental motion in epoxy resins is not possible, but this has not yet been achieved for the simpler polymethylene chain. However, the specific role of absorbed water in epoxy resins is clearly established.

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