

The Thermal Degradation of an Amine-Cured Epoxide Resin at Temperatures between 200°C. and 310°C.

J. C. PATTERSON-JONES and D. A. SMITH, *Department of Materials, The College of Aeronautics, Cranfield, Bedford, Great Britain*

Synopsis

This paper describes the nonoxidative thermal degradation of an epoxide resin based on the diglycidyl ether of bisphenol A crosslinked with *p,p'*-diaminodiphenyl methane. Temperatures of degradation lay between 200 and 310°C. and the process was followed concurrently by three means: changes in dielectric properties, changes in infrared spectra, and weight loss. Dielectric properties support the contention that there is a dehydration step during degradation. It is proposed that vacuum curing at high temperature can produce optimum crosslinking. Evidence of phenol and *N*-methyl aniline as degradation products is advanced, and possible degradation mechanisms are discussed.

INTRODUCTION

Epoxide resins are being increasingly used in the fields of electrical engineering, adhesives, and surface coatings. In some of these applications they may be exposed to temperatures in excess of 180°C., though apart from possible aerospace applications they are not likely to be exposed to temperatures much above 350–400°C. Temperatures below 350°C. we shall describe as "low temperatures" and those above as "high temperatures." In this paper is described an investigation into the so-called low-temperature degradation of an epoxide resin made by the reaction of the diglycidyl ether of bisphenol A with *p,p'*-diaminodiphenyl methane. Low-temperature degradation does not lead to large quantities of gaseous products, which can be readily analyzed, but the resin network is chemically changed, which gives rise to changes in physical properties such as dielectric loss, infrared absorption characteristics, and weight losses.

The subject of thermal degradation of epoxides has been reviewed by Bishop and Smith,¹ and only those papers dealing with low-temperature degradation are considered here, together with relevant work on dielectric loss in epoxides and the infrared spectra of epoxide resins.

Work on weight loss and dimensional changes due to thermal degradation of epoxide resins at low temperatures has been reported by Jacobi and Andre,² Lemon,³ and Ehlers.⁴ These workers found that in general

anhydride-cured resins are more stable than amine-cured materials, and there was evidence that resins based on epoxyated novolacs may be more stable than those based on the diglycidyl ether of bisphenol A.

Neiman et al.⁵ investigated the oxygen uptake of amine-hardened and anhydride-hardened resins at temperatures between 160 and 250°C. and found evidence of the formation of peroxy structures in the resin. They also found that the anhydride-cured material had the better oxidation resistance. Park and Blount⁶ also investigated low-temperature oxidative degradation of epoxides with infrared spectroscopy, and further work on these lines is reported by Conley⁷ and Anderson⁸⁻¹⁰ who studied low-temperature degradation by thermogravimetric analysis. Lee¹¹ used this method in conjunction with other techniques. The general impression was confirmed that epoxyated novolacs and anhydride hardeners are superior in respect of heat resistance to the diglycidyl ether of bisphenol A and amine hardeners.

Anderson and Freeman¹² described exploratory work on the low-temperature degradation of epoxides with the use of DTA (differential thermal analysis), and this approach was further investigated by Anderson.^{13,14} Anderson^{13,14} used a nitrogen atmosphere and examined hardened resins and unreacted materials. A large exothermic peak was observed between 300 and 400°C., and this was attributed to isomerization of the epoxy group, which appeared to occur simultaneously with other degradation reactions; indeed, it is a degradation reaction in incompletely cured resin.

Similar results were obtained by Lee,¹¹ and DTA was used to examine laminates based on epoxy resin by Learmonth and Wilson.¹⁵

A number of workers have studied the infrared spectra of epoxide resins and included studies of the curing process.¹⁶⁻²¹ Sugito and Ito²² also studied the pyrolysis products of epoxide resins by infrared spectroscopy, mainly as a method of identifying the hardeners.

The dielectric properties of epoxide resins were studied by von Kobale and Löbl.²³ The properties of resins hardened with both tetrahydrophthalic anhydride and *p,p'*-diaminodiphenyl methane were examined under a variety of cure conditions. Plots of power loss ($\tan \delta$) versus temperature over a wide range of frequencies displayed two maxima, one at high frequencies and low temperatures, believed to be associated with movement of the hydroxyl group, and the other at low frequencies and high temperature, believed to be associated with relaxation of the resin network. The effects of a number of experimental parameters on these regions were studied, and absolute rate theory was applied to the high-temperature loss region. Dasgupta and Mital²⁴ studied dielectric loss for an epoxide resin, a hardener (phthalic anhydride), and various cured combinations of these materials. A wide frequency range was used (5 cps to 50 Mc./sec.). Havan, Gringras, and Katz²⁵ studied the changes in loss tangent and dielectric constant accompanying the isothermal curing of a commercial epoxide resin with diethylene triamine. Attempts were made to use the curves of loss tangent versus time as a means of monitoring cure. To the

best of our knowledge the degradation of epoxide resins has not been previously reported, with dielectric properties as a means of assessment of network breakdown.

In the work described in this paper the low-temperature degradation of epoxide resins was investigated by simultaneously studying the effect of temperatures from 220 to 309°C. on the infrared spectra and dielectric properties of cured resin.

This work was supported by a secondary exploratory investigation of the chemical nature of the volatiles evolved and by weight loss studies. The latter were mainly undertaken to determine at what temperature degradation became appreciable. The aim was to elucidate the reactions occurring in the molecular network during degradation, even though some of the structures produced by such changes would remain in the partially degraded solid resin and not appear as volatile compounds. There are already data suggesting the presence of fragments of the molecular network in the tar formed when epoxide resins are pyrolyzed.²⁶ It was hoped that fresh studies would reveal where the first ruptures occurred in the resin network, whether at the "cure link" or at some part of the structure. In view of the complexities of oxidative degradation it was decided degradation *in vacuo* would be studied, at least in preliminary work.

EXPERIMENTAL METHODS

Starting Materials

It was felt desirable to use a resin whose chemical structure was known as well as possible, and for this reason purified diglycidyl ether of bisphenol A (DGEBA) was made to react with purified *p,p'*-diaminodiphenyl methane (DDM).

A commercial sample of DGEBA was recrystallized from ethanol. The purified material was melted and the molten material evacuated for 3 hr., to remove traces of ethanol.

Required for DGEBA: C 74.1%, H 7.1%, Cl 0%. Found: (a) C 73.8%, H 7.2%, Cl 0.55%; (b) C 73.9%, H 7.0%, Cl 0.35%. The melting point was 39.1–42°C. Clearly, some chlorinated structures were present, possibly due to incomplete formation of the epoxide group due to dehydrochlorination. The manufacturers stated that the 2,4'-disubstituted materials, instead of those of the normal 4,4' form, may be present in 1 or 2% quantities.

The hardener, *p,p'*-diaminodiphenyl methane, was purified by recrystallizing commercial material from water and then vacuum-drying. Anal. recrystallized material. Required for DDM: C 78.8%, H 7.1%, N 14%, Cl 0%. Found: (a) C 78.1%, H 7.1%, N 14.2%, Cl 0.3%; (b) C 78.5%, H 7.0%, N 14.5%, Cl 0%.

Preparation of Samples for Degradation

Recrystallized DGEBA was weighed, melted, evacuated for 20 min., and reweighed, and the weight loss associated with evacuation was obtained. DDM (28.8% on the final weight of DGEBA) was added, and the mixture heated to a mobile liquid, which was evacuated for 20 min. to get rid of air bubbles. After evacuation the mixture was weighed; the weight loss associated with evacuation was never more than 0.1%. Elemental analysis was used to check that one component was not significantly more volatile than the other. The liquid mixture was then cast in airtight polythene molds and cured for 20 hr. at 95°C. The resulting disks had diameters of 5.5 cm. and thicknesses of 0.13 cm. and were trimmed before being subjected to degradation procedures.

Two disks were prepared for each experiment, one being used for dielectric studies and the other for infrared studies.

Degradation of Samples

Degradation of samples was carried out at a pressure of 0.7 mm. Hg, to minimize oxidation. There is evidence that further curing took place and that this process overlaps with degradation; this will be discussed later. Disks of cured resin, previously weighed, were clipped onto a clean, flat aluminum plate, to avoid distortion during heating. This assembly was then placed in a massive, brass degradation vessel. The vessel was sealed by bolts, a copper gasket being used, and was then connected by rubber pressure tubing to a simple vacuum line assembly. The procedures for degradation were as follows:

(1) Disks of resin, previously weighed, were clipped to their aluminum plates, to prevent distortion, and placed in the degradation vessel, which was closed and connected via the traps to the pump.

(2) The apparatus was pumped down, one of its two traps immersed in liquid air.

(3) The degradation vessel was placed in an oven at the desired temperature, and the temperature of the outside wall of the brass reaction vessel was measured with a chromel-alumel thermocouple. Time in the degradation vessel was measured, and a time-temperature history for each degradation experiment was thus recorded. Pumping was continued throughout the degradation cycle.

(4) At the end of each degradation experiment the degradation vessel was removed from the oven and the vacuum line isolated from the pump and the degradation vessel. By warming one of the traps to room temperature the degradation products that were volatile at room temperature were distilled into a special trap, which was sealed off and removed.

(5) Condensable products remaining in the first trap were removed by being dissolved in methanol, and these materials together with the materials volatile at room temperature were subjected to normal chemical analysis.

The results on room-temperature volatiles were not conclusive.

(6) Disks removed from the cooled reaction vessel were reweighed and physically examined; one disk was used for infrared spectra and the other for dielectric studies.

Infrared Spectroscopic Investigation of Degraded Resin Disks

Infrared spectra of cured and degraded disks were obtained by filing the resin disks and incorporating the filings into KBr disks in the usual way. The KBr was Analar grade and was carefully dried before use. It showed negligible hydroxyl absorption after 10 min. of evacuation before pressing into KBr disks.

Dielectric Measurements

The dielectric properties of the degraded resin disks were measured at nine fixed frequencies in the range 210 cps to 90 kc./sec. and over the temperature range of -185 to $+240^{\circ}\text{C}$. The disks formed the dielectric of a parallel-plate capacitor or cell, whose capacitance and loss were measured on a dielectric bridge. The construction of the cell is given in Figure 1. The resin disk was placed between two flat aluminum electrodes. One electrode was circular, of diameter 5.5 cm.; the other was circular and approximately 1 cm. wide. The electrodes were cemented to Bakelite plates that were backed with steel plates, so that the whole assembly could be bolted together without distortion of the electrodes. The steel backing plates and bolts were all earthed. Terminals from the electrodes and guard ring were connected to the bridge by means of leads insulated with PTFE and each sheathed in a copper spiral, to eliminate mutual-capacitance effects. After measurements at high temperatures some degradation of the Bakelite plates occurred, but this did not appear to impair their insulation properties.

A dielectric bridge designed and built by W. P. Baker (AEI Ltd., Manchester) was used to measure the loss tangent ($\tan \delta$) at a number of pre-determined frequencies between 210 cps and 90 kc./sec.

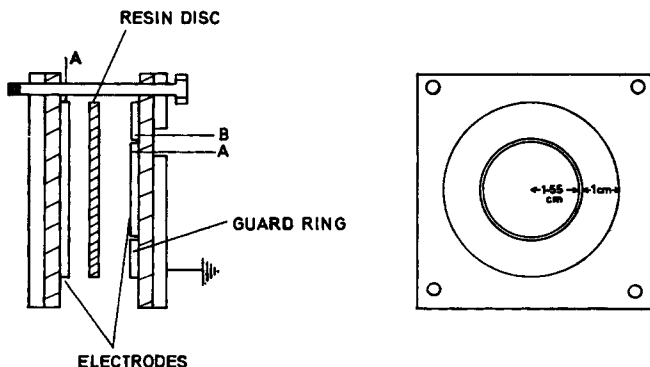
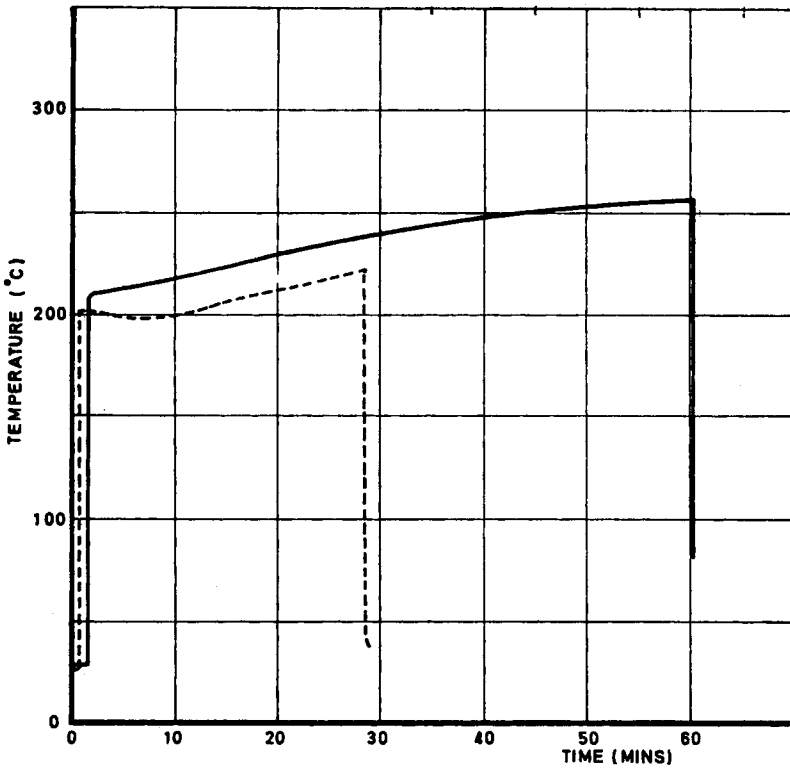
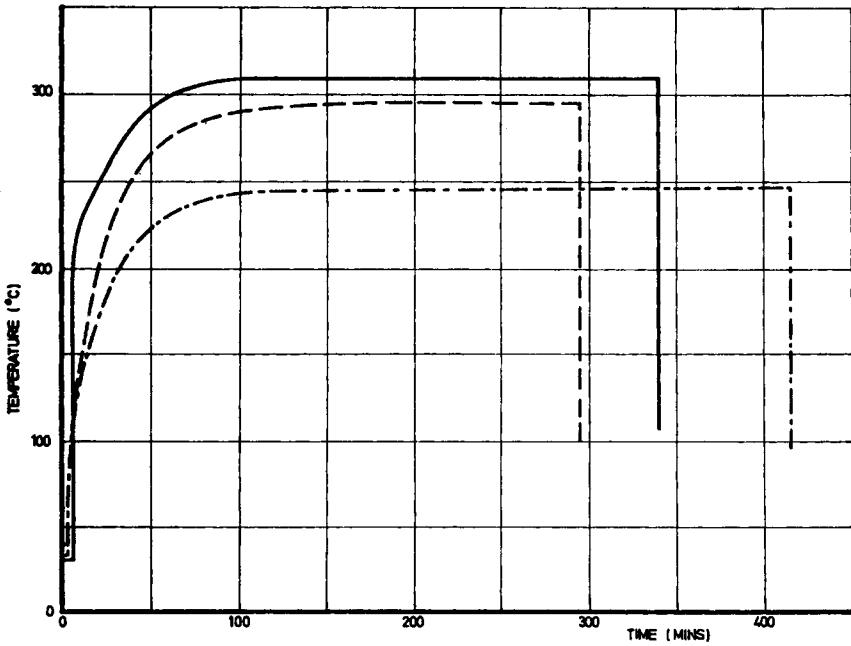


Fig. 1. Dielectric cell.



(a)



(b)

Fig. 2. Temperature-time cycles: (a) Experiments III (---) and (—) IV. (b) Experiments V (···), VI (---), and VII (—).

TABLE I

Expt. no.	Cure sched. ^a	Degrad. cycle	Press, mm. Hg	Wt. loss, %	Infrared spectrum	Dielec. studies
I	Plus 16½ hr. in air at 130°C.	not deg.	—	—	similar to that of material cured 20 hr. at 95°C.	performed
II	Plus 16½ hr. at 135°C. + 16 hr. at 180°C. in air.	not deg.	—	—	increased absorption at 1700 and 1660 cm. ⁻¹ , especially at surface; surface red.	not performed
III		30 min. at 200–225°C.	0.7	0.0	little diff. to that of undeg. material	performed
IV		60 min. at 210–255°C.	0.7	0.06	little diff. to that of undegraded material	performed
V		420 min. at 240°C.	0.5	0.26, 0.19%	little diff. to that of undeg. material	performed
VI		290 min. at 290°C.	0.6	7.87, 4.94%	diff. to that of undeg. material	performed
VII		340 min. at 309°C.	0.6	20.8, 17.5, 9.7, 26.0%	diff. to that of undeg. material	not performed, disks distorted and embrittled

^a Schedule: 20 hr. at 95°C. all experiments; in experiments I and II additional schedules as given. Two disks all experiments except VII, in which four were used.

For readings in the temperature range -185°C. to room temperature the cell was wrapped in two separate layers of polythene sheeting, which prevented condensation of water from the atmosphere onto or into the cell. The wrapped cell was placed in a massive iron cylinder, which was cooled to liquid-air temperature and then placed in a thermos flask. Readings at temperatures between liquid-air temperatures and room temperature were taken while the cell and cylinder slowly warmed to room temperature. The maximal rate of temperature rise was less than 1°C./min. , which enabled the dielectric bridge to be easily balanced. For readings at temperatures greater than room temperature the cell was placed in an oven which maintained the temperature within $\pm 1^{\circ}\text{C.}$ of the desired value. Helium was circulated around the cell for readings greater than 140°C. , to prevent oxidation of the resin disks.

The temperature of the cell was measured with a chromel-alumel thermocouple, the hot junction sunk into one of the Bakelite plates of the cell. The temperature variations across the sample were minimal because of the electrodes, and the steel backing plates evened out any temperature variations. Dielectric heating of the samples was negligible.

The time-temperature histories of the degraded samples are shown in Figure 2, and the following table supplies details of the results of seven degradation experiments. All initial curing at 95°C. was done in airtight polythene molds.

In experiment VII the volatile products of degradation were collected in the vacuum line in larger quantities, and the main effort on the chemical analysis of volatile breakdown products was devoted to the materials obtained in this experiment. In addition, considerable quantities of tar were found in the reaction vessel in experiment VII.

Infrared Spectroscopic Results

It was noted that under nonoxidative conditions only those materials degraded above 290°C. (experiments VI and VII) showed any change in infrared spectra from undegraded material. Under oxidizing conditions changes occur by 180°C. (Experiment II.) Only in experiment VII are there very marked changes in the spectrum, compared with those of undegraded material. One may also note that weight loss became quite large in experiment VII.

Significant changes in the spectra were as follows.

(1) Reduction in a band at $2.9\text{--}3.0\ \mu$ (O—H and N—H) relative to that at $3.5\ \mu$ (C—H), which probably indicates a reduction in the number of OH and/or NH groups; this is more notable in experiment VII (Fig. 11).

(2) Changes around $7\ \mu$ connected with the OH group (possibly a reduction in the number of groups).

(3) A relative increase in bands at 6.8 and $10.6\ \mu$, probably due to an increase in —CH=CH_2 groups; this was again notable in experiment VII.

Changes in infrared spectra associated with experiment VI are, in general, slight and difficult to interpret.

Dielectric Results

Experimental Accuracy. The power loss ($\tan \delta$) was measured at nine fixed frequencies between 210 cps and 90 kc./sec. and over a temperature range of -185 to 240°C . Experiments designed to test reproducibility of results showed that, when values of $\tan \delta$ were of the order of 10^{-2} , values could be quoted to 0.5×10^{-2} . The disks of experiment I, cured at 130°C ., were unstable when measurements of $\tan \delta$ near the original cure temperature were attempted. Only values at a frequency of 1.05 kc./sec. are quoted for discussion.

Values of $\tan \delta$ at temperatures of about 220°C . and above are time-dependent. The reported values of $\tan \delta$ at these temperatures have therefore only qualitative significance. The time dependence is possibly due to degradation during measurement.

Significance of the β Loss Region. Contour plots of $\tan \delta$ as a function of temperature and frequency for experiments IV, V, and VI are shown in Figures 3-5. Figure 6 shows $\tan \delta$ as a function of temperature at 1.05 kc./sec. for experiments III to VI; Figure 7 gives a similar result for experiment I, in which an undercured, undegraded material was examined. The results of experiment III are for an apparently fully cured material that has not been degraded.

All the results show that in the frequency-temperature range investigated the samples have two distinct dispersion regions, a low-temperature region

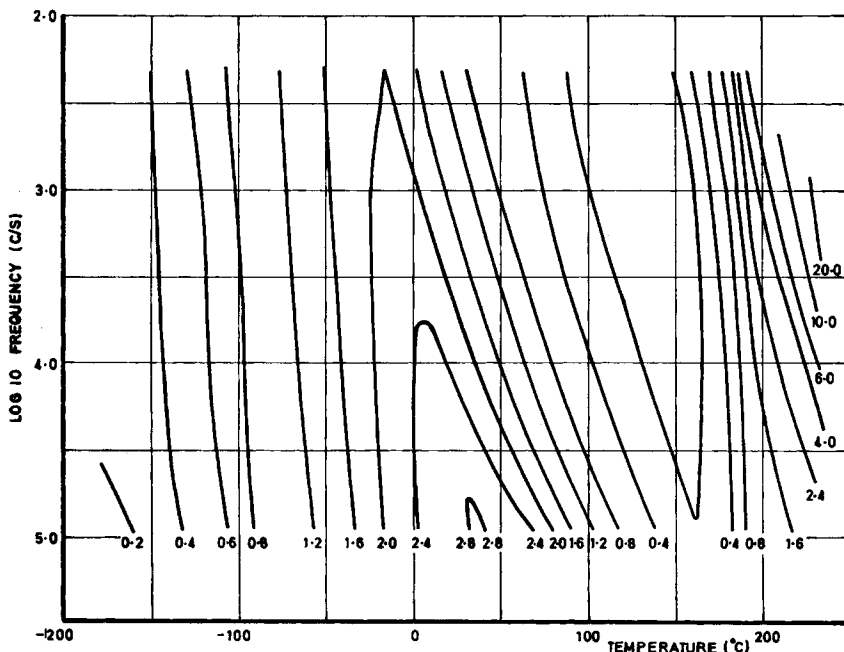


Fig. 3. Contour diagram: power loss $\tan \delta$ ($\times 10^{-2}$), log frequency, and temperature, experiment IV.

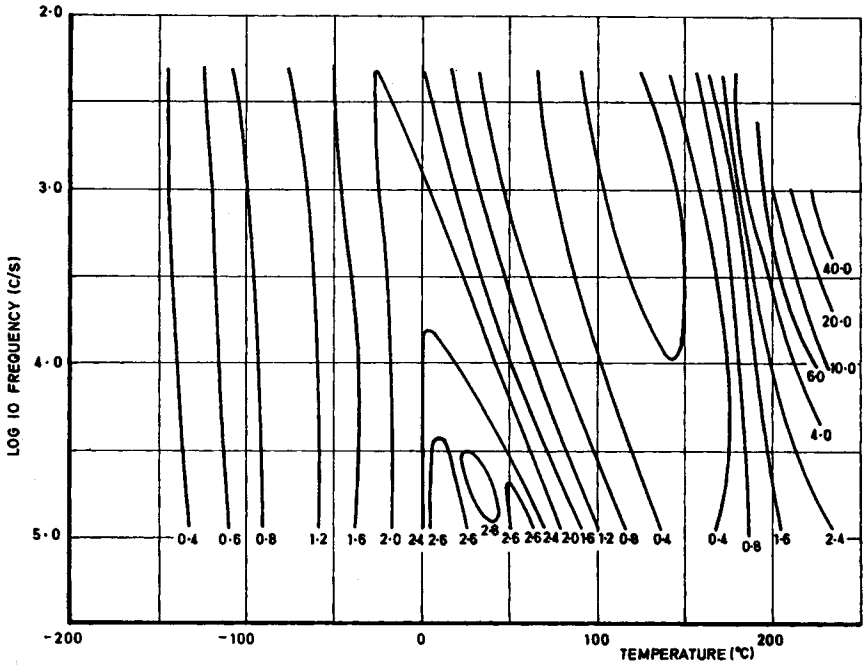


Fig. 4. Contour diagram: power loss $\tan \delta (\times 10^{-2})$, log frequency, and temperature, experiment V.

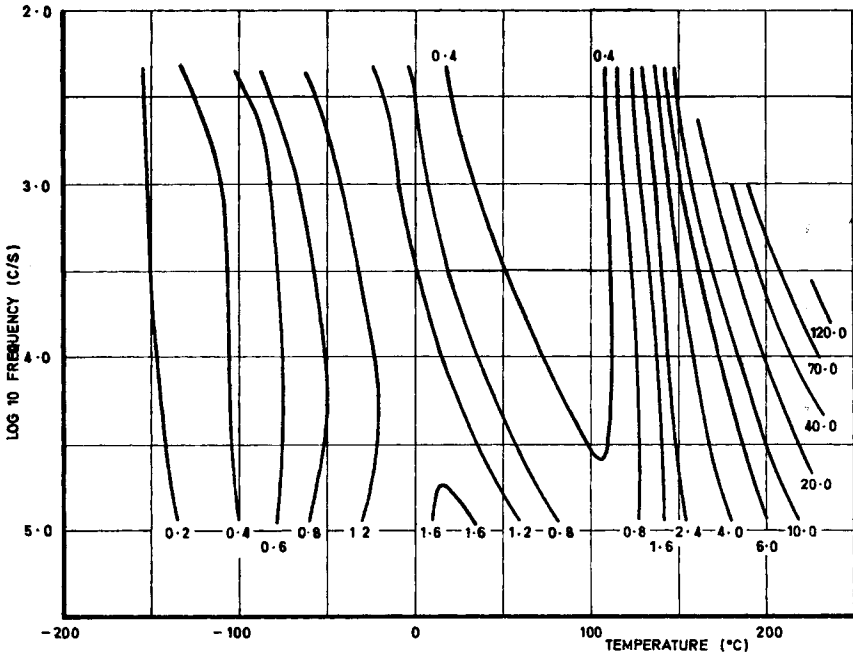


Fig. 5. Contour diagram: power loss $\tan \delta (\times 10^{-2})$, log frequency and temperature, experiment VI.

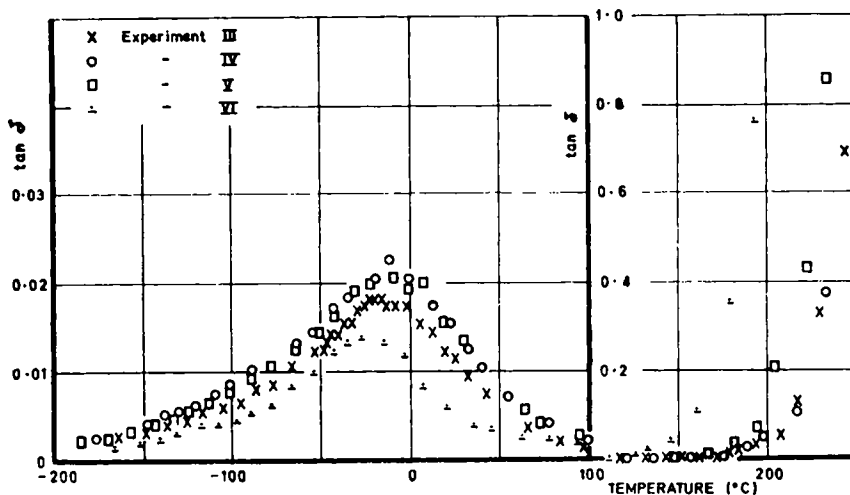


Fig. 6. Power loss $\tan \delta$ versus temperature at 1.05 kc./sec., experiments III-VI.

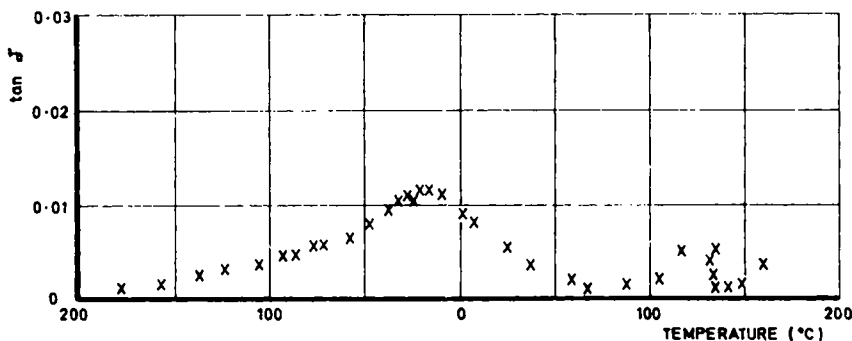


Fig. 7. Power loss $\tan \delta$ versus temperature at 1.05 kc./sec., experiment I.

β and a high-temperature region α . The β region is broad and characterized by relatively low values of $\tan \delta$. An Arrhenius plot of f_{\max} versus $1/T$, where f_{\max} is the frequency of maximum absorption and T is the absolute temperature, for the results on undegraded samples gave an apparent activation energy of 16.5 cal./mole. This suggests that the loss is of the dipole-radical type, as opposed to the dipole-elastic type. The β peak is probably associated with a dipole movement independent of the main chain; this interpretation is consistent with the temperature-frequency range in which the loss occurs. It is possible that the β loss peak is formed from two overlapping loss peaks. The structure of the resin shows that the pendant hydroxyl group is the only group that could be responsible for a dipole-radical loss. The movement of any other dipole in the network structure would involve a change in the configuration of the network, bringing about a dipole-elastic loss. Groups such as epoxide, primary amine, and chlorine are likely to be present in the cured network in such

small amounts that their contribution to dielectric loss will be negligible. It seems reasonable to suppose that the dispersion region is concerned with dipole-radical loss due mainly to hydroxyl groups.

Figure 7 shows the results of measurements of $\tan \delta$ as a function of temperature at a frequency of 1.05 kc./sec. for the resin disk of experiment I. This disk had only received a preliminary cure at 130°C. and was not fully cured. It is clear from Figures 6 and 7 that, as the disks were more fully cured, so the maximal value of $\tan \delta$ in the loss region increased, the greatest value being recorded for the disk in experiment IV, which had in fact been cured up to a temperature such that some slight degradation had occurred. For increasingly degraded specimens in experiments V and VI the maximal value of $\tan \delta$ in the β loss region decreased. It is known from the work of Lee,¹¹ and from the work done in these laboratories that water is evolved when DDM-cured epoxide resins are degraded and that this is produced by a dehydration reaction involving the hydroxyl groups. Although concentration of hydroxyl may not be the only factor controlling the β absorption, the results show a direct relation between the concentration of hydroxyl groups and the maximal value of $\tan \delta$ of the β peak. The concentration of hydroxyl groups increases with increasing cure but decreases as degradation proceeds. Thus, in Figure 6 and 7 materials from experiments I and III were undercured, that of experiment IV was cured (and, possibly, slightly degraded), and materials from experiments V and VI were progressively degraded. This agrees with weight loss data and infrared studies and is evidence that hydroxyl groups are largely responsible for the loss associated with the β peak.

The many possibilities for hydrogen bonding and the random nature of the resin network probably account for the broadness of the β loss region. Von Kobale and Löbl quoted curves of $\tan \delta$ versus temperature for a commercial epoxide cured with tetrahydrophthalic anhydride. They also obtained a β loss region at lower temperatures, but their α loss region differed considerably from that observed for DDM-cured material. They associated the β loss region with hydroxyl groups and quoted an activation enthalpy of 11 kcal./mole. The similarities of this figure with activation enthalpies for ice and terylene are quoted as evidence, though in itself this is a dubious argument.

Significance of the α Loss Region. The following points were noted concerning the high-temperature, or α , loss region.

(1) In the temperature-frequency ranges studied no maxima in the values of $\tan \delta$ were found in any of the experiments. Weight loss showed that degradation is appreciable above 240°C., and measurements of $\tan \delta$ were not continued much above this temperature.

(2) Very high values of $\tan \delta$ (approaching unity) were recorded toward 240°C. It is questionable whether these very high values of $\tan \delta$ are of exact quantitative significance, since they may be highly time-dependent owing to degradation during the actual measurements.

(3) When undegraded disks were examined (experiment I), a shifting

of the α peak, due to cure during measurement, was observed. The disks were cured at 130°C. The graph of $\tan \delta$ versus temperature showed a rise in $\tan \delta$ as 130°C. was approached, but a maximum was not realized. The value of $\tan \delta$ at 135°C. is lower than would be expected, and successive measurements at this temperature show a progressive decrease in $\tan \delta$. When the temperature of measurement was raised to 160°C. and then lowered, the result indicated by extrapolation a peak in the region above 160°C. Thus, the actual measurements caused a shifting of the $\tan \delta$ readings (Fig. 7) in undercured materials such as those in experiment I. No true α loss region could be obtained.

(4) Inspection of Figure 6 shows the effect of thermal degradation on the α loss region. Results for experiments III and IV show rises of $\tan \delta$ in the α loss region, which almost lie on the same line, though the β loss evidence suggests that the experiment IV material was more highly cross-linked than that of experiment III. A comparison of weight losses suggests that a very slight degradation had commenced in experiment IV. The discs of experiment IV were postcured and degraded at a higher temperature and for a longer time than that of experiment III. The α loss regions for experiments V and VI, on increasingly degraded specimens, were shifted progressively to lower temperatures (Fig. 6).

Von Kobale and Löbl²³ investigated the dielectric properties of a commercial, nondegraded epoxide resin cured with tetrahydrophthalic anhydride. Two distinct loss regions were found, as in our own work. The low-temperature region was a broad region characterized by relatively low maximal values for $\tan \delta$.

Unlike the results for DDM cured epoxide resin they found a well-defined complete peak in the high-temperature loss region, the maximal values of $\tan \delta$ being in the region of 0.1. Von Kobale and Löbl clearly showed the relation of this region with the properties of the network and characterized the losses as dipole-elastic losses. Clearly this region lay in a temperature range where the anhydride-cured material was stable, enabling a complete peak to be observed. This accords with the fact that anhydride-cured resins are more thermally stable than amine-cured materials.

In our work also the temperature-frequency ranges of the α , or high-temperature, loss region is such that it would be unlikely to be due to dipole-radical losses, even if there were another pendant dipole present to account for such losses. The loss is therefore associated with network relaxation. This does not itself explain why no definite peaks were observed in the curves of $\tan \delta$ versus temperature.

The results noted in (3) above, for disks made in experiment I, may be explained as follows, assuming that the α loss region is closely associated with the glass transition temperature. After the gel point, during polymerization, the remaining liquid attaches itself to the network and also increases the degree of crosslinking. As cure proceeds and building onto the network becomes progressively replaced by crosslinking, there comes a time when

the degree of crosslinking is such that the glass transition temperature of the network corresponds to the cure temperature. At this stage crosslinking must almost cease, because molecular motion is frozen in all but the remaining liquid phase.

This is illustrated in the disks of experiment I, which were postcured at 130°C. As the measurement temperature approached 130°C., a rise in $\tan \delta$ was noted, signifying the approach of the α region associated with the glass transition temperature. As the temperature was further raised, molecular motion became possible, and further cure reactions took place, until the glass transition temperature corresponded to the new cure temperature, i.e., the temperature of the new measurement. Raising the temperature to 160°C. provided the opportunity for further cure, until the glass transition temperature again corresponded to 160°C. Subsequent measurements below 160°C. confirmed the appearance of a peak characterizing the glass transition temperature somewhere above 160°C. In effect, cure during measurement made impossible a clear observation of an α loss region for the disk made in experiment I. In the subsequent experiments the postcure was done in the degradation chamber *in vacuo*, since postcure overlaps degradation. Experiment II showed the necessity of vacuum cure, oxidative degradation being appreciable by 180°C.

As will be shown, purely chemical evidence suggests that degradation proceeds by rupture of the bonds in the network, and this process is appreciable at 240°C. The scission is most probably of a homolytic nature, and though most of the free-radical ends will recombine, a fraction of them will not, leading to partial breakdown of the network. It is possible that dipole-radical effects are associated with these "free ends" and that such effects will be superimposed on the dielectric loss due to relaxations of the network. This assumes that the free ends formed by rupture have a polar character. This may explain the very high values of $\tan \delta$ found in cases in which degradation is taking place. Chemical reaction at high temperature may produce changes in the nature and concentration of free ends with time, so that values of $\tan \delta$ in these temperature regions will be time-dependent. High values of $\tan \delta$ may also be due to water formed in the degradation reaction.

The breakdown of the network, caused by bond scission, will also be associated with an increased mobility of the network and therefore a movement of the glass transition temperature, and an associated α loss region at lower temperatures may be expected. This is clearly seen in the curves for experiments V and VI in Figure 6, in which increasing degradation moves the α loss region to lower temperatures.

Practical Aspects of the Dielectric Studies. Study of the curves in Figure 6 shows that undercure is associated with a low maximum for the β loss region and a difficulty in obtaining a sharp rise for the α loss region (Fig. 7). As cure proceeds, the β loss maximum increases, and a sharp α loss rise is detected (Fig. 6, experiment III). Experiment IV shows the greatest cure (height of the β loss peak), and significant degradation has

not occurred (α loss region similar to that in experiment III). The onset of degradation is shown by a shift of the α loss region to lower temperatures and a decrease in the maximum of the β loss region (experiments V and VI). The greatest crosslinking of this hardener-resin system is achieved by 20 hr. at 95°C. in an airtight mold, followed by 1 hr. at 240°C. *in vacuo*. A vacuum is essential, oxidative degradation is appreciable by 180°C. and should be prevented. Optimal electrical and mechanical properties may be expected from high-temperature vacuum cure. Extensive cure times at 240°C. should not be used, degradation overlaps with cure.

If the dehydration theory is correct, the water generated in a degrading epoxide resin would adversely affect its electrical insulation properties.

Chemical Analysis of Degradation Products

With the use of the vacuum line apparatus described under "Degradation of Samples" and using the procedures of experiment VII (temperature 309°C., time-temperature cycle, Fig. 2b) four disks were degraded and the degradation products collected in the vacuum line. At the end of the degradation process the disks were brittle, distorted, dark brown, and opaque, and a quantity of viscous tar was found in the degradation chamber. After the degradation chamber was shut off from the vacuum line, the first trap was warmed, and some of the more volatile materials were distilled into the capsule, but their analysis did not yield conclusive results. The remaining, less volatile, materials were extracted in methanol. The resulting methanol solution was evaporated, and the resulting yellow liquid was first treated with caustic soda solution, to extract acid compounds. The remaining material was dissolved in ether. Acidifying the caustic soda solution, followed by continuous extraction with ether, gave material which, after evaporation of ether, proved to be substantially phenol (infrared spectrum, tosyl derivative, m.p. 91.5°C., infrared spectrum identical with that of tosyl derivative of phenol).

The nonacid components (in ether solution) were then extracted with dilute hydrochloric acid solution, to extract bases. The extracts were neutralized with caustic soda, yielding an emulsion, which was continuously extracted with ether. After being dried this ethereal solution was evaporated and gave two liquid phases, a mobile, brown liquid and a dark-brown oil. The mobile phase yielded a tosyl salt identical with the tosyl salt of *N*-methyl aniline (infrared spectrum).

All the amines were redissolved in hydrochloric acid and reacted with sodium nitrite solution. The yellow materials formed were extracted with ether, dried, and evaporated, to yield a yellow oil and crystals. The presence of crystals suggests a *p*-nitroso derivative of *N,N*-dimethyl aniline; there was also infrared spectral evidence of this compound in the spectra of the residues of basic components.

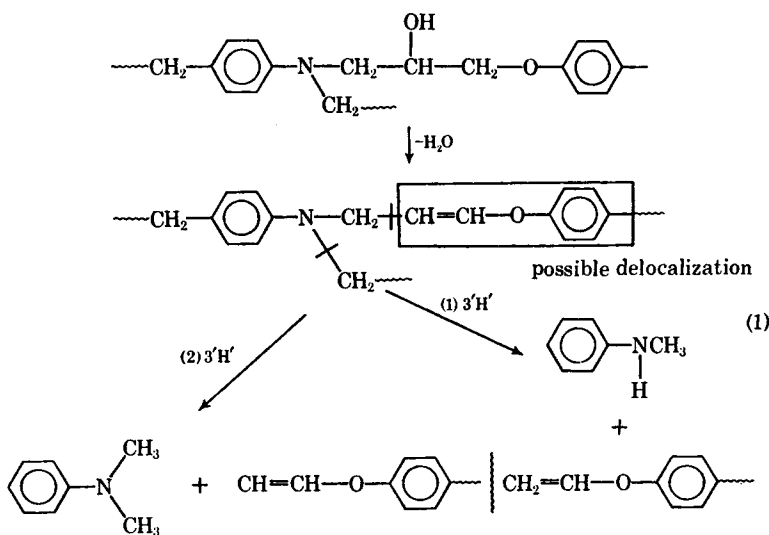
In the remaining neutral compounds there was some evidence of the existence of carbonyl compounds (formation of traces of 2,4-DNPH).

Some exploratory work was done on degradation at lower temperatures, at which no tar was found, but quantities of phenol were still observed with smaller amounts of other products, particularly amines.

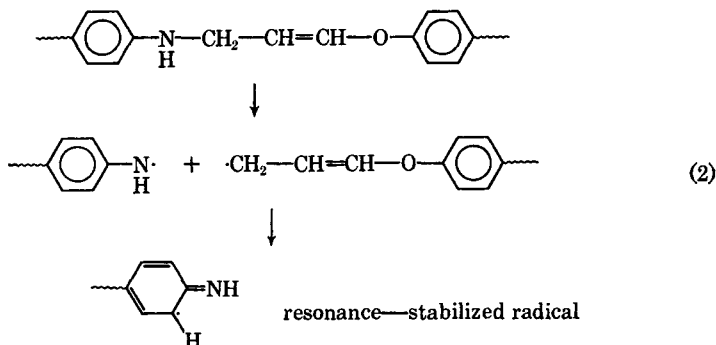
DEGRADATION REACTIONS

The dielectric evidence strongly supports the view that dehydration is concurrent with the breakdown of the network, and infrared evidence suggests that this breakdown is associated with the appearance of the $-\text{CH}=\text{CH}_2$ group. The chemical evidence shows these processes are associated with the production of *N*-methyl aniline, phenol and, possibly, *N,N*-dimethyl aniline, with other materials not certainly identified. Other workers and more recent work in these laboratories, have shown water is evolved as a degradation product. It is also significant that aniline has not been detected in significant quantities.

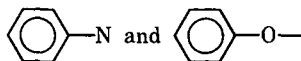
The additional evidence regarding the amines suggests some modification of the degradation schemes advanced by Keenan and Smith.²⁶ They suggested that the C—N bond was more likely to rupture than the C—C bond, but the presence of secondary and tertiary amines and the absence of aniline challenge this statement and, indeed, both ruptures may be concurrent. The present data do not clearly indicate whether dehydration precedes bond scission or not but, assuming that it does, the following reaction scheme seems reasonable:



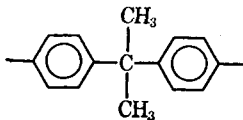
The double bond produced in dehydration is likely to be *trans* for steric reasons, and some evidence that it exists.²⁶ It is possible that resonance-stabilized free radicals are produced by a reaction such as



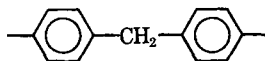
This rupture of the "cure link" is an alternative of the scheme of eq. (1). From then on, in the absence of more precise data, the proposed reaction mechanisms are more speculative; some were described by Keenan and Smith.²⁶ Further evidence concerning the amine degradation products necessitates a modification of these schemes, but *a priori* one may still assume that the



bonds are less easily ruptured than other bonds. The group

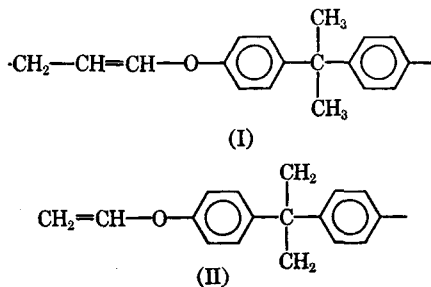


is probably somewhat unstable, for steric reasons. It is possible that the



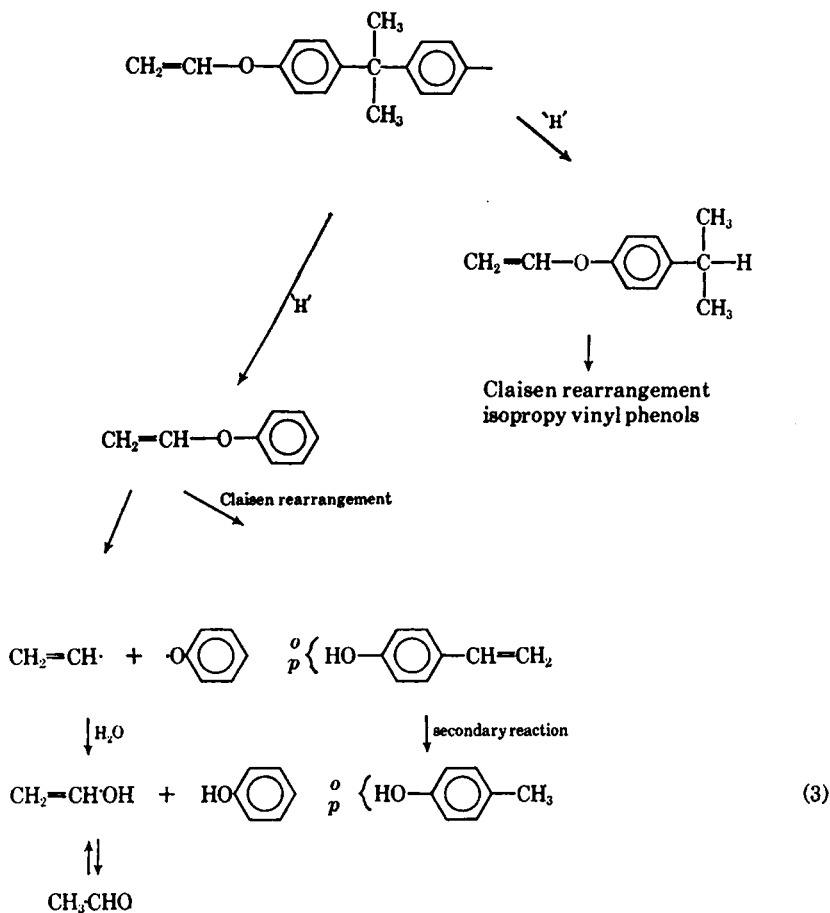
is relatively more stable owing to more favorable steric considerations and the possibility of hyperconjugation of the aliphatic hydrogen atoms.

Once the "cure link" has ruptured, there are two molecular species derived from DGEBA that may undergo further degradation:



Whereas formerly species (I) was thought to predominate, increasing evidence suggests that species (II) is present in considerable amounts. The degradation reactions of species (I) were discussed at length by Keenan and Smith²⁶ and may lead to the formation of a range of propenyl and isopropenyl phenols and cresols, probably by secondary reactions.

Considering species (II), one may postulate the following reactions:



Rupture of the DDM part of the network, in addition to substituted anilines, which have been found, might also be expected to yield *N*-substituted *p*-toluidines. These have not been found, to our knowledge.

Work with tagged carbon atoms may help to elucidate the degradation reactions of the DGEBA part of the network with more certainty, and kinetic studies may throw valuable additional light on this question.

CONCLUSIONS

Our evidence supports the theory that in epoxides cured with aromatic amines degradation is associated with a dehydration reaction and initial rupture at the "cure link," giving *N*-substituted anilines. The theory harmonizes with views put forward in an earlier paper.²⁶ Subsequent degradation produces phenol and a range of other compounds. The production of the OH group during cure reactions and its disappearance during dehydration-degradation reactions is associated with changes in the β loss region in plots of $\tan \delta$ versus temperature, and this correlates with changes in the high-temperature, α loss, region, which indicates the onset of breakdown of the resin network. Thus, in a practical sense some idea of the optimal degree of crosslinking is obtained. For this the vacuum cure appears to be essential, owing to the onset of appreciable oxidative degradation at 180°C. The dielectric evidence is correlated with infrared and weight-loss evidence.

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