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FINAL TECHNICAL REPORT

PHYSICAL AGING AND ITS INFLUENCE ON THE RELIABILITY OF NETWORK EPOXIES AND EPOXY-MATRIX COMPOSITES

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Time-dependent variations have been observed in mechanical and physical properties of polymeric network epoxies and also carbon-fiber-reinforced composites with epoxy-matrices. These property variations are the result of differences in specimen preparation conditions and/or thermal histories which the materials have experienced (1 - 7). In general, with slower cooling rate from above the glass temperature, Tg, and/or increasing the sub-Tg annealing time, the density increases, while impact strength (8), fracture energy (8), ultimate elongation (9), mechanical damping (5), creep rates (10), and stress-relaxation rates (5) decrease.

Of particular concern in the processing and application of structural epoxies is the loss of ductility of such materials on sub-Tg annealing, i.e., thermal aging at temperatures below the glass transition of epoxy resin. This sub-Tg annealing process, more commonly known as "physical aging" (10), is confirmed to be thermoreversible (5). That is, with a brief anneal at temperatures in excess of the resin Tg, the thermal history of an aged epoxy can be erased. A subsequent quench from above Tg would render a "rejuvenated" epoxy. In other words, the polymer embrittles during sub-Tg annealing. But with an aging history erasure above Tg, the ductile behavior can be restored (5,10).

If epoxies are to be strong candidates as structural matrices of composites materials, it is of primary importance

that an understanding of the nature of this volume recovery process as well as an assessment of the magnitude of its effects be achieved. To date, there is a general consensus that the property changes in glassy polymers on sub-Tg annealing are the result of relaxation phenomena associated with the non-equilibrium nature of the glassy state (11, 12). However, a basic understanding on the changes in the molecular level is still lacking. Fortunately, substantial progress has been made in the past few years in characterizing the glassy state from the molecular point of view by powerful techniques such as proton-decoupled cross-polarized magic-angle-spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy (13). Combining such techniques with other conventional instrumental tools, which measures excess thermodynamic properties, it is now possible to ascertain the changes in properties that can be attributed to relaxations of excess thermodynamic state functions such as enthalpy and volume. This paper addresses the pertinent relations between excess thermodynamic properties and the time-dependent behavior of epoxy glasses. Also, an attempt is made to describe the molecular nature of this relaxation process.

Moisture is a well-known plasticizer for macromolecules (14). Specifically, water penetrates into an epoxy network and can lower the glass temperature of the resin (15). In this report, moisture for the first time has been utilized as a probe to characterize the densification process during epoxy aging. Also, using the same rationale, heavy water is used to diffuse into the epoxy resin in order to study the interactions of moisture with the aging polymer by hydrogen-2 (deuterium) NMR spectroscopy.

Experimental

The epoxy used in this study was Fiberite 934 resin supplied by Fiberite Corporation, Winona, Minnesota, U.S.A. The chemical formulation of this resin is shown in Figure 1. The chemical constituents are 63.2% by weight of tetraglycidyl- 4,4'-diaminodiphenyl methane (TGDDM tetrafunctional epoxy), 11.2% of diglycidyl orthophthalate (DGOP difunctionsl epoxy), 25.3% of the crosslinking agent 4,4' - diaminodiphenyl sulfone (DDS crosslinker), and 0.4% of the boron trifluoride/ethylamine catalyst complex (16, 17).

The neat epoxy resin was prepared by casting. The as-received B-stage material was subjected to degasification at 85°C inside a vacuum oven. The softened resin was then transferred into a preheated silicon-rubber mold. The curing schedule was 121°C for 2 hour, 177°C for 2.5 hour, followed by a slow cooling at ca. 0.5°C per minute to room temperature (23°C).

Thornel 300 carbon-fiber-reinforced Fiberite 934 epoxy laminates (ca. 60% fiber and 40% resin by volume) were fabricated from prepreg tapes manufactured by Fiberite Corporation. The details of this fabrication process have been disclosed elsewhere (4, 5).

With the exception of five specimens (which were to be tested in the as-fabricated condition), all specimens were postcured for 16 hour at 250°C, followed by a slow cooling to room temperature at a rate of 0.5°C per minute. Testing was then performed on the five as-postcured specimens. The other postcured specimens were heated to 260°C for 20 minute and then immediately air-quenched to room temperature. Five of these quenched specimens were immediately tested, others were sub-Tg annealed in darkness at either 80, 110, or 140°C (in nitrogen) for time increaments of 10, 10^2, 10^3, 10^4, and up to 10^5 min. Time zero was taken as the time

when a mercury thermometer placed adjacent to the specimens reached the sub-Tg annealing temperature. At each decade of aging time, five specimens were removed from the environmental chamber and store at room temperature prior to testing.

In order to demonstrate the "thermoreversibility" of physical aging , the following requenching procedure was carried out. Specifically, some 10^4 min.-aged specimens were heated to above Tg for 20 minute (260°C), followed by air quenching to room temperature. Five of these requenched specimens were tested immediately. while the rest were subjected to "re-aging" in darkness at either 80, 110, or 140°C in nitrogen for time increments of 10, 10^2, 10^3, 10^4, and up to 10^5 minute. At least five specimens were tested for each decade of aging time.

The techniques reported in this paper for the study of volume recovery in carbon/epoxy composites is summarized as follows:

1. Instron 1122 tensile tester was utilized to study the time-dependent stress-strain behavior of the neat resins. Dog-bone-shaped epoxy specimens were prepared in accordance to ASTM: D1708-66. Strain rate used was 5×10^{-5} sec^{-1}.

2. Dynamic mechanical analysis was performed on 8-ply Thornel 300/Fiberite 934 composites that were symmetrically reinforced in configuration of $(\pm 45^\circ)_{2s}$. A dynamic mechanical thermal analyzer interfaced with a Hewlett Packard 85 computer was kindly supplied by Professor R.E. Wetton of polymer Laboratories/Loughorough University, Loughborough, United Kingdom. This instrument utilized a sinusoidal bending mode of mechanical deformation on a double cantilever beam (18). Both mechanical dispersions and dynamic storage modulus were measured in nitrogen from -100°C to 300°C at 1 Hz and 5°C per minute heating rate.

3. Differential scanning calorimetry was used to measure both the extent of cure as well as the progress of enthalpy recovery in the neat epoxy resin. A Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a scanning-auto-zero unit for baseline optimization was utilized to measure the heat capacity of the polymeric network glasses. Each disc-like, 0.8mm thick specimen of diameter 5mm was measured from 50 to 280°C in nitrogen at a heating rate of 10°C/min. Each specimen was scanned (160°C cooling rate from 280 to 50°C after the first scan.) The enthalpy recovery measurements were made by superimposing the first and the second scans for each specimen using a data-analysis method suggested by M.G. Wyzgoski (19).

4. Density measurements were made at 23°C on spherical neat resins of 5mm diameter using the flotation method in accordance to ASTM: D-1505. The density gradient column (model DC1) was supplied by Techne Incorporated, Princeton, New Jersey. Calcium nitrate solution column was set up which could measure density that ranges from 1.210 to 1.290.

5. Hardness measurements were made on 500Å gold-decorated epoxy square plates (2.5cm. by 2.5cm., 2mm thick) using a Leitz miniload micro-hardness tester, supplied by Ernst Leitz Company, Midland Ontario, Canada. A load of 200gm was applied to the specimen. ASTM D-785 and ASTM D-1706 test procedures were consulted.

6. Thermal mechanical analysis was performed on 2.5mm thick neat epoxy discs of 6mm diameter using a Perkin Elmer TMS-2 analyzer. The expansion mode was utilized in order to study the thermal expansion behavior of the network epoxies. Each specimen was measured from 50°C to 260°C at 5°C per minute heating rate in helium atmosphere. Similar to the DSC experiment

described earlier, each specimen was scanned twice from 50°C to 260°C. After the first scan, a cooling rate of 160°C per minute was utilized to quench the system from 260°C to 50°C. The first and second scans were then superimposed at the high-temperature "rubbery" domain in order to measure the volume recovery during sub-Tg annealing. Thermal expansivity was measured at the linear expansion regions below and above the epoxy glass temperature.

7. Moisture sorption kinetics by neat epoxies were measured using gravimetric analysis using a Mettler balance which was accurate to ± 0.05 mg. This technique was described in details elsewhere (20). Another method was used to monitor the sorption kinetics of heavy water diffusing into neat epoxies. This technique involved the use of solid state hydrogen-2 NMR spectroscopy. By the use of the normalized Free Induction decay (FID) NMR signal, one can readily determine the amount of heavy water sorbed by the epoxy specimen. Cylindrical-shaped 20 mm-long epoxy specimens of 5 mm diameter were immersed in heavy water at 23°C for 2 months and 40°C for 1 month before the NMR experiment. The hydrogen-2 NMR experiment involved locating the non-spinning heavy-water-saturated solid polymer in a magnetic field of 5 Tesla while pulsing the material with a radio frequency of 30.7 MHz. This technique was used to study the moisture-epoxy interactions in the molecular level (14).

8. In order to study the molecular aggregation during the volume relaxation of network epoxies, CP/MAS carbon-13 (natural abundance) NMR was utilized. The Hartman-Hahn cross-polarization technique (21) was used with a cross-contact time of 1 msec for transfer of proton polarization to carbon nuclei.

The proton-decoupling was achieved at the radio frequency of 56.4 MHz. Carbon-13 14.2 MHz spectra were measured in a 1.4 Tesla magnetic field. Room temperature (23°C) experiments were performed at 54.7° MAS at 1 KHz. The brittle, aged epoxies posed some experimental difficulties in using higher spinning rates (e.g., 4 KHz) at which the spectrum would have a higher resolution. The probe was constructed using a double-tuned/single-coil circuity. The spinner was constructed using an Andrew-type rotor driven by compressed air.

9. A Bruker WM-500 NMR Spectrometer was used to study the carbon-13 resonances for epoxy components (TGDDM and DDS) dissolved in deuterated chloroform ($CDCl_3$). TGDDM or DDS components were dissolved in solvent-containing 10 mm NMR tube. 125 MHz carbon-13 NMR spectra were measured at 23°C using a superconducting magnetic field of 11.7 Tesla.

Results and Discussion

In previous communications (4,7,9,22), we reported the importance of physical aging processes in affecting time-dependent changes in mechanical properties of TGDDM-DDS network epoxies and their carbon-fiber-reinforced composites. Recently, by means of a transport experiment, we have conclusively demonstrated the time-dependent "free volume collapse" in neat, fully-crosslinked TGDDM-DDS epoxies by water diffusion experiments (6,23). In addition, the mechanical damping and stress relaxation rates of such epoxies were observed to decrease, while tensile modulus of the carbon-fiber-reinforced epoxies was suggested to increase by our stress-relaxation studies (22).

In this paper results from various instrumental techniques will be discussed and critically reviewed. Thermal analysis

performed by differential scanning calorimetry (DSC) of as-cast epoxy indicated the material was not fully crosslinked --- an exotherm with a maximum peak temperature at 263°C was detected during the first scan from room temperature to 300°C, using a heating rate of 20°C per minute. Because it is obvious that continued "chemical aging" such as increase in crosslink density can change the physical and mechanical properties of an epoxy, it was important to this study that all possibilities of continuous chemical aging be eliminated to permit a full evaluation of the effect of the physical aging phenomenon on mechanical behavior. The Fiberite 934 epoxies and their composites were given a postcuring treatment of 16 hours at 250°C in nitrogen. After postcuring, DSC confirmed that the epoxy matrix was in a fully-cured state with a regular step-function increase in heat capacity at a Tg range of 180°C to 270°C. This result was also confirmed, using dynamic mechanical analysis and Fourier transform infrared spectroscopy (24).

Stress-Strain Analysis

Tensile tests were performed on neat epoxy resins in the following conditions: as-cast, as-postcured, as-quenched, and aged at decade increments from 10 to 10^4 minute at 140°C in nitrogen while stored in darkness. A summary of the observed resin stress-strain behavior is shown in Figure 2. As can be seen, the epoxy polymer was found to be extremely sensitive to thermal history. The as-cast specimens exhibited the highest value of ultimate-tensile-strength (UTS) and by far the greatest values of strain-to-break (ϵ_B) and toughness. Toughness here is defined as the area under the stress-strain

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curve, which is different from the dynamic toughness values obtained from impact tests. As reported earlier in the carbon/epoxy composites investigations (4, 23), the postcuring treatment resulted in a significant reduction in these mechanical properties. This effect is undoubtably due to the completion of the crosslinking reactions in the thermoset.

Oddly enough, the postcured specimens given an air-quench from above Tg exhibited a loss in strength, ductility, and toughness --- significantly greater than that of the as-postcured specimens (Figure 2). This observation was unexpected, based on the free-volume concept. A rapid quench will result in a larger deviation from the equilibrium glassy state; thus, a relatively large amount of free volume will be frozen into the epoxy. Because more free volume can be interpreted to mean higher chain mobility and shorter molecular relaxation time, an increase in free volume was anticipated to result in an increase in epoxy tensile properties instead of a severe decrease.

Quenched specimens given a brief thermal annealing at 140°C for 10 minute were to exhibit toughness similar to that observed for as-postcured specimens (Table 1). Even though the strength for 10 minute annealed specimens was not totally restored compared to the as-postcured specimens, the ductility for the former was much improved. This rapid restoration of mechanical properties over that observed in as-quenched behavior is an artifact of the quenching process and not an indication of the inherent tensile behavior of the epoxy material itself.

One explanation for these observations is the presence of residual thermal stresses, which can develop in the bulk

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material as the result of rapid thermal changes. The skin and the core of the bulk epoxy would experience a different cooling rate during the air-quench, and rapid cooling of the specimen would not permit the time-dependent relaxation of these stresses. The fact that a brief thermal annealing results in restoration of epoxy tensile properties suggests that the residual thermal stresses have been removed and have not caused irreversible damage in specimen.

Thermal annealing at 140°C in inert and dark atmosphere for times investigated up to 10^4 minute was found to have a severe effect on the polymer tensile behavior, as seen in Figure 2 and Table 1. The continual reduction in the stress-strain curve with decrement interval increases in exposure time at 140°C is shown in Table 1. These observed decreases in strength, ductility, and toughness are interpreted to be the results of the physical aging process occuring in the glassy polymer. As an additional check to assure that compositional changes were not occuring in the laminate with thermal exposure, specimen weights were followed. No resolvable weight change was observed in any of the aged specimens.

The detailed influences of physical aging on UTS and ϵ_B of Fiberite 934 epoxies are shown in Figures 3 and 4, respectively. To summarise the effects of thermal history on the ductility of network epoxies, the results are presented in Figure 5. Ductility (ϵ_B) was found to decrease from 2.1% to 1.0% while strength was found to <u>decrease</u> for 35.5% during this period of 10^4 minutes aging at 140°C. The decreases in UTS and ϵ_B appeared to be linear as a function of <u>logarithmic</u> aging time (see Figures 3 and 4)

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Likewise, toughness decreased with time to a reduction of 80.6% after 10^4 minutes of 140°C aging (Table 1). The scatter in the results for modulus (E) and yield strength (σ_y) was large, however. In general, E was found to remain essentially constant at ca. 11 GPa (11,000 MPa). While σ_y was found to decrease with aging time (see Table 1).

Dynamic Mechanical Analysis

Dynamic mechanical analysis of polymeric materials, including epoxies (25-43), is an established tool in measuring the mechanical dispersion peaks as well as other parameters such as the dynamic storage modulus of the macromolecules. Wetton has reported some effects by sub-Tg annealing on the modulus and damping peaks a low-Tg epoxies (44). In this investigation on high-performance/high-Tg epoxy-matrix composites, we have observed decrease of damping and increase in dynamic storage modulus of the composite as a function of physical aging time (5). Figure 6 shows a specific example of a 140°C/10^2 min.-aged carbon/epoxy composite having a glass transition maximum peak temperature near 242°C. The onset of the Tg is near 175°C. It is rather easy to characterize the α mechanical dispersion peak (tanδ or loss tangent) for this system. This composite, which is ± 45° carbon-fiber-reinforced, shows a dynamic storage modulus of the epoxy matrix in the glassy-state of ca. 15 GPa. At the onset of the glass-to-rubber transition (see Figure 6), the modulus drops gradually from 15 GPa (175°C) to about 3 GPa (300°C), as the rubbery plateau is reached.

With physical aging at 140°C in nitrogen/dark atmosphere, however, the dynamic storage modulus is demonstrated to be very sensitive to aging time. We observed the modulus increased

from 13 GPa (10 min.-aged) 18 GPa for samples aged up to 10^5 min. at 140°C (see Figure 7). These results agrees with the observations made in the stress relaxation experiments reported earlier (5) in which the epoxy tensile modulus increased with sub-Tg annealing.

The mechanical dispersion peaks in low-Tg epoxies, e.g., Epon 828 resin, were subject to numerous studies (26,28-31,35-38, 42). The α peak can undoubtedly be attributed to the large-scale cooperature segmental motion of the macromolecules. The β relaxation near -55°C, however, is subjected to much controversies (29,36). One postulated origin of the dispersion peak is the "crankshaft mechanism" (29,42,45) at the junction point of the network epoxies (Figure 8). The "crankshaft motion" for linear macromolecules was first proposed (46-49) as the molecular origin for secondary relaxations, which involved restricted motion of the main chain requiring at least 5 and as many as 7 bonds (50). This kind of crankshaft rotation needs an energy of activation in the order of 11 to 15 Kcal/mol and most likely requires creation of free volume in order that the crankshaft may rotate (50). While it is difficult to prove or disprove the crankshaft mechanism in the epoxy β relaxation (38), it is the purpose of this paper to show the effects of physical aging on the magnitude of secondary loss peaks in TGDDM-DDS net work resins.

Figure 9 shows the effects of thermal histories on the mechanical dispersion peaks in Fiberite 934 epoxy composites. The as-fabricated materials show by far the largest damping (T_β spans from -100°C to ca. 20°C for this epoxy system). Postcuring completes the crosslinking and results in a

significantly lower-damping composite. (see Figure 9). In other words, a fully-crosslinked epoxy matrix after postcuring would most likely have a smaller amount of free volume, hence a lower damping system compared to as-fabricated material.

With a quench from above Tg, which conceivably would have created a larger amount of trapped free volume compared to the as-postcured matrix, the loss tangent data near -55°C indeed showed a higher-damping as-quenched material.

Physical aging affects significantly the mechanical damping in both the α and β relaxation peaks. Figure 10 shows the decrease in the area under the β loss peak as a function of aging time at 140°C in nitrogen. This gradual decrease in damping can be explained by the relaxation model in which the epoxy network loses mobility and free volume during its asymtotic approach towards the equilibrium glassy state, and, as a result, the ability to dissipate energy is reduced. This is a significant observation in view of the fact that the area under this secondary mechanical dispersion peak is often correlated with the impact resistance of the polymer (51). Upon requenching from above Tg and re-aging such material, the thermoreversible nature of physical aging can be demonstratively shown. The effect of 140°C aging on the β-transition in the epoxy matrix of requenched specimens is shown in Figure 11.

The α mechanical dispersion peak corresponding to the glass transition (175 to 270°C) is also affected by sub-Tg annealing. Damping decreases from 10.3940 (arbitrary units) for 10 min.-aged samples to about 9.4735 for 10^5 min.-

aged specimens. On requenching and reaging, the area under the α dispersion peak again decreases from 10.2110 (10 min. reaging) to about 9.5673 for 10^5 min.-reaged samples. In the β region, damping decreases from 6.0170 to 5.8670 in the first aging experiment from 10 min. to 10^5 min. at 140°C. Reaging results in again a T_β damping decrease from 5.8851 to about 5.4970 (arbitrary units of mechanical damping measured from area under the peak).

With sub-Tg annealing at 140°C the maximum peak temperature of Tg tended to shift to higher temperatures. For example, the value was 242.0°C for 10 min.-aged samples. In the two aging/reaging experiments, Tg shifted to 253.0°C for both 10^5 min.-aged and reaged samples. T_β, however, appeared to be less sensitive to physical aging time and the β maximum peak temperature stayed at the -55°C region rather constantly.

Differential Scanning Calorimetry

DSC was utilized to study both the state of the cure (extent of crosslinking) as well as the kinetics of enthalpy relaxation in network epoxies (5, 12, 52, 53). DSC results confirmed a fully-crosslinked epoxy network having no exotherm at temperatures up to 280°C.

In an earlier communication (5), we reported enthalpy relaxation studies at 140°C aging. In this paper, both 110°C and 80°C sub-Tg annealing data are disclosed for neat-epoxy aging. Figure 12 shows the DSC scans of fully-cured epoxy samples that were quenched from above Tg and then subjected to aging at 110°C. The full line is the first scan, and the dotted line represents the second scan taken right after

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cooling from the initial one. The following observations were made:

1. The enthalpy relaxation peak appears near the onset of the transition from the glassy state to the rubbery state. This peak appears after only 10 min. of aging at 110°C.
2. During sub-Tg annealing, the relaxation peak shifts to higher temperature and grows in magnitude.
3. This recovery phenomenon is thermoreversible. Upon re-aging material that is cooled from above Tg, the relaxation peak will reappear and grow with annealing time (see Figure 13).

Compared to the 140°C enthalpy relaxation data reported earlier (5), the 110°C aging kinetics are definitely slower. A series of 80°C sub-Tg annealing experiments were also performed using similar postcured-and-quenched specimens. "Aging peaks" were again observed for 80°C annealing even though this time the magnitude of the relaxation peak was much smaller compared to 110°C aging data. In 80°C aging, the peak temperature shifted from the 100°C (10 min.) to 125°C (10^5 min.). In the case of 110°C aging, that peak temperature shifted from 130°C to 180°C (10 min. to 10^5 min. aging). In an earlier report, we noticed a shift from 160°C (10 min.-aged) to 210°C (10^5 min.-aged) for 140°C sub-Tg annealing (5).

As mentioned earlier, the relaxation enthalpy was measured by superimposing the first and second DSC scans for each specimen. Figure 14 shows the relaxation-enthalpy loss versus logarithmic sub-Tg annealing time at 140°, 110°, and 80°C. One can follow clearly a linear relationship between this enthalpy relaxation process and the logarithmic aging time. It is interesting to

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observe that a linear relationship was also reported earlier in this paper between the decrease in ultimate tensile properties and the logarithmic aging time.

In Figure 14, it is clearly demonstrated that aging kinetics slow down as one increase the temperature increment, ($Tg - T_a$), i.e., the recovery process is a thermally-stimulated phenomenon which requires segmental mobility of the polymer in its glassy state. So the lower the sub-Tg annealing temperature, T_a, the slower is the aging kinetics.

An attmept is made to calculate the activation energy for the enthalpy relaxation process, based on the information displayed in Figure 14. Since there exists a linear relationship between ΔH (decrease in enthalpy) and aging time, we can analyze the activation energy assuming the Arrhenius equation holds. Figure 15 shows the Arrhenius plot. From the slope, we can estimate the activation energy to be 5.9 Kcal/mol.

This activation energy of 5.9 Kcal/mol. is very close to the typical hydrogen bond dissociation energy for a majority of hydrogen-bonded systems (54-56). It is suggested that during the resin contraction (densification) process in volume relaxations, hydrogen bonds may be broken and re-formed in this network polymer.

The activation energy for epoxy polymer relaxation of 5.9 Kcal/mol. estimated from the Arrhenius analysis is a low value compared to enthalpy relaxation in inorganic glasses such as the B_2O_3 system as reported by Moynihan et al. (57) having ΔH activation energy values of the order of 90 Kcal/mol. This simply suggests that relations in epoxy polymer-network-

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glasses (PNG) may have different mechanism compared to structural relaxation in inorganic glasses. The low value estimated may also suggest that the relaxation mechanism at 140°C versus those at 110°C and 80°C in this epoxy system may be different from each other.

Density

The density of the epoxy PNG was followed closely as a function of its thermal history. We found postcuring by far caused the most drastic decrease in density (4.65% decrease) from 1.290 gm/cm^3. for as-cast epoxy to 1.230 gm/cm^3 for as-postcured/slowly-cooled epoxy. This decrease in room-temperature-density can be explained partially by escape of unreacted DDS crosslinker in the epoxy system during postcuring. On the other hand, Aherne et al., (58) who also observed density drop with Epon 828 epoxy postcuring, argued from a free-volume explanation for the observation. A Priori, one would assume from the crosslink-density point of view that a postcured system (presumably with a higher crosslink density) would have a higher density. That may actually be the case at the postcure temperature. At 23°C, however, Gillham et al. believed that the higher-crosslinked system may be quenched further from the hypothetical equilibrium glassy state and thus resulted in a higher value of free volume, i.e., lower epoxy density (59).

With an air-quench, the fully-crosslinked epoxy now possesses a higher free volume compared to the as-postcured material. Hence density again drops from 1.230 to 1.215 gm/cm^3. (1.22% drop).

With sub-Tg annealing, an increase of 0.82% in the resin

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density was observed during the 140°C aging. This fits the "free volume collapse" model in which the resin densifies. We observed an aged epoxy PNG (10^5 min./140°C) having a density of 1.225 gm/cm^3 compared to 1.215 gm/cm^3 for freshly quenched material. Figure 16 summarizes our observations.

Hardness

The hardness of a material is related to its resistance to scratching or denting. The hardness value is actually inversely proportional to the "depth of penetration". We observed that hardness value for epoxy PNG is very dependent on its thermal history and is also a time-dependent parameter during physical aging. M-scale of the Rockwell hardness index is reported. As-cast epoxy has a low hardness value of M70$\pm$3. With postcuring the value increased to M97$\pm$3. This represents a 39% increase of hardness with postcuring, which agrees with the observations in tensile testing in which we reported resin embrittlement with postcuring (see Figure 2).

With an air-quench, the epoxy hardness dropped slightly for about 4% to M93$\pm$3. This is reasonable since the excess trapped free volume in the as-quenched PNG may well soften the system.

With aging at 140°C, the epoxy hardened from M93$\pm$3 to M110$\pm$3 for 10^4 min. aged material (an 18% increase). This hardening process actually is accompanying the embrittlement phenomenon that the polymer is experiencing.

With a requenching of 10 min.-aged epoxy, we observed a drop of 7% in the hardness, probably due to a restoration of free volume in the resin, as manifested in a softened hardness index of M92.5$\pm$2.5. Hence, once again, we have demonstrated

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the thermoreversibility of the physical aging process. Figure 17 summarizes our observations.

We understand that this hardness value only reflects the surface properties of the epoxy PNG. In this experiment,-the "skin" properties show significant time-dependent changes. It is therefore reasonable to expect the "core" or bulk properties to experience similar time-dependent variations in microhardness.

Thermal Mechanical Analysis

Thermal Mechanical Analysis (TMA) was utilized by Ophir (60) to study the densification of Epon 828 epoxy. In this investigation, it is again proven to be a useful tool to study the physical aging in Fiberite 934 epoxies. The glass transition temperature can be easily characterized by a slope change as the resin trasits from the glassy state to the rubbery state (see Figure 18). Hence, in glassy material, it is typically represented by two thermal expansity parameters, one below Tg (glassy thermal expansivity) and one above Tg (rubbery thermal expansivity).

Figure 18 shows the thermal expansion behavior of a fully-crosslinked epoxy as a function of aging time at 140°C sub-Tg annealing. By superimposing the first scan (for aged material) and the second scan (for as-quenched material) at the high-temperature rubbery region, it is possible to monitor the development of aging in the resin, i.e., the progress of the densification process.

As shown in Figure 18, the aged glass typically has a lesser volume in the glassy state as compared to the as-quenched state. It is obvious from the data that the longer the aging time, the larger is the amount of volume lost due to sub-Tg annealing

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at 140°C. This observation also fits well into our "free-volume-collapse" model as discussed earlier.

Figure 19 shows the thermal expansion behavior of requenched epoxies. Upon reaging, the densification process was again measurable. Data shown in Figure 19 therefore supports the thermoreversible nature in physical aging.

By analyzing the linear portion of the thermal expansion curves below and above Tg, it is possible to calculate the expansivity of each specimen taking into account its individual thickness. Through such analysis, significant variations were observed in the thermal expansivity of epoxy PNG both below and above its Tg.

Figure 20 shows the expansivity variations as a function of thermal history. As-cast epoxy has a value of $5.43 \times 10^{-5}\ {}^{\circ}C^{-1}$ (below Tg). Expansivity below Tg decreased with postcuring to $5.20 \times 10^{-5}\ {}^{\circ}C^{-1}$, which is reasonable because postcuring resulted in a network which has higher crosslink-density hence lesser moblility. Quenching, which introduced a thermal shock and also residual thermal stresses, caused the epoxy to be less expansible below Tg ($4.98 \times 10^{-5}\ {}^{\circ}C^{-1}$), inspite of the increased free volume through quenching. In this experiment, similar to the results suggested by the stress-strain analysis, residual thermal stresses seem to override the importance of free volume considerations in affecting the glassy expansivity of the as-quenched resin.

With 10 minutes of sub-Tg anneal at 140°C, the thermal expansity below Tg decreased to $4.78 \times 10^{-5}\ {}^{\circ}C^{-1}$. Throughout

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the 140°C aging experiment, this parameter kept decreasing. After 10^5 minutes of aging, the value decreased to 4.30×10^{-5} °C^{-1}. During physical aging, the glassy state expansivity decreased 13.7%. This time, the free volume decrease dictates the thermal expansivity in the glassy state during sub-Tg annealing.

To erase resin history, aged samples were quenched from above Tg. With the requenching, glassy-state expansivity was restored to a high value of 5.22×10^{-5} °C^{-1}, comparable to as-postcured value. Requenching obviously have introduced a significantly larger amount of free volume in the resin and thus made the resin more expansible (see Figure 20).

Reaging the resin at 140°C again caused a decrease in glassy-state expansivity. This time, reaging caused a decrease of 25.7% in that parameter. This is a significantly larger decrease compared to the first round of aging. However, evaluating the % decrease for 10^4 minute data in to two series of aging indicated that the aging kinetics was probably similar. Specifically, in both series, a decrease of ca. 13.0% was registered in both cases. (see Figure 20).

Figure 21 shows the thermal expansity of the epoxy above its Tg as a function of thermal history. Rubbery-state expansivity is generally an order of magnitude larger compared to the glassy-state expansivity. (see Table 2) As-cast epoxy has an expansivity above Tg of 3.22×10^{-4} °C^{-1}. With postcuring and quenching, this parameter tend to increase due to interplay of free volume variations and factors involing residual thermal stresses (see Figure 21).

With postcuring and slow cooling, the resin actually

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physically ages, i.e., contracts, when it goes through the temperature range from 175°C to 23°C and resulted in lost free volume. At temperatures above Tg where enough thermal energy is available, the resin can catch up its lost volume in an attempt to reach thermodynamic equilibrium. Hence the apparent rubbery-state expansivity is larger for postcured resin (3.77×10^{-4} $^{o}C^{-1}$) compared to that of as-cast resin.

As is clearly indicated by the data in Figure 21, expansity above Tg for epoxies tend to increase with aging at 140°C. This increase in expansivity in the rubbery-state undoubtely can be traced to a "catching-up-process" for lost volume during physical aging. At temperatures above Tg, there are enough thermal energy around for the system to utilize in order to reach equilibrium. Since volume was lost during physical aging, the high temperatures provide the thermal energy to recover for the "lost volume". The longer the glass subjected to aging, the higher would be its tendency to recover the lost volume, hence manifested in a larger value of thermal expansivity above Tg. We observed an increase from 3.14×10^{-4} $^{o}C^{-1}$ to 5.11×10^{-4} $^{o}C^{-1}$ (62.7% increase).

With requenching and reaging, expansivity above Tg again increased with reaging time (96.6% increase), demostrating once again the thermoreversiblity of physical aging. Table 2 summarizes all the results observed in the TMA investigations.

Moisture Sorption Kinetics

140°C aged epoxy glasses were subjected to 40°C moisture penetration. Figure 22 shows the results of this transport

experiment. We observed both a decrease of initial sorption kinetics as well as a decrease of equilibrium sorption level as a function of aging time. This supports the idea that during sub-Tg annealing, the resin contracts and densifies, resulted in lesser amount of free volume.

In another series of diffusion experiments, as-postcured, epoxies were first immersed in 23°C heavy water for 2 months. Then the temperature of the epoxy/heavy water interacting system was increased to 40°C. The continuous influx of heavy water into the epoxy can be easily monitored by deuterium NMR spectroscopy. The free-induction-decay signal as normalized by the specimen weight showed an increase as a function of sorption time (see Figure 23). For example, a 2 months room-temperature-sorption results in an epoxy having 2.10% of moisture (determined by gravimetry). With 667 h of additional sorption at 40°C, 3.14% of moisture resided in the epoxy. Correspondingly, the sorption kinetics for NMR FID signal showed an increase from 275 (arbitrary units) for 2 months/23°C diffusion to ca. 990 with additional 667 h of diffusion at 40°C (Figure 23). In general, the epoxy-water gravimetry experiment and the epoxy-heavy water deuterium NMR agrees well with each other.

In addition to detecting the heavy water content, we also utilized the deuterium NMR technique to study epoxy/moisture interactions. Figure 24 showed the 4.65 ppm nuclear magnetic resonance of freely-tumbling heavy water. Figure 25 shows the NMR spectrum of deuterium as it resides inside

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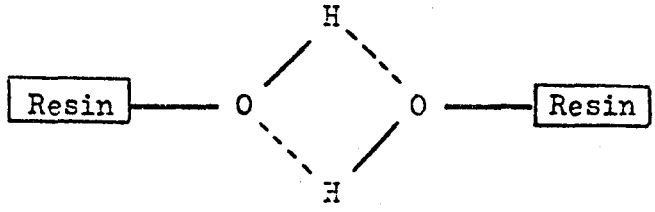
an as-quenched epoxy after the diffusion was carried for 2 months at 23°C and then 1 month at 40°C.

In Figure 25, we can clearly see the sharp component (with little broading) that is due to isotropically tumbling heavy water. The wide broadening of the deuterium resonance could be due to deuterium oxide trapped by the hydrogen bonds of epoxy resin. It is well known that the deuterium of heavy water can exchange with the protons in the epoxy (61) so the broadening may only reflect deuterons that have exchanged and now resided in the epoxy network. Experiments using deuterated resin can clarify this point.

In the TGDDM-DDS epoxies, hydrogen bonds may be formed among the polar groups. Figure 26 summarized such possible hydrogen bonding possibles. To propose one example, hydroxyl groups may hydrogen bond in the following fashion:



Similar to water, it is also known that heavy water is highly associated by hydrogen bonding. It is very likely that the heavy water hydrogen bonding system disrupts the epoxy hydrogen-bonding system (Figure 27), thereby causing swelling in the moisture-saturated-resin network (6,20,62) The epoxy-heavy water interacting model is proposed in Figure 28 in which some freely tumbling moisture molecules would reside in voids (free volume) hence giving rise to the sharp NMR

component, whereas some moisture would be trapped by the epoxy hydrogen bonds, resulting in the NMR broad component. From the NMR broadening, it can be estimated that the correlation time for heavy water among the epoxy hydrogen bonds is in the order of 10^{-7} sec.

Earlier we reported that physical aging affects the "swelling efficiency" and diffusivity of epoxy as moisture is transported into the network (6). In conjunction with this earlier communication (6), we can now summarize the findings for interactions between moisture and aging epoxies:

1. As epoxies densify, the amount of moisture uptake decreases.
2. As epoxy densify, the "swelling efficiency" (6,10) of aged epoxy is increased.
3. Diffusivity (6) decreases with physical aging.
4. Moisture can either resides in the free volume or disrupts the epoxy hydrogen bonds.

Proton-Decoupled CP/MAS NMR

For the first time, proton-decoupling, cross-polarization, and magic angle spinning NMR techniques are applied to study the Fiberite 934 TGDDM-DDS system. Figure 29 shows a carbon-13 spectrum of as-cast epoxy. In the spectrum, the aromatic carbons (residing in downfield between 100 to 150 ppm) can clearly be resolved from the aliphatics (20 to 80 ppm). By integration, the population of aliphatic and aromatic carbons was shown to be roughly the same (Figure 29).

In order to study physical aging in the molecular level, CP/MAS NMR was a used to study the epoxy densification process.

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Figure 30 shows the spectral difference between as-cast, 10 min.-aged, and 10^5 min.-aged epoxies. Postcuring and aging clearly has resulted in much spectral changes (see Figure 30). Of greatest interest was the observation that the sharp and highest aromatic resonance at 127 ppm (as-cast epoxy) tended to shift downfield with aging, With aging to 10^5 min., this resonance peak shifted to ca. 131 ppm. We can interprete this downfield shift of this aromatic resonance to molecular aggregation of the phenyl rings in the resin causing "ring-current effects" (63) during volume relaxation in the epoxy resins.

Solution Carbon-13 NMR

125 MHz carbon-13 spectra of the TGDDM and DDS in deuterated chloroform solutions are shown in Figures 31 and 32 respectively. The spectra shows sharp components of resonance peaks for the aromatics between 110 to 150 ppm and for the aliphatics between 40 to 80 ppm. The large peak at 77 ppm is due to $CDCl_3$ or deuterated cholroform carbon-13 resonance. The solution work was done in order to help peak assignments for the CP/MAS NMR studies.

Conclusions

For the first time, it is now possible to characterize the molecular aggregation during physical aging in network epoxies by spectroscopic technique. Other important findings are summarized: with progress of PNG physical aging,

- Damping decreases
- Ultimate mechanical properties decreases

- Stress relaxation rates (also creep rates) decreases
- Moisture sorption decreases
- Moisture diffusivity decreases
- Density increases
- Modulus increases
- Hardness increases
- Moisture-epoxy interaction increases (i.e., swelling increases)
- Thermal expensivity varies: glassy-state expansivity decreases; rubbery-state expansity increases

Abstract

Matrix-dominated physical and mechanical properties of a carbon-fiber-reinforced epoxy composite and a neat epoxy resin have been found to be affected by sub-Tg annealing in nitrogen and dark atmosphere. Postcured specimens of Thornel 300 carbon-fiber/Fiberite 934 epoxy as well as Fiberite 934 epoxy resin were quenched from above Tg and given annealing at 140°C, 110°C, or 80°C, for time up to 10^5 minute. No weight loss was observed during annealing at these temperatures. Significant variations were found in density, modulus, hardness, damping, moisture absorption ability, thermal expansivity. Moisture-epoxy interactious were also studied. The kinetics of aging as well as the molecular aggregation during this densification process were monitored by differential scanning calorimetry, dynamic mechanical analysis, density gradient column, microhardness tester, Instron, and solid-state nuclear magnetic resonance spectroscopy.

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Acknowlegments

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Tables Caption

1. Mechanical properties of Fiberite 934 epoxy as a function of thermal history and sub-Tg annealing time.

2. Thermal expansivity of Fiberite 934 neat epoxies as a function of thermal history.

THERMAL HISTORY	AS-CAST	POSTCURING 16 hr 523K (250°C)	ANNEALING 533K (20 min) +QUENCHING 296K (23°C)	SUB-Tg ANNEALING			
				10 min 413K (140°C) N_2 atm	10^2 min 413K (140°C) N_2 atm	10^3 min 413K (140°C) N_2 atm.	10^4 min 413K (140°C) N_2 atm
UTS, MPa	102.20 ± 1.16	17.71 ± 1.14	13.76 ± 1.13	14.73 ± 1.11	13.30 ± 1.11	11.66 ± 1.19	9.50 ± 1.01
ϵ_B, %	2.6 ± 0.82	1.7 ± 0.90	1.5 ± 0.90	2.1 ± 0.58	1.6 ± 0.55	1.2 ± 0.55	1.0 ± 0.50
TOUGHNESS J/cm^3	2.69	0.30	0.21	0.31	0.10	0.07	0.06
E, MPa	13000	12381	11063	11817	8965	8666	10399
σ_Y, MPa	7.59	4.47	3.55	2.66	2.37	2.00	1.80

* TOUGHNESS (J/cm^3) = UTS x ϵ_B

Table 1

THERMAL HISTORY		α(BELOW Tg) $\times 10^5$ K^{-1} (ca. 60 – 160°C)	α(ABOVE Tg) $\times 10^5$ K^{-1} (ca. 200 – 240°C)
AS-CAST		5.43	32.2
AS-POSTCURED		5.20	37.7
AS-QUENCHED		4.98	52.9
140°C AGED	10	4.78	31.4
	10^2	4.63	32.4
	10^3	4.40	33.9
	10^4	4.32	40.1
	10^5 min	4.30	51.1
		DE-CREASE WITH AGING	IN-CREASE WITH AGING
AS-REQUENCHED		5.22	38.8
140°C REAGED	10	5.13	26.2
	10^2	5.00	33.3
	10^3	4.82	34.5
	10^4	4.56	36.6
	10^5 min	3.88	51.5
		DE-CREASE WITH AGING	IN-CREASE WITH AGING

Table 2

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Figure Captions

1. Chemical constituents of Fiberite 934 epoxy resin.

2. Stress-strain behavior of Fiberite 934 neat resins as a function of thermal history.

3. Ultimate tensile strength of fully-crosslinked Fiberite 934 epoxy as a function of log sub-Tg aging at 140°C.

4. Ductility of Fiberite 934 epoxy as a function of log sub-Tg aging at 140°C.

5. Ductility of Fiberite 934 epoxy as a function of thermal history.

6. Dynamic mechanical analysis of 10^2-min.-aged $(\pm 45^\circ)_{2S}$ Thornel 300/Fiberite 934 composite showing the loss tangent and the dynamic storage modulus.

7. The influence of physical aging time on the dynamic storage modulus of Thornel 300/Fiberite 934 composites.

8. Proposed "crankshaft motion" at the junction point of a crosslinked TGDDM-DDS epoxy.

9. Secondary mechanical dispersion peaks of Thornel 300/Fiberite 934 composites as influenced by their specimen thermal history.

10. The influence of physical aging time on the secondary loss peaks of Thornel 300/Fiberite 934 composites.

11. The influence of requenching followed by reaging on the secondary loss peaks of Thornel 300/Fiberite 934 composites.

12. The influence of 110°C physical aging on the endothermic enthalpy relaxation peak of neat Fiberite 934 epoxies.

13. The effect of 110°C reaging on the enthalpy relaxation peak of as-requenched Fiberite 934 epoxies.

14. Enthalpy loss at 80°C, 110°C, and 140°C aging as a function log sub-Tg annealing time.

15. Arrhenius analysis of the enthalpy loss data of Figure 14.

16. Density of neat Fiberite 934 epoxy as a function of thermal history.

17. Hardness of neat Fiberite 934 epoxy as a function of thermal history.

18. Thermal expansion behavior of neat Fiberite 934 epoxies as influenced by aging history at 140°C.

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19. Thermal expansion behavior of neat Fiberite 934 epoxies as influenced by requenching (erasure of thermal history) and subsequent reaging at 140°C.

20. Glassy-state thermal expansivity (60-160°C) of Fiberite 934 epoxies as a function of thermal history.

21. Rubbery-state thermal expansivity (200-240°C) of Fiberite 934 epoxies as a function of thermal history.

22. Moisture absorption behavior of fully-crosslinked Fiberite 934 epoxy as influenced by 140°C sub-Tg aging.

23. Heavy water absorption by Fiberite 934 epoxy as a function of immersion time at 40°C as monitored by deuterium NMR spectrocopy.

24. Deuterium NMR spectrum of isotropically-tumbling heavy water molecules.

25. Deuterium NMR spectrum of heavy water absorbed by an as-quenched Fiberite 934 epoxy.

26. Various hydrogen bonding possibilites by polar groups in Fiberite 934 epoxy (N.B.: Diglycidyl orthophthalate is given the acronym of DGOP).

27. Hydrogen-bonded network of Fiberite 934 epoxy (N.B.: π electrons may also participate in hydrogen bonding).

28. Proposed model for "heavy water-epoxy interactions" (N.B.: Heavy water may form aggregates in the voids or disrupt the epoxy hydrogen bonds).

29. Proton-decoupled CP/MAS carbon-13 NMR spectrum of an as-cast Fiberite 934 epoxy showing also the integration of the aromatic (downfield) and aliphatic (upfield) carbons.

30. The effect of physical aging on the spectral changes in proton-decoupled CP/MAS carbon-13 NMR measurements.

31a. 125 MHz carbon-13 solution NMR spectrum of TGDDM moiety dissolved in deuterated chloroform.

31b. Same spectrum as Figure 31a on TGDDM/$CDCl_3$ solution with higher resolution to show doublets near 45 and 50 ppm (doublets due to TGDDM gaving 2 conformational isomers arising from "umbrella-like" inversion at the pyramidal-bonded nitrogen atom).

32a. 125 MHz carbon-13 solution spectrum of DDS crosslinking agent dissolved in deuterated chloroform.

32b. Same spectrum as Figure 32a on DDS/$CDCl_3$ solution showing only peaks between 110 and 150 ppm.

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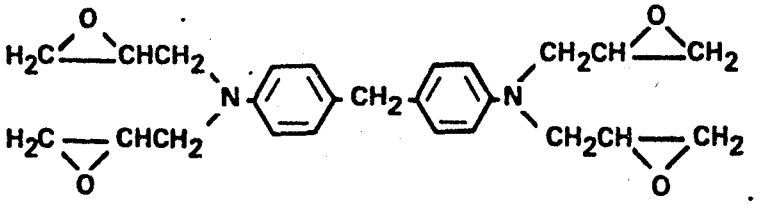
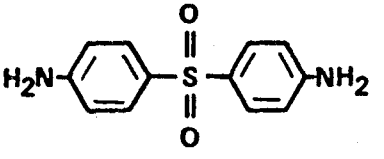
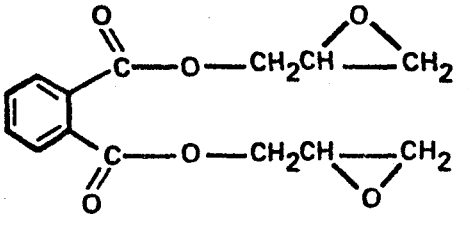
FIBERITE 934 EPOXY RESIN



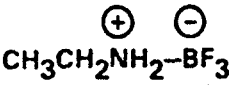
TETRAGLYCIDYL 4,4' DIAMINODIPHENYL METHANE (63.2%)



4,4' DIAMINODIPHENYL SULFONE (25.3%)



DIGLYCIDYL ORTHOPHTHALATE (11.2%)



BORON TRIFLUORIDE/ETHYLAMINE COMPLEX (0.4%)

Figure 1

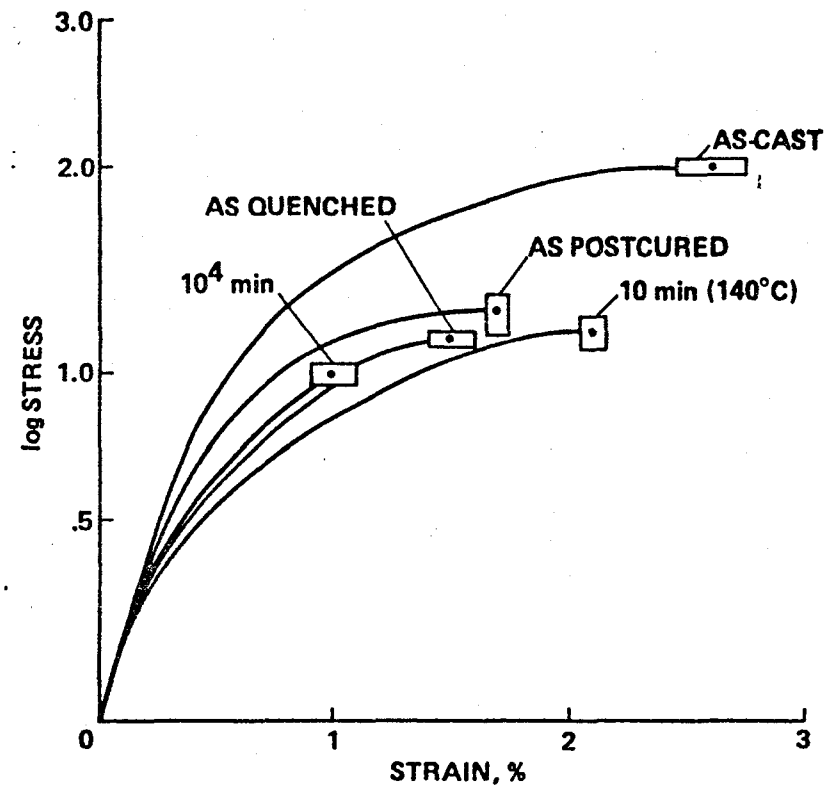


Figure 2

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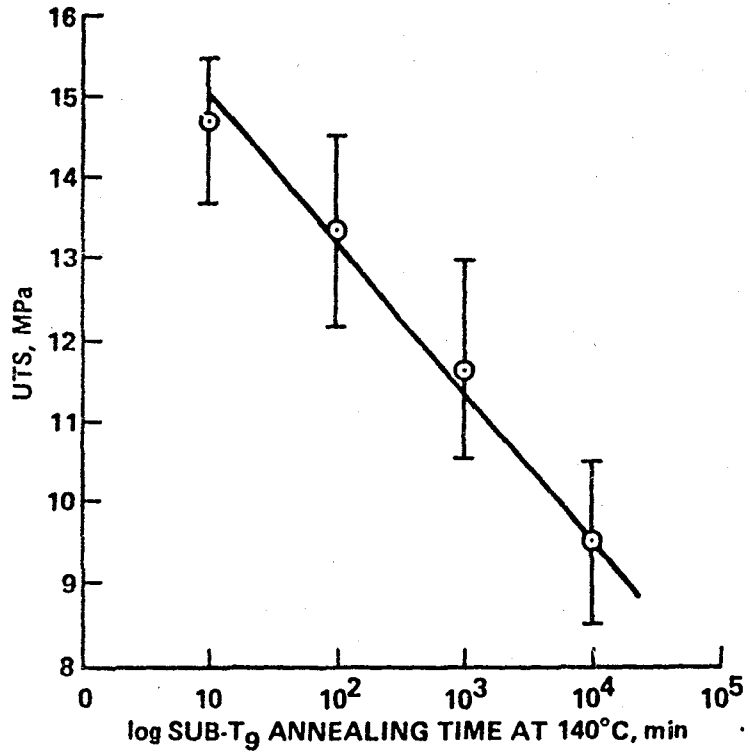
16
15
14
13
12
11
10
9
8
UTS, MPa
0
10
10^2
10^3
10^4
10^5
log SUB-T_g ANNEALING TIME AT 140°C, min

Figure 3

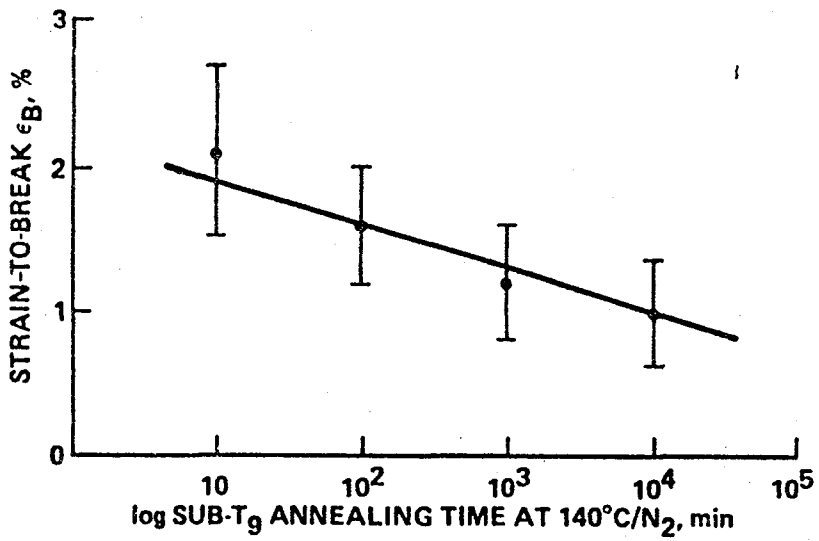

Figure 4

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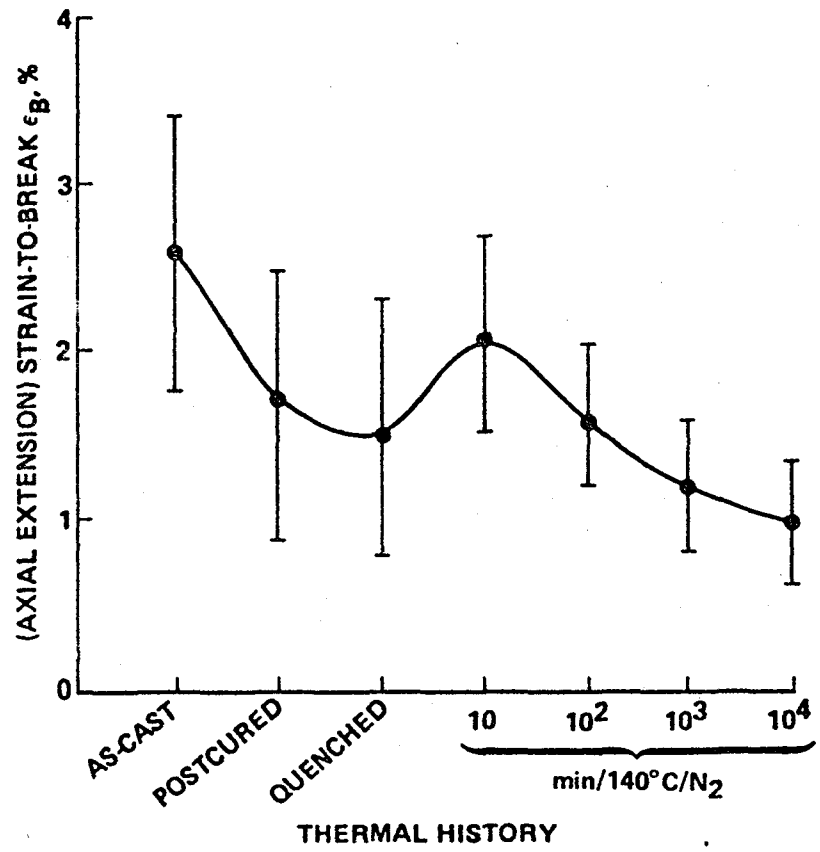

Figure 5

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DYNAMIC MECHANICAL ANALYSIS OF GRAPHITE/EPOXY COMPOSITES

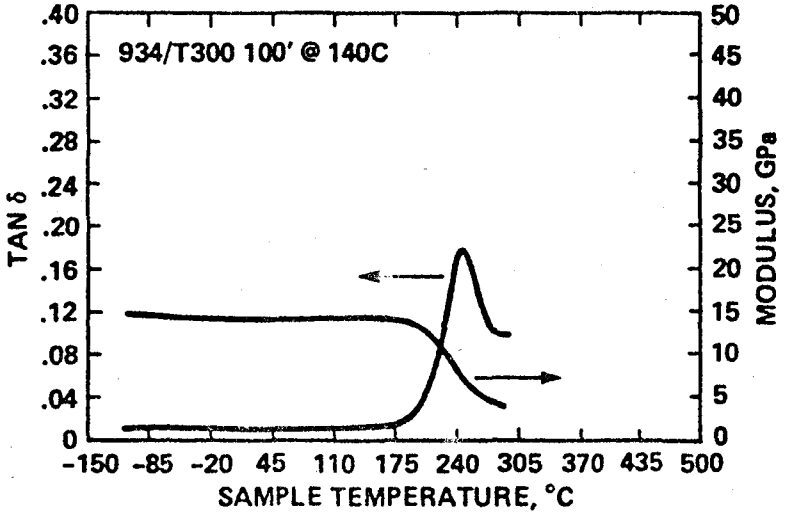

Figure 6

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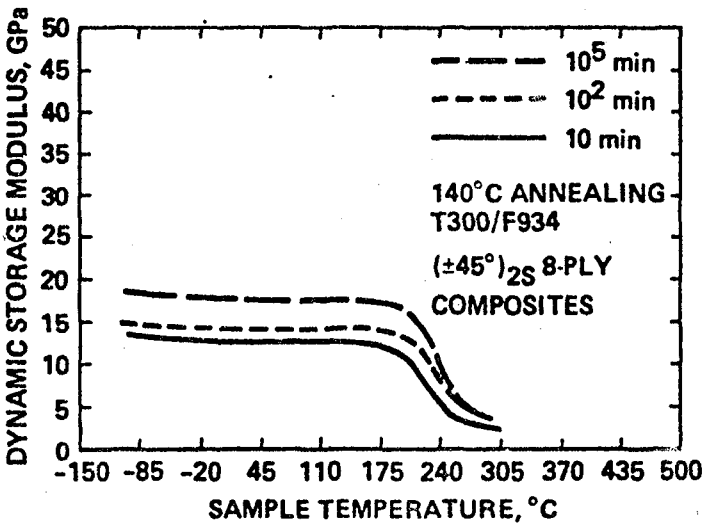

Figure 7

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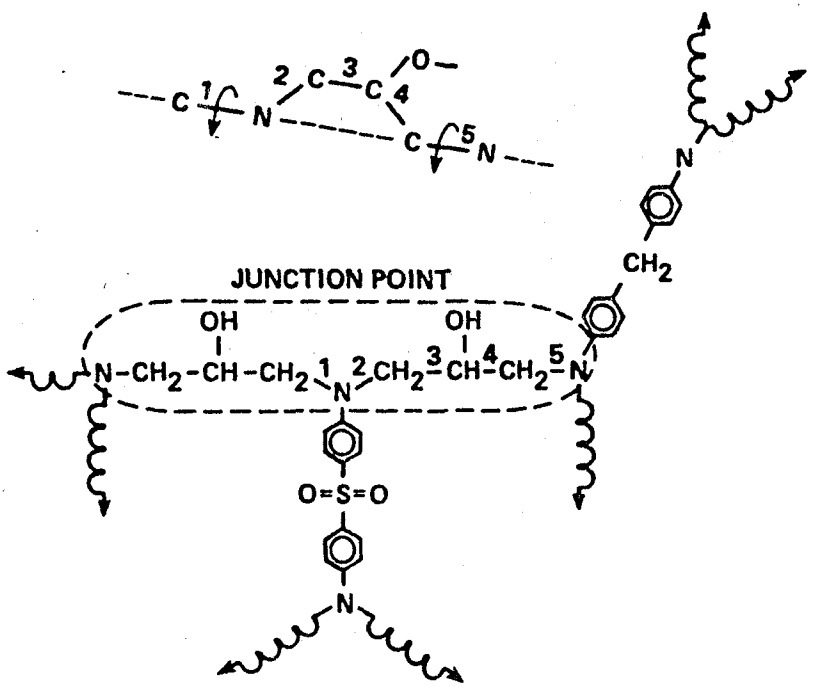

Figure 8

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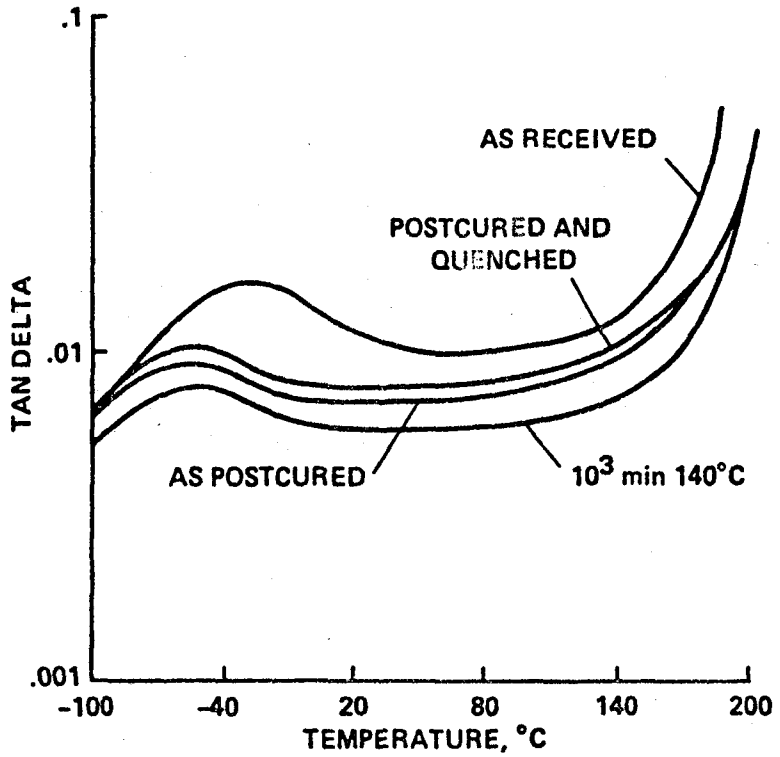

Figure 9

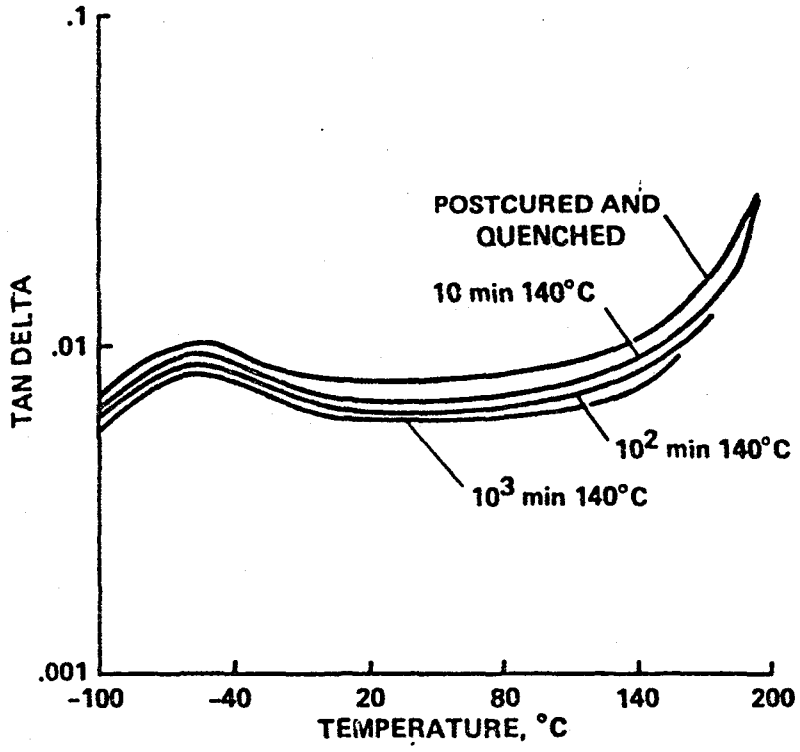

Figure 10

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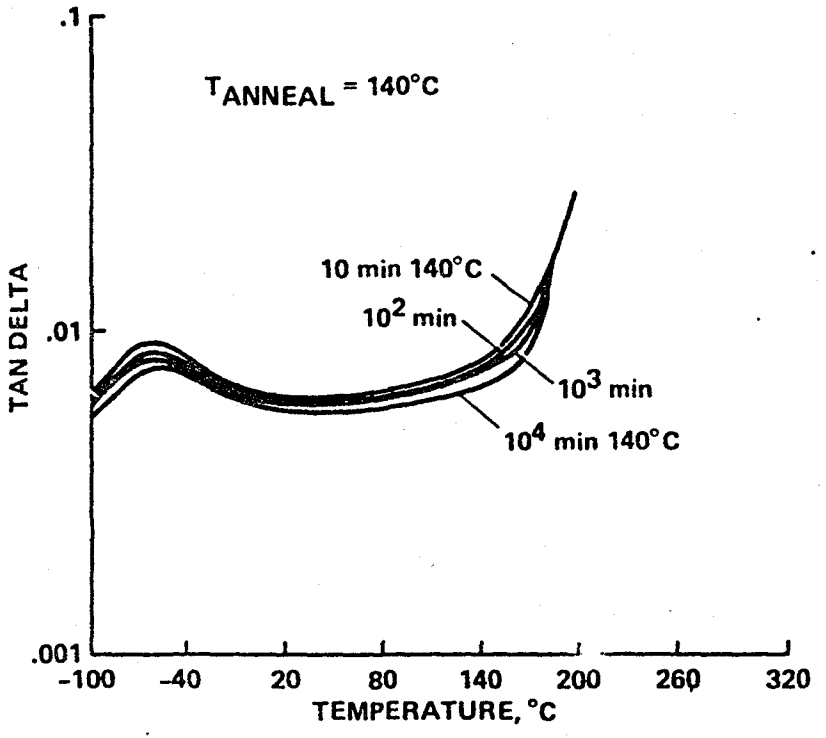

Figure 11

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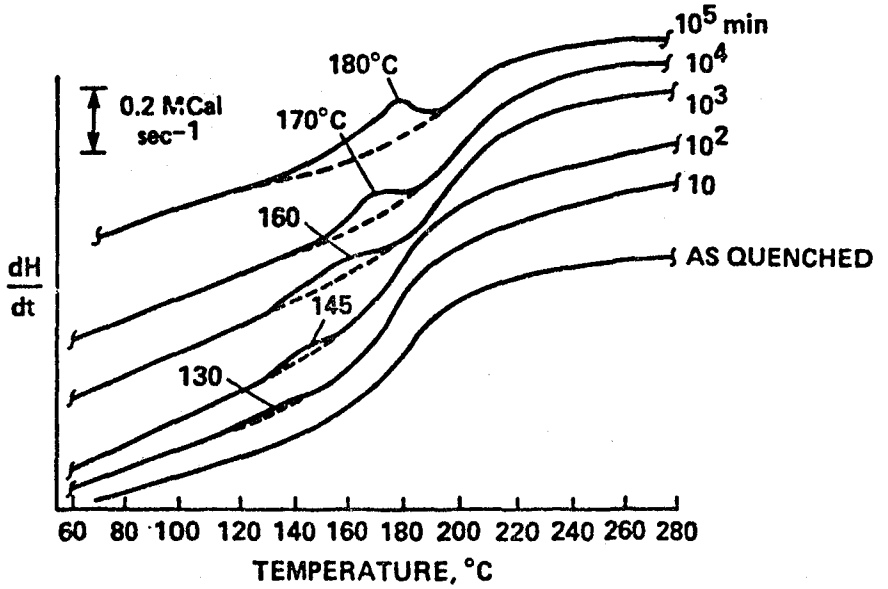

THERMAL HISTORY: QUENCHED AND AGED IN NITROGEN

HEATING RATE: 10°C/min

——— FIRST SCAN

- - - - RESCAN

Figure 12

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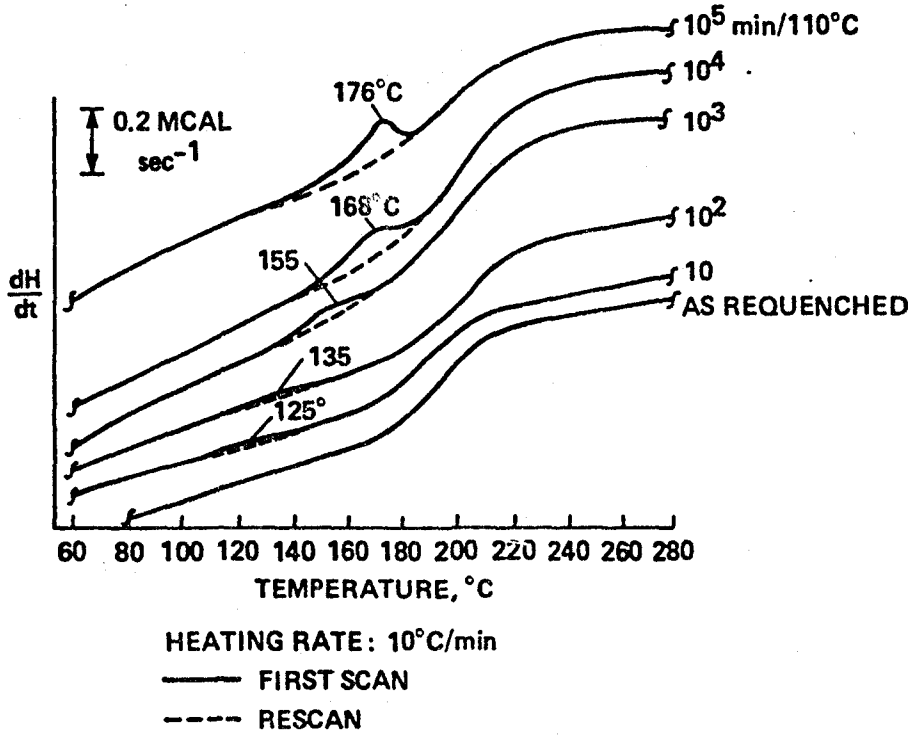

Figure 13

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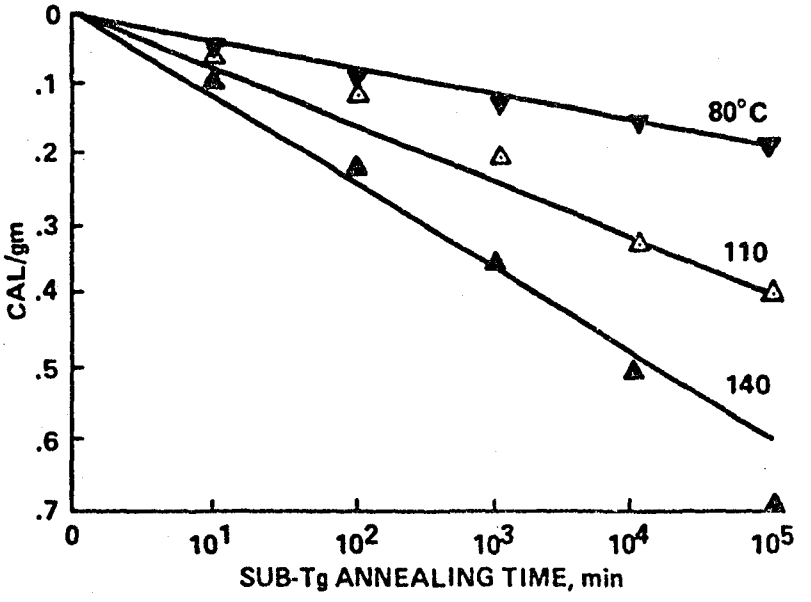

Figure 14

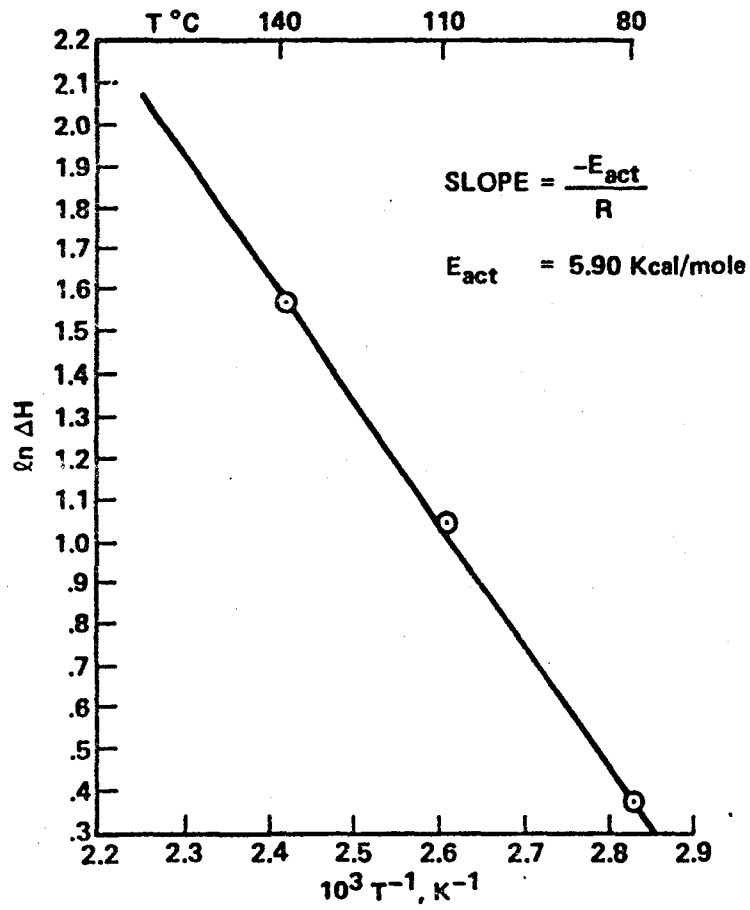

Figure 15

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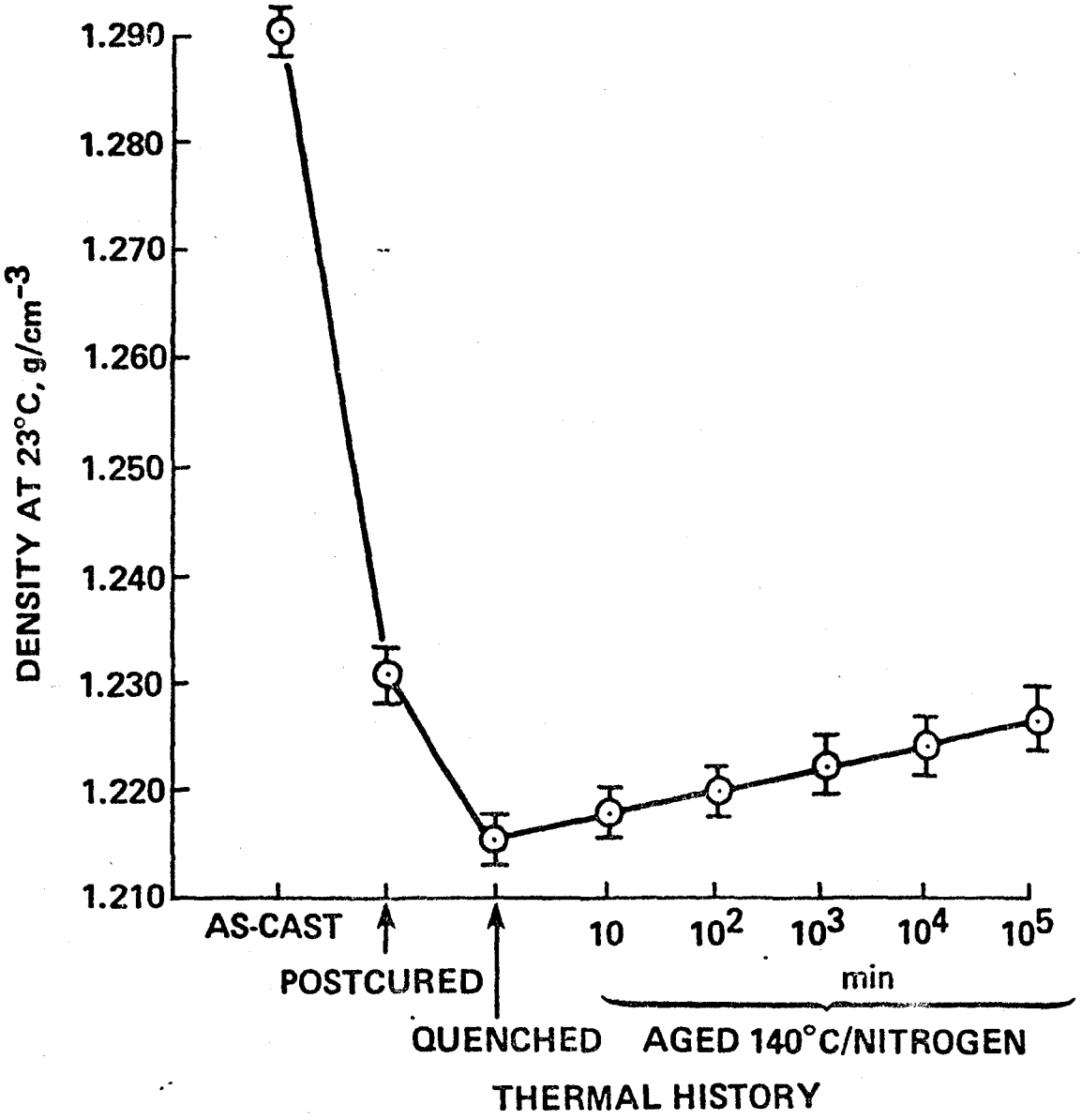
FIBERITE 934 EPOXY AS A FUNCTION OF THERMAL HISTORY



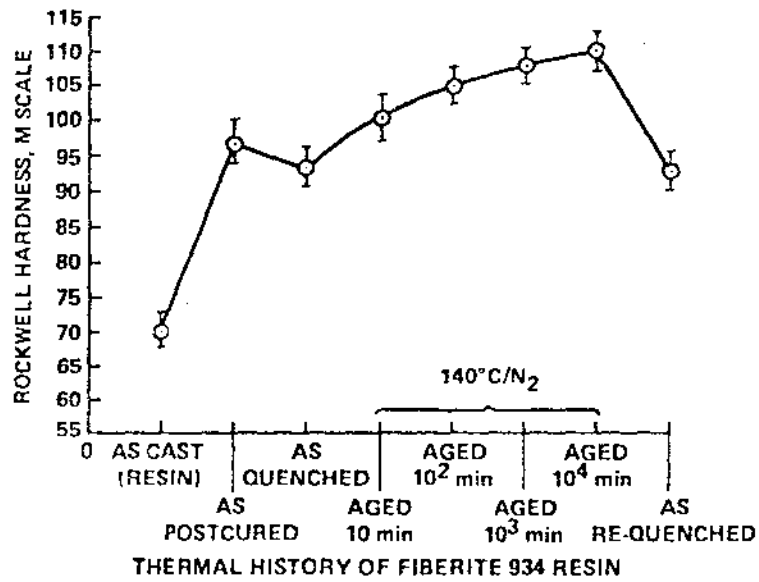


Figure 17

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Figure 18

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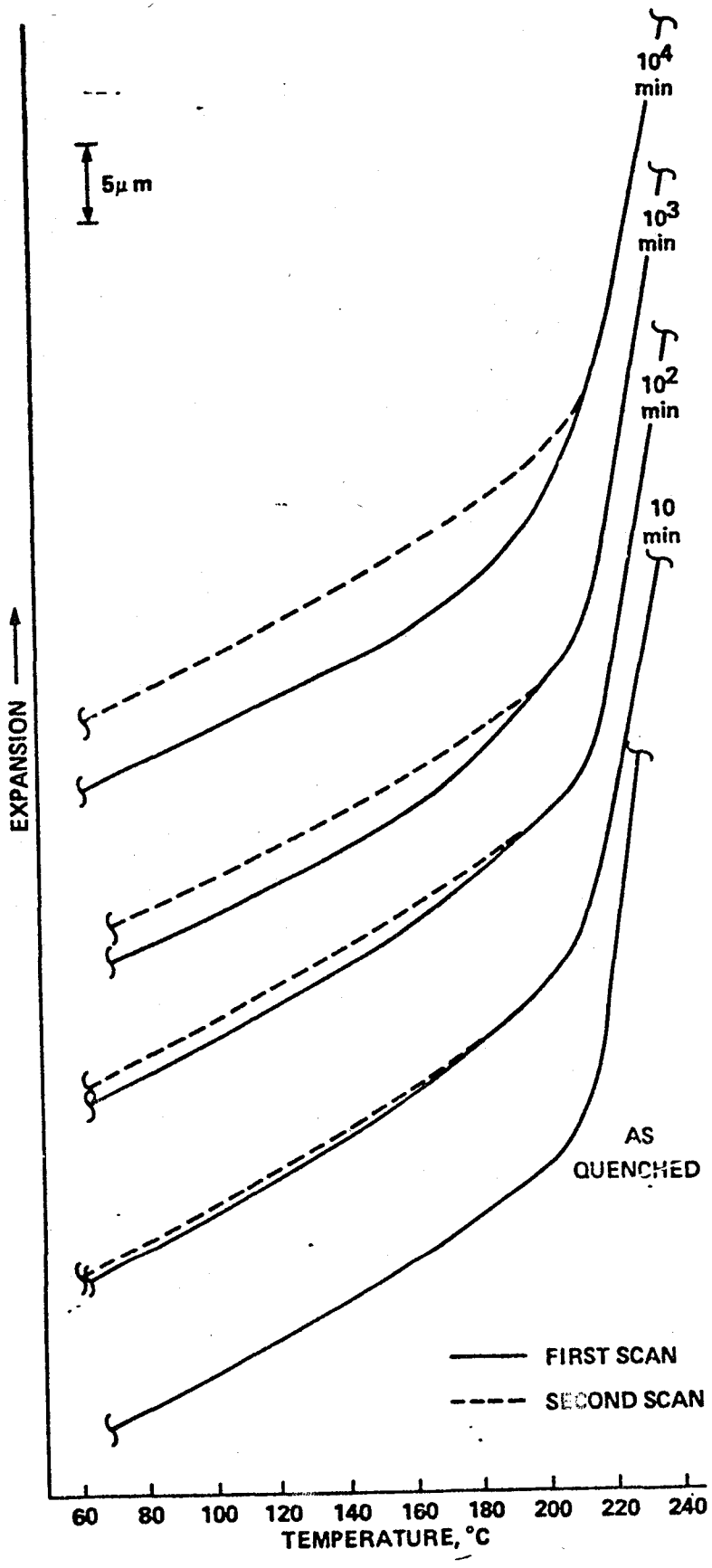

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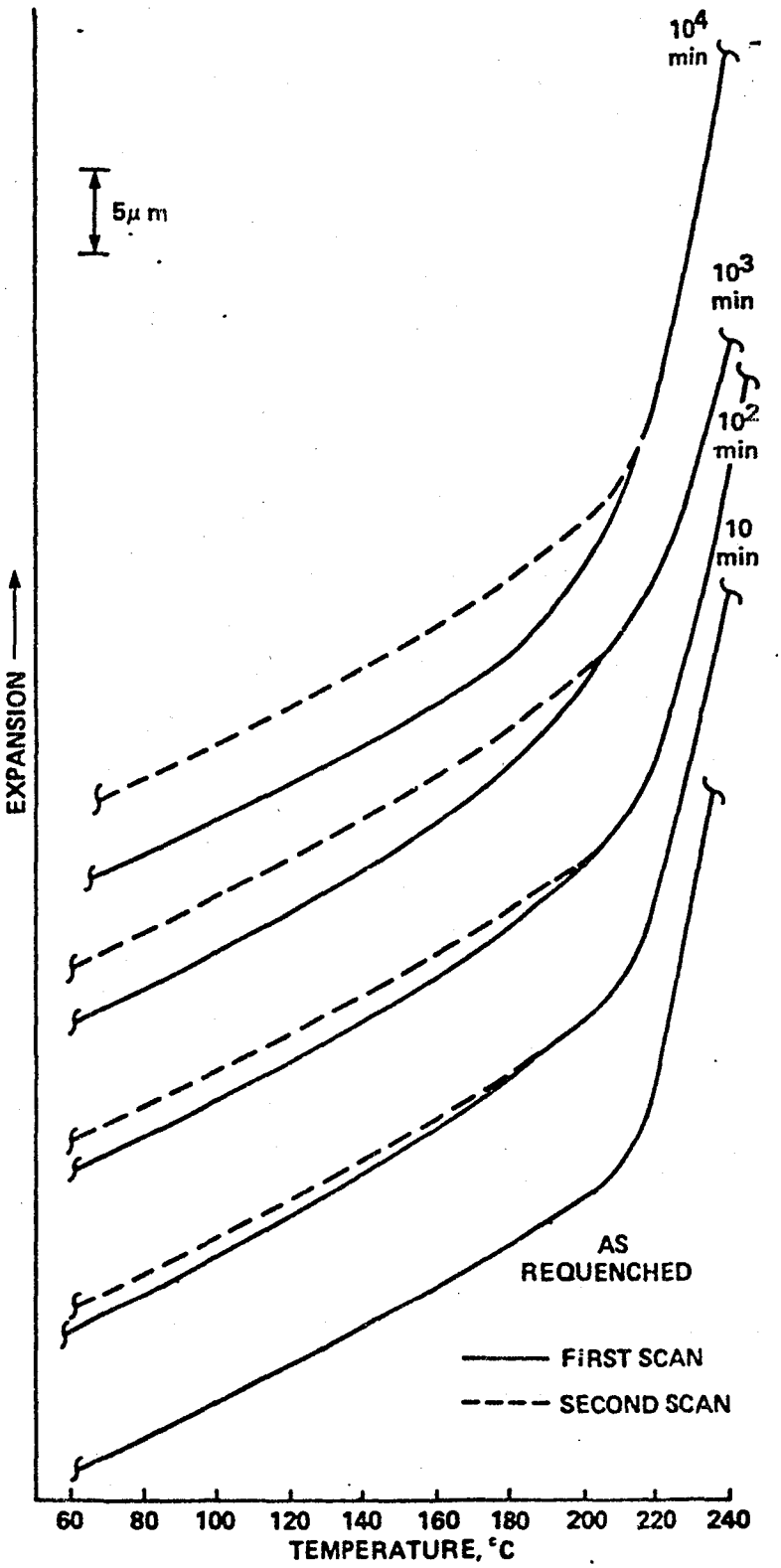

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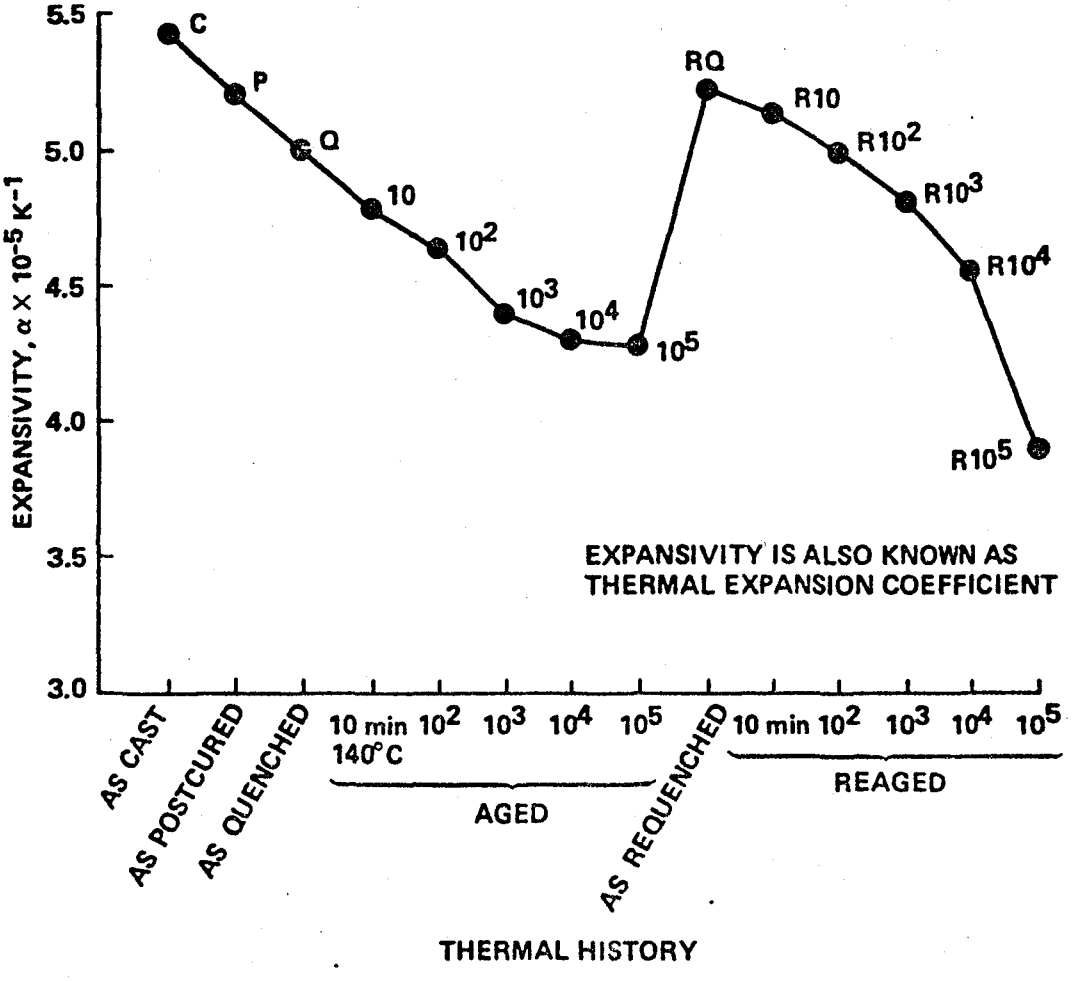

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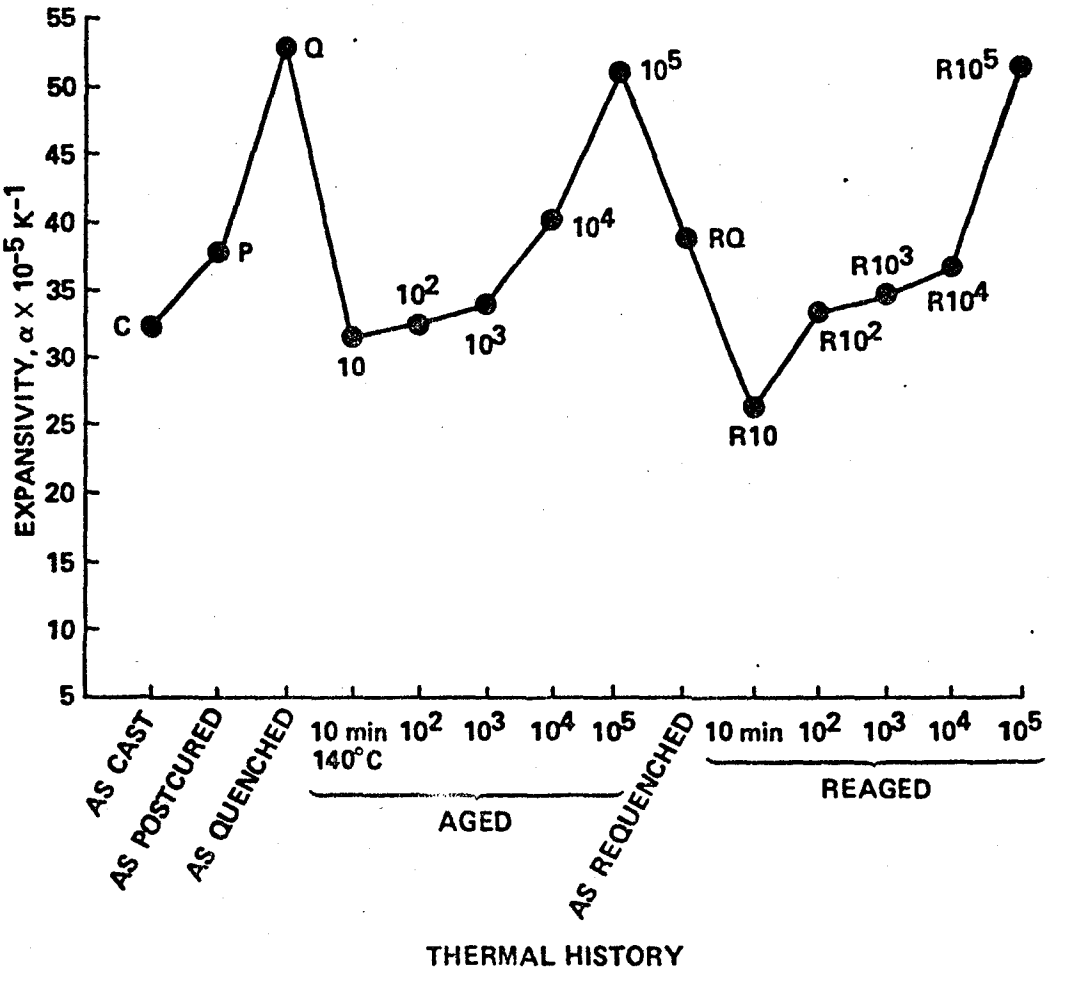

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SORPTION BEHAVIOR OF WELL-CURED FIBERITE 934 NEAT RESIN AS A FUNCTION OF SUB-Tg ANNEALING TIME

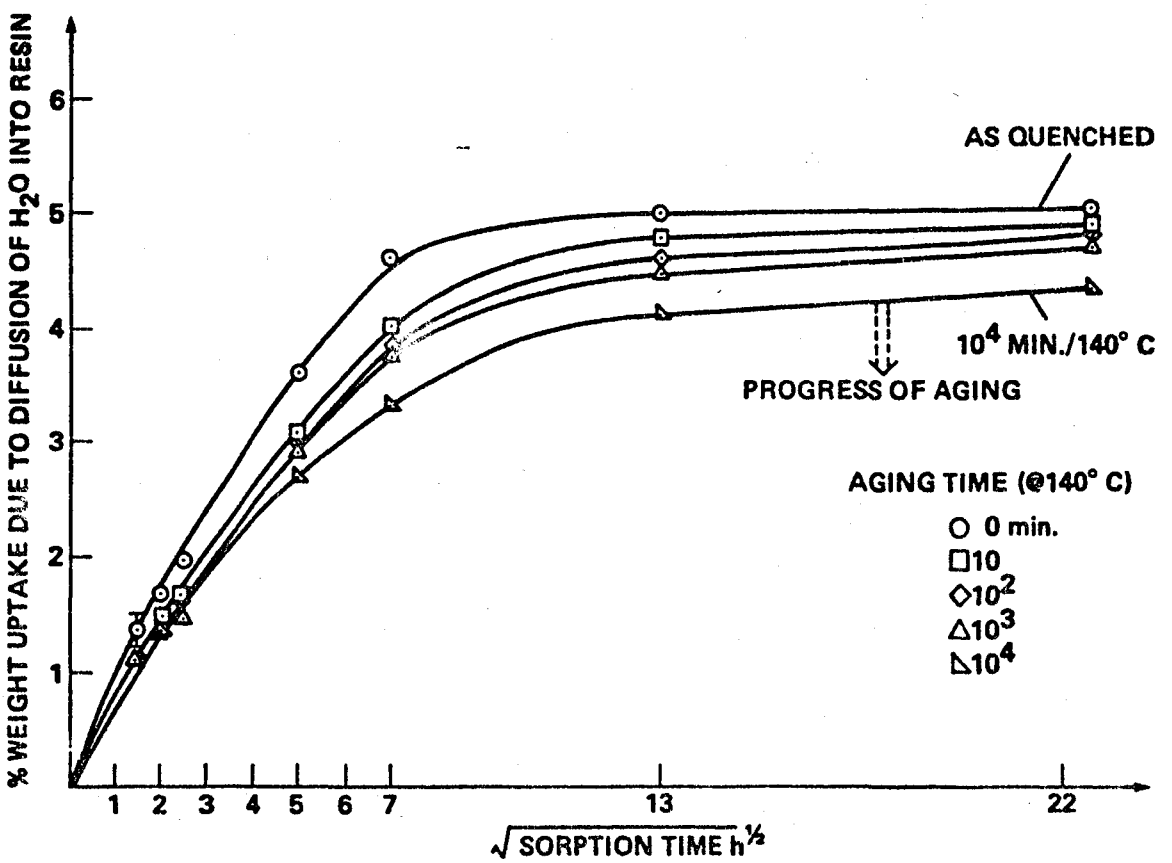

Figure 22

DEUTERIUM OXIDE-UPTAKE BY EPOXY AS FOLLOWED BY DEUTERIUM NMR SPECTROSCOPY

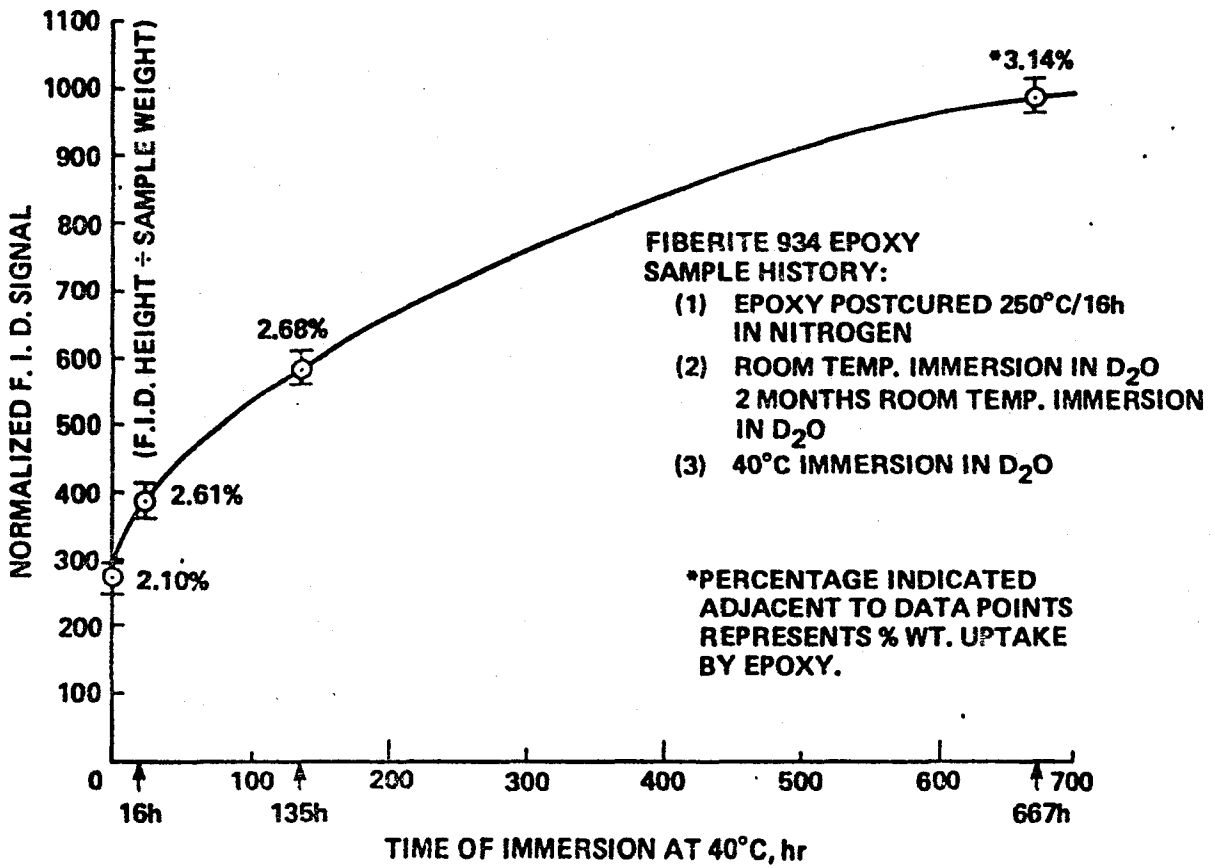

Figure 23

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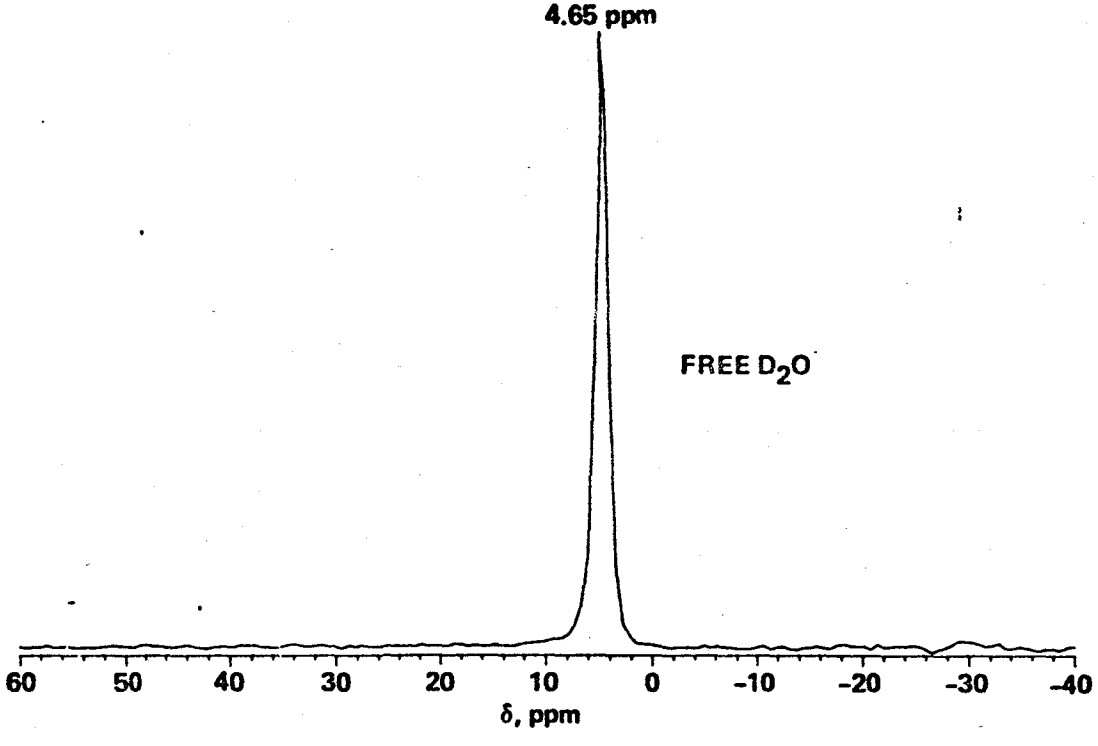

Figure 24

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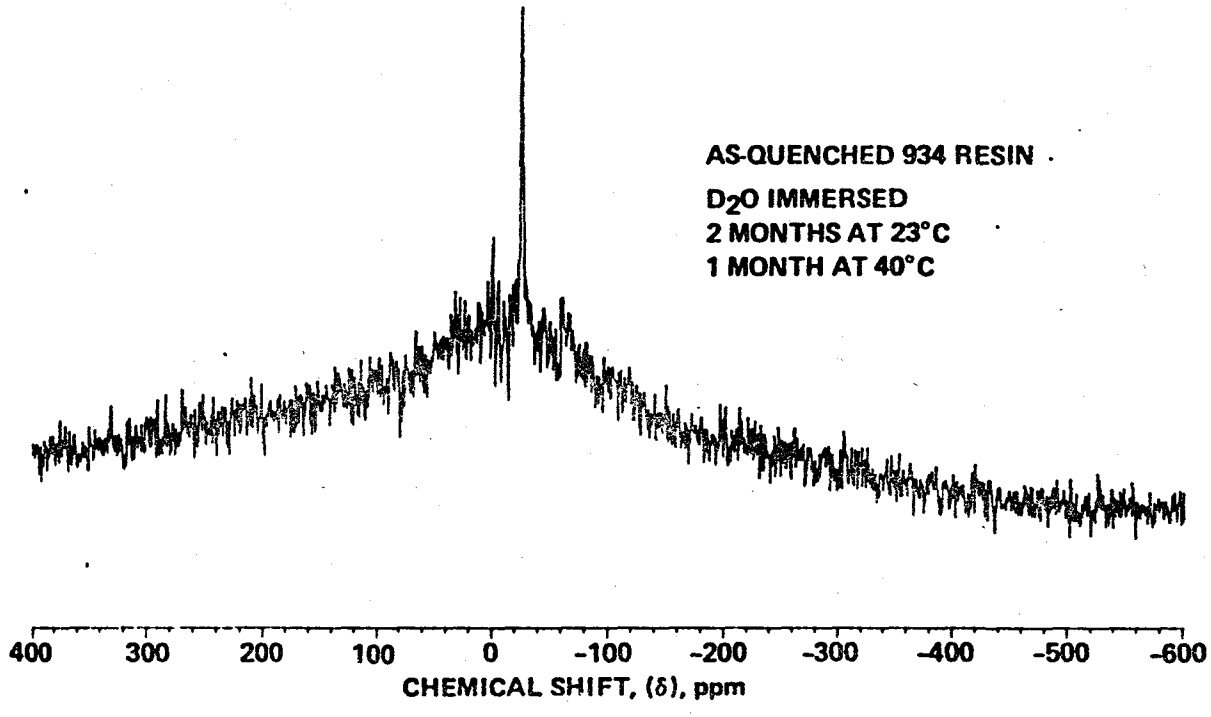

Figure 25

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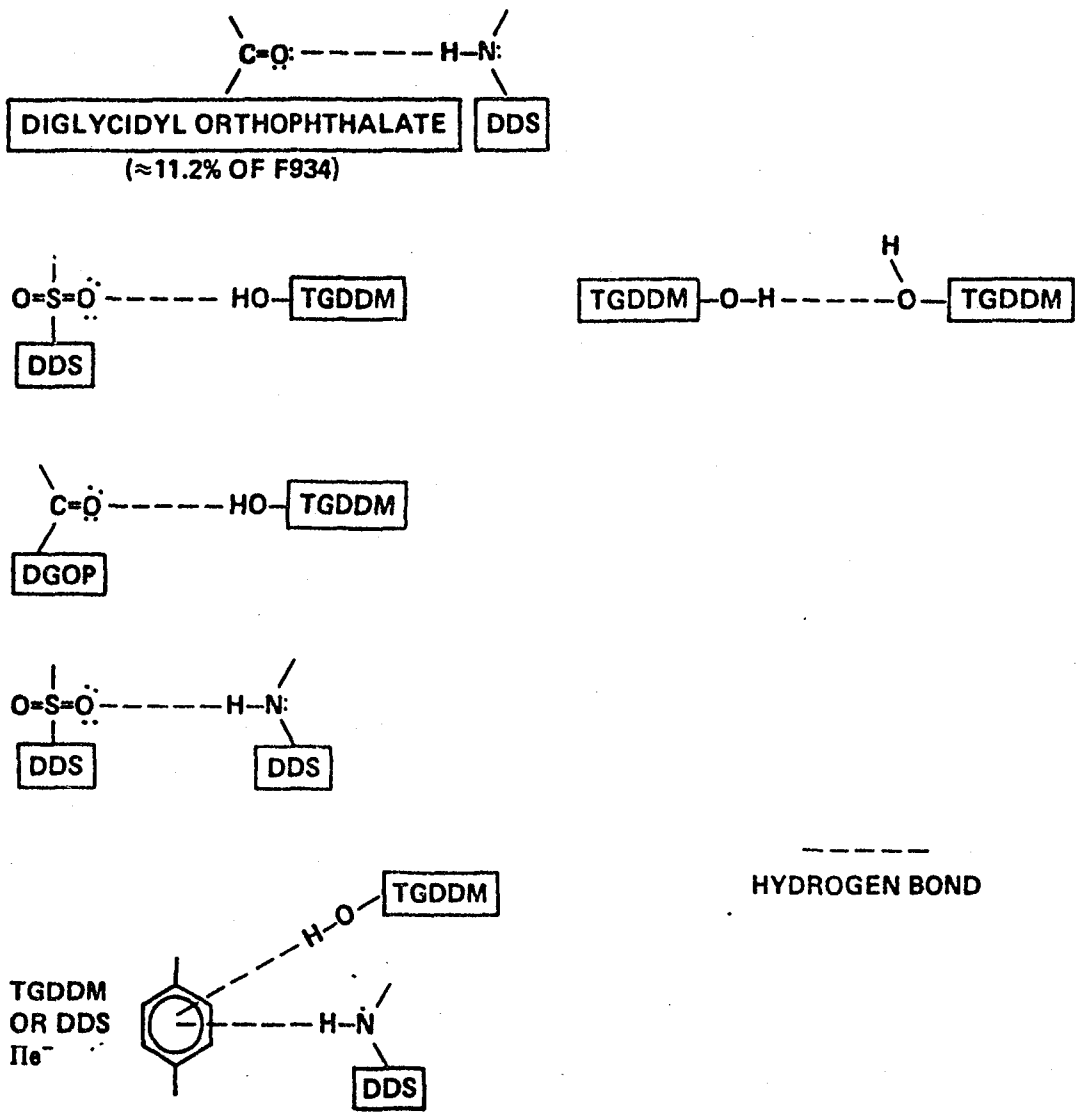
VARIOUS HYDROGEN BONDING POSSIBILITIES IN F934 EPOXY RESIN



HYDROGEN BONDING IN FIBERITE 934 EPOXIES

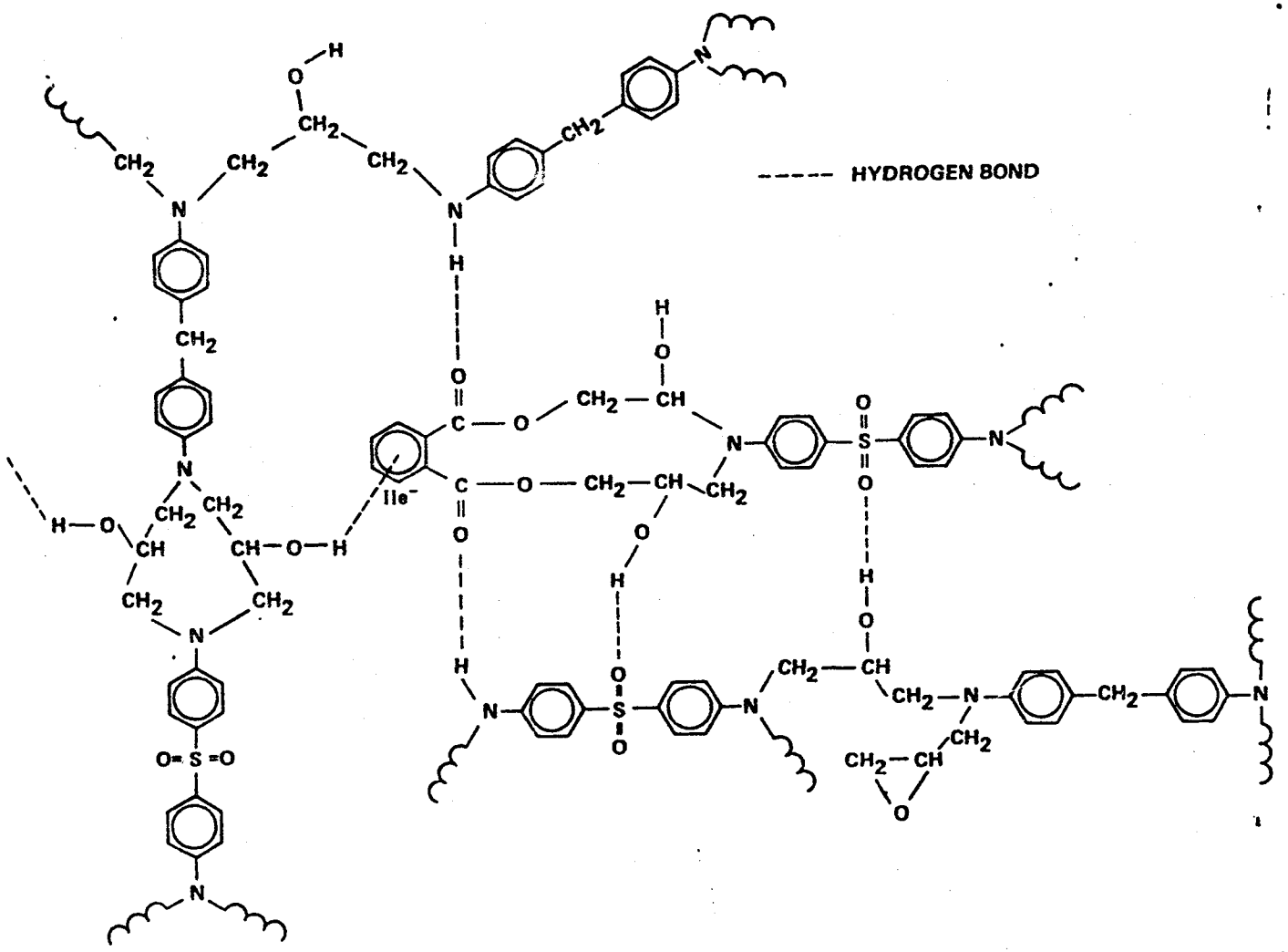


Figure 27

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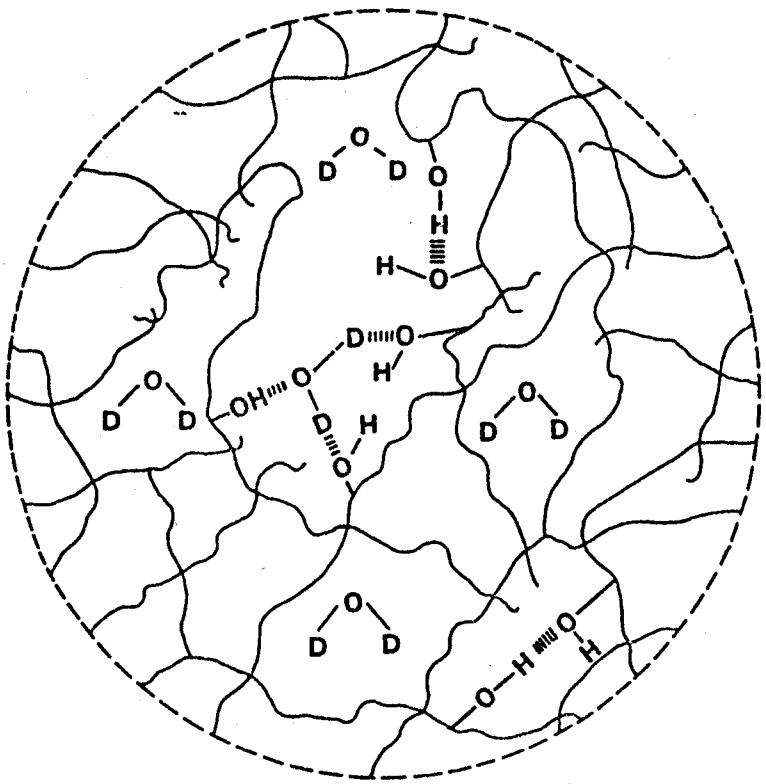
INTERACTIONS BETWEEN DEUTERIUM OXIDE AND EPOXY NETWORK



D_2O RESIDES IN VOIDS/FREE VOLUME → FREELY TUMBLING D_2O

D_2O RESIDES IN BETWEEN EPOXY—OH⋯HO— HYDROGEN BONDS (CORRELATION TIME ≈ 10^{-7} sec) → BOUND D_2O

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CROSS-POLARIZED MAS CARBON-13 NMR SPECTRUM

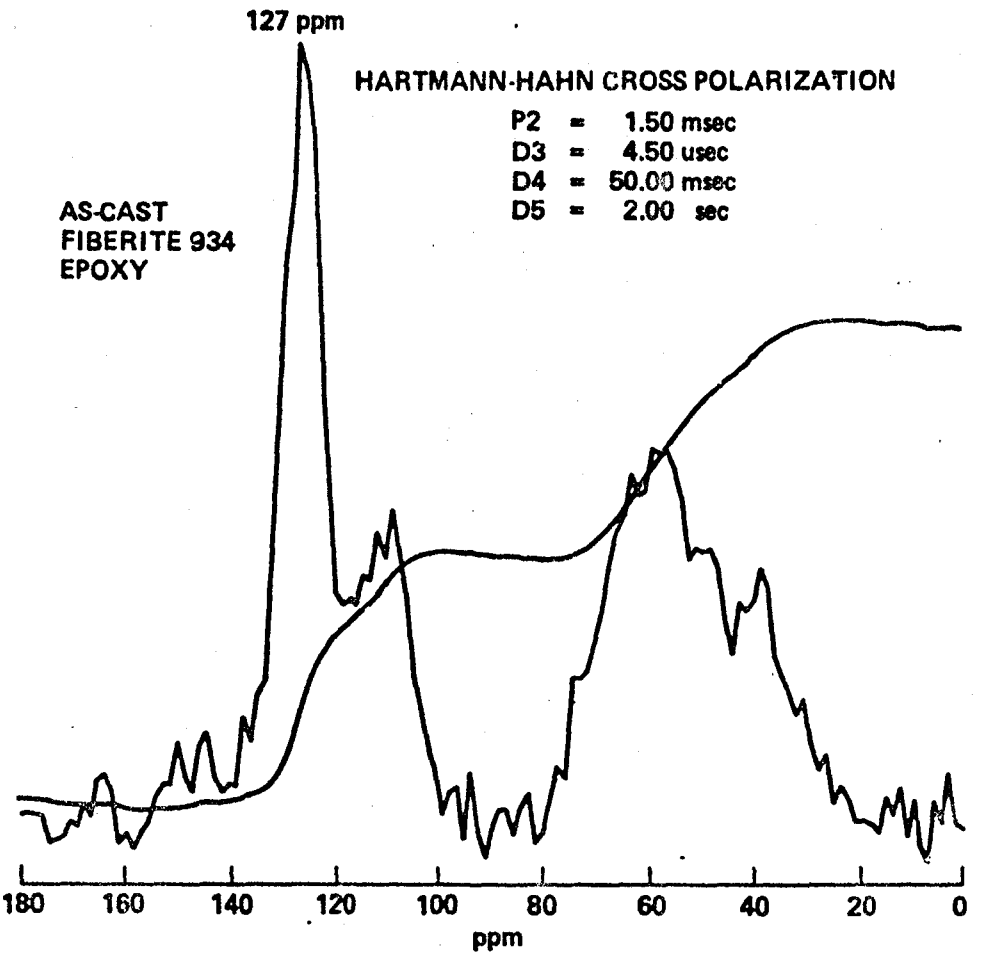

Figure 29

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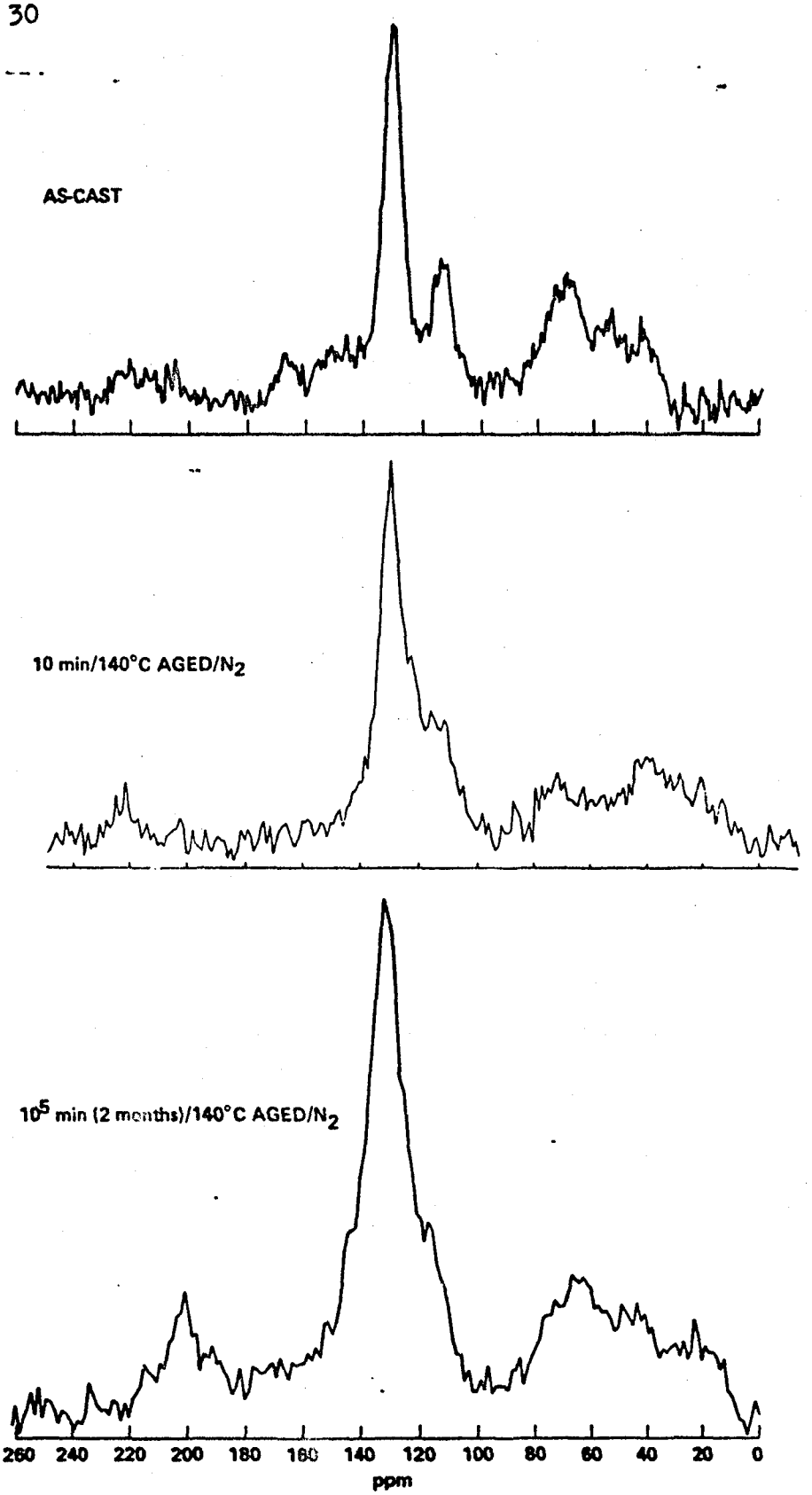
Figure 30



125 MHz CARBON-13 NMR SPECTRUM OF TGDDM IN $CDCl_3$

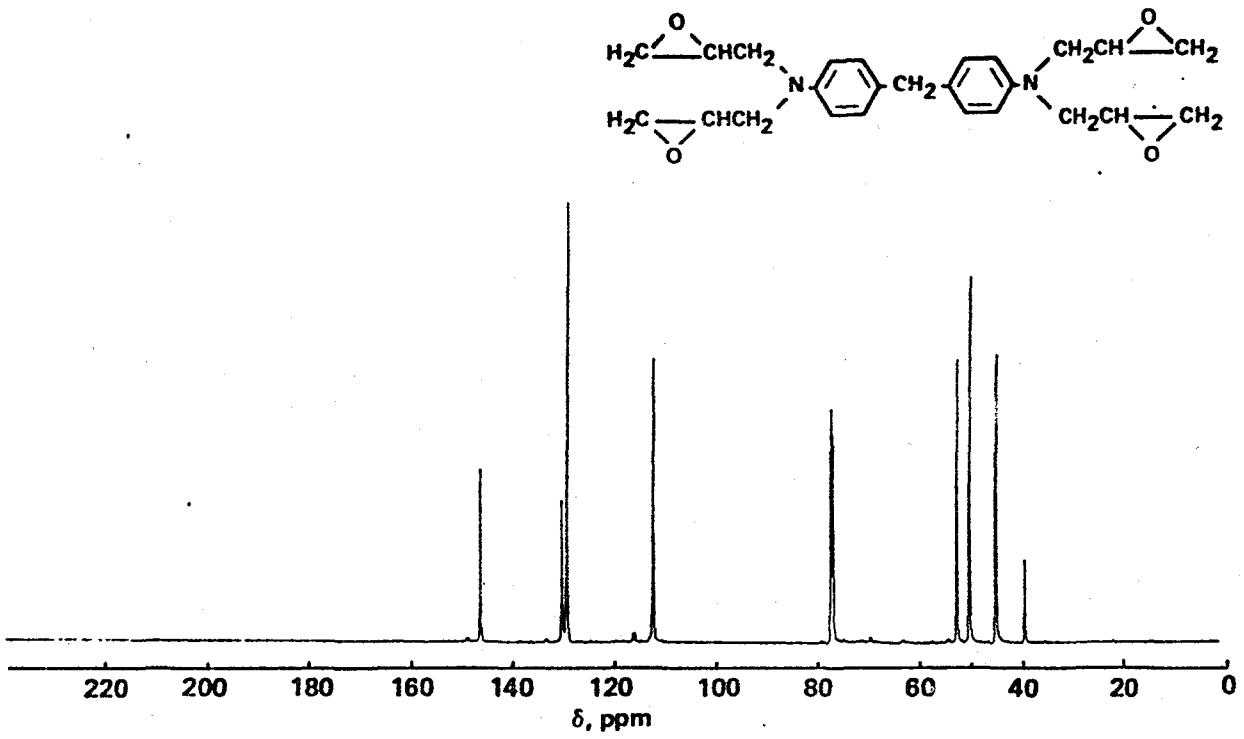


Figure 31a

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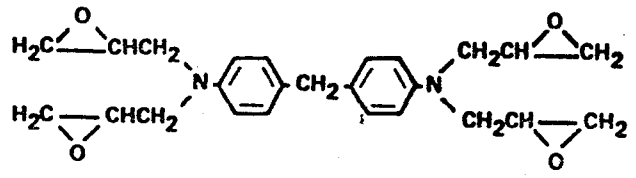
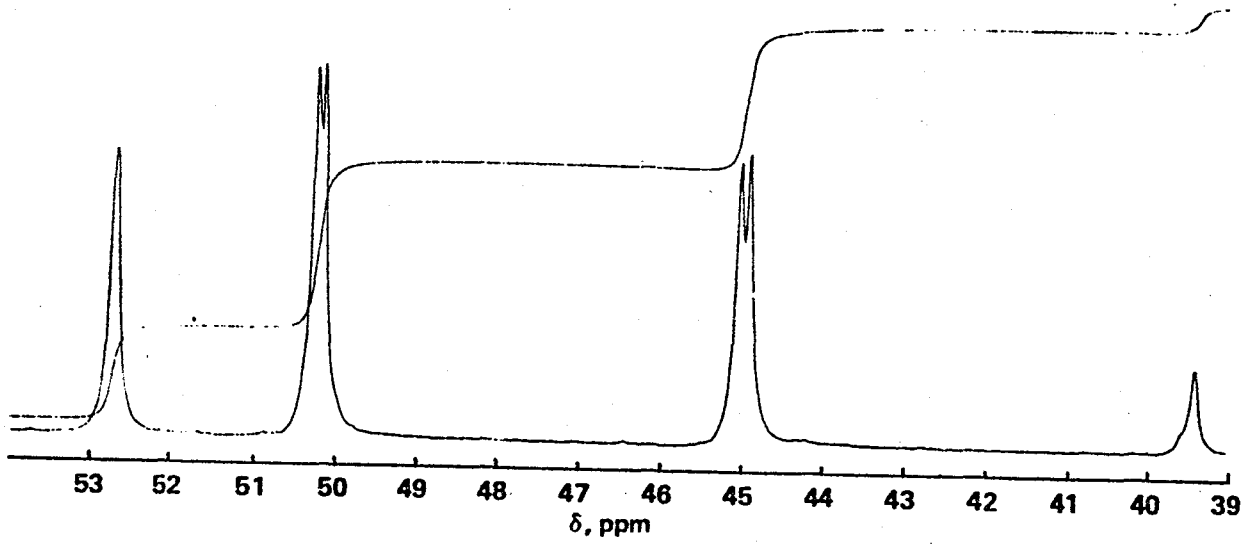
125 MHz CARBON-13 NMR SPECTRUM OF TGDDM IN $CDCl_3$

PEAKS BETWEEN
70 -150 ppm NOT SHOWN





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PROTON-DECOUPLED CARBON-13 125 MHz NMR SPECTRUM OF DDS*/$CDCl_3$ SOLUTION

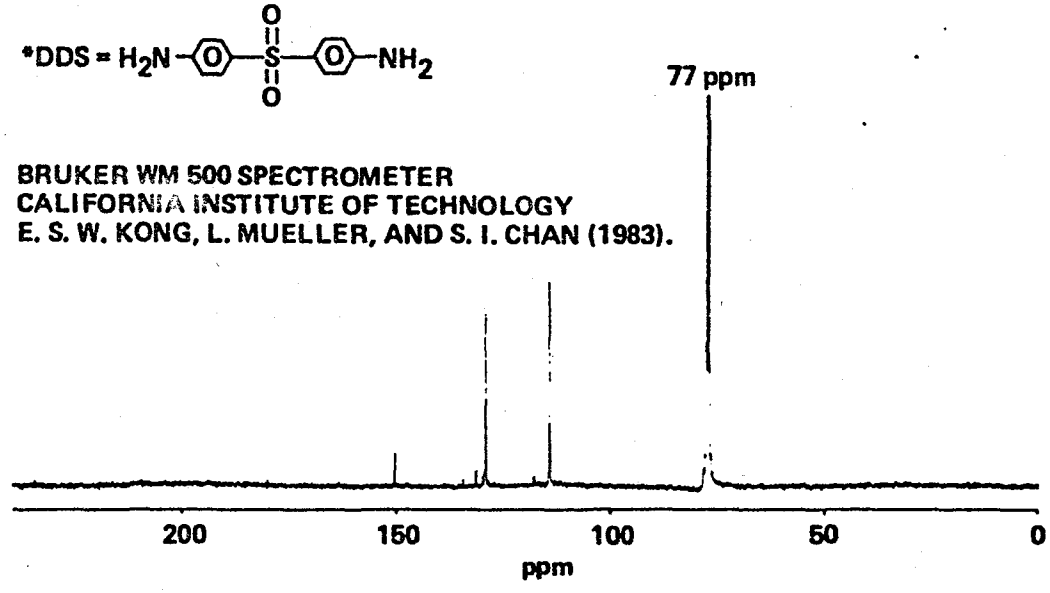

Figure 32a

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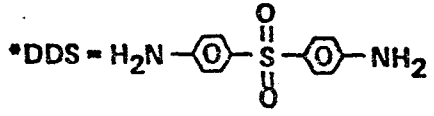
PROTON-DECOUPLED CARBON-13 125 MHz NMR SPECTRUM OF DDS* MONOMER/$CDCl_3$ SOLUTION



BRUKER WM 500 SPECTROMETER
CALIFORNIA INSTITUTE OF TECHNOLOGY
E. S. W. KONG, L. MUELLER, AND S. I. CHAN (1983).

LARGE PEAKS NEAR 77 ppm NOT SHOWN

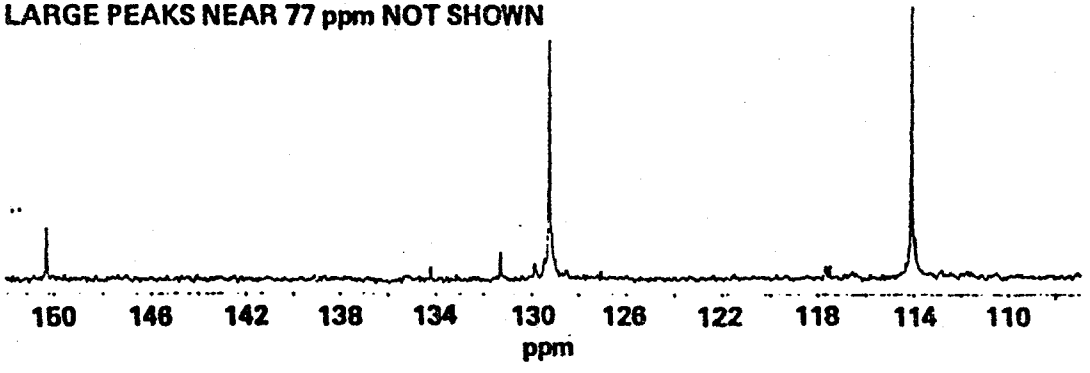


Figure 32b

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3 1176 01328 7371