The Thermal Degradation In Vacuo of an Amine-Cured Epoxide Resin

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Synopsis

The degradation in vacuo of the cured resin from stoichiometric amounts of the diglycidyl ether of bisphenol A and *p,p'*-diaminodiphenylmethane was studied at temperatures of 303.7 and 304.0 ± 0.2°C. The condensible products of the degradation at these temperatures were collected and the major components were isolated as pure compounds. These were identified as water, bisphenol A, 2-(benzofur-5-yl)-2-(*p*-hydroxyphenyl)propane, N,N,N',N'-tetramethyl-*p,p'*-diaminodiphenylmethane, phenol, *p*-isopropylphenol, *p*-isopropenylphenol, N,N-dimethylaniline, N-methylaniline, N,N-dimethyl-*p*-toluidine, benzofuran, and N-methyl-*p*-toluidine. The presence of 2,2-bis(benzofur-5-yl)propane was suspected. The gaseous degradation products were identified as acetaldehyde, chloromethane, carbon dioxide, carbon monoxide, methane, ethane, ethene, and nitrogen. Tentative reaction mechanisms are proposed to account for the formation of the products identified. The possible nature of some of the minor degradation products is discussed. The results are related to those of previous studies of the degradation of the same and similar resin–hardener systems.

INTRODUCTION

Studies of the thermal degradation of epoxide resins have ranged from those concerned with their performance as materials under stringent service conditions to basic investigations[1] of the molecular changes which the resins undergo during degradation.

Early workers[2,3,4] studied the degradation of cured and uncured resins by the analysis of the gaseous products, which formed only some few per cent of the total products. The remainder of the products was not investigated in any detail. The reaction schemes proposed for the degradations concerned only the production of gaseous species from epoxide groups and diphenylpropane units.

Lee[5,6] degraded a variety of epoxide resins both uncured and cured with amine and anhydride hardeners. It was shown that in all cases large quantities of phenolic products were formed. Gaseous products were shown to be only minor products. Lee proposed several detailed reaction schemes to account for the formation of the condensible products. In these, cured and uncured resins were not distinguished since the results

showed that phenolic products were formed in both cases. In particular, Lee investigated the degradation of a low molecular weight bisphenol A-type resin both uncured and cured with p,p'-diaminodiphenylmethane. For the uncured resin degraded at 350°C, the major volatile products were water and toluene, and at 450°C, the major volatiles were toluene, methylcyclopentadiene, and water. The major condensibles of the degradation at 475°C were phenol, cresols, ethyl-substituted phenols, isopropylphenol, isopropenylphenol, and bisphenol A. For the same resin cured with p,p'-diaminodiphenylmethane, the major volatile product of the degradation at 350°C was water (29.7 mole-%). At 450°C, the major volatiles were methylcyclopentadiene, carbon monoxide, water, carbon dioxide, acetaldehyde, chloromethane, and methane. The condensible products of the degradation at 475°C of the cured resin were similar to those of the uncured resin. No nitrogenous compounds were reported.

Keenan and Smith[7] used the hot filament technique to study the degradation of the adduct of the diglycidyl ether of bisphenol A and p,p'-diaminodiphenylmethane. The volatile products were chromatographed. Using thin-layer chromatography and infrared spectra, an attempt was made to characterize the tarry residues remaining on the pyrolysis head after degradation. The chemical structure of the cured resin was examined and the strengths of the chemical bonds were discussed. Reaction schemes were proposed which supplemented those of Lee.[5,6]

Paterson-Jones and Smith[8,9] investigated the changes in the dielectric properties of the same resin–hardener system which followed its degradation at temperatures from 200°C to 310°C. The results supported evidence for a dehydration reaction and showed that the adduct was degraded by scission of chemical bonds. Chemical analyses indicated the presence of phenol, N-methylaniline, and N,N-dimethylaniline among the reaction products. The need to consider the chemical and physical structure of the cured resin when proposing reaction mechanisms was emphasized.
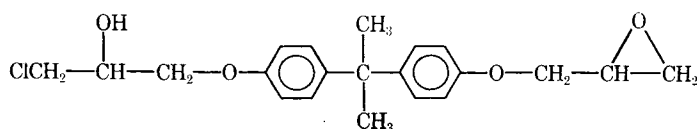
Sugita[10] identified phenol, p-isopropylphenol, p-isopropenylphenol, p-ethylphenol, aniline, and possibly p-toluidine among the products of the degradation at 500°C of a commercial bisphenol A-type resin cured with p,p'-diaminodiphenylmethane.

This paper reports the identification of the gaseous products and major condensible products of the relatively low temperature degradation of the cured resin from the diglycidyl ether of bisphenol A and p,p'-diaminodiphenylmethane.

EXPERIMENTAL

Starting Materials

The diglycidyl ether of bisphenol A (DGEBPA) and the p,p'-diaminodiphenylmethane (DDM) used for the preparation of the samples have been described in an earlier paper.[9] The DGEBPA was a fairly pure sample containing as impurities some 3.8 mole-% of molecules with the structure

$$\underset{ClCH_2}{}-\underset{\overset{\displaystyle OH}{|}}{CH}-CH_2-O-\langle\bigcirc\rangle-\underset{\overset{CH_3}{|}}{\overset{CH_3}{\underset{|}{C}}}-\langle\bigcirc\rangle-O-CH_2-CH\overset{O}{\overbrace{}}CH_2$$

and a smaller percentage of molecules with o,p'- instead of p,p'-substitution.

Cure

A quantity of DGEBPA was weighed into a glass beaker, melted, and evacuated for 20 min.   The weight loss was 0.037%.   A quantity of DDM calculated as 0.2912 of the final weight of DGEBPA was added and the mixture was heated and stirred to obtain a homogeneous solution.   The solution was again evacuated (weight loss 0.037%).   The homogeneous deaerated solution was poured into a polythene mould, cured for 210 min at 94°C, and postcured for 30 min at 165°C.   The cured resin was in the form of bars with rounded ends of dimensions 0.318 cm × 0.318 cm × 2.54 cm (between centers).

Apparatus

The degradation apparatus is shown in Figure 1.   A glass reaction vessel A was connected to a foretube B which led via three traps, C, D, E (the first two of which were detachable), to the pumping system.   The last two traps, F, H, prevented back diffusion of oil vapors from the diffusion and
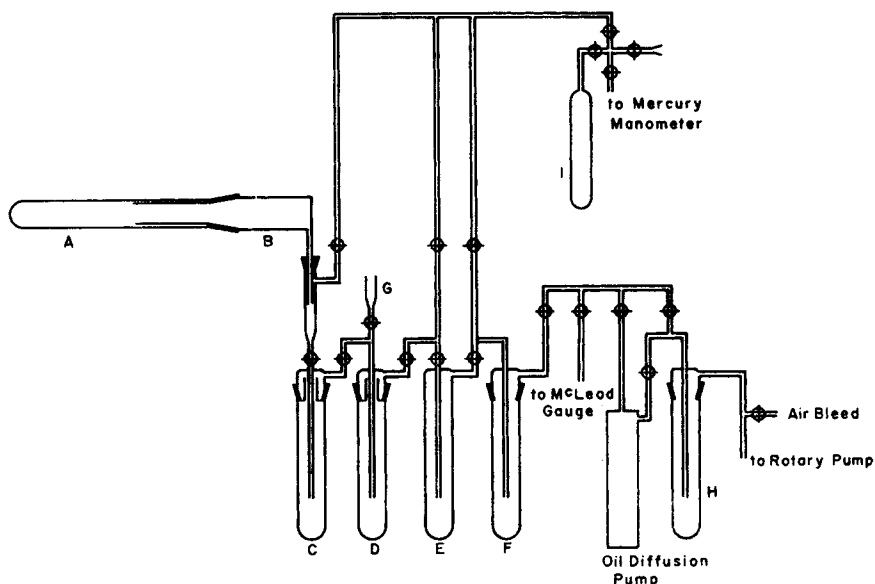

Fig. 1.

rotary pumps. Low pressures were measured by means of the McLeod gauge. Facilities were provided for the storage of gaseous products from trap E in trap I, from which samples could be removed at pressures measured on the mercury manometer. The reaction vessel was heated by surrounding it with a tube heater.

Experiments showed that the temperature inside the reaction vessel varied with time by less than 0.4°C after stabilization at the required temperature. Temperature variations over the portion of the reaction vessel containing the resin bars were within 2°C. Experiments were carried out to determine the rate of heatup of the reaction vessel after its insertion in the previously stabilized heater. A typical result is given in Table I. The degradations were clearly isothermal only after an appreciable time. Calculations showed that the resin bars followed the temperature of the reaction vessel closely.

TABLE I
Rate of Heatup of Reaction Vessel

Time, min	Temperature, °C
0	25.5
5	261.6
10	286.5
20	293.5
30	298.1
40	302.6
50	303.9
60	304.2
90	304.1
120	304.2

A Pye Model 15 Series 105 automatic preparative gas chromatograph was used for the separation and collection of condensible products.

Degradation Procedure

A quantity of resin bars was weighed into the reaction vessel which was then èvacuated for $5^1/_2$ hr to remove adsorbed air and moisture. The heater was placed in position and pumping was continued for the duration of the degradation. During degradation the three traps were maintained at temperatures of $-12.2°C$, $-77°C$, and $-196°C$, respectively. After a predetermined time the heater was removed. Pumping was continued until the reaction vessel reached room temperature. The reaction vessel and foretube and the three traps were isolated. Gaseous products were distilled into the storage trap leaving no residue in trap E. Products collected in the foretube and the remaining two traps, C and D, were dissolved and the solutions were reserved for analysis. The reaction vessel and degraded bars were washed with solvent and the washings were added to the foretube solution. The resin bars were dried under vacuum and reweighed.

Degradation Data

Experiment I. Time of degradation 150 min; final isothermal temperature, 303.7°C; initial vacuum, 10^{-6} mm Hg; initial weight of resin, 15.1294 g; weight loss, 23.7%; linear shrinkage 3%. Products in the reaction vessel and foretube were dissolved in chloroform. Products in the −12.2°C and −77°C traps were dissolved in dry methanol.

Experiment II. Time of degradation 150 min; final isothermal temperature, 304°C; initial vacuum, 10^{-5} mm Hg; initial weight of resin, 18.32245 g; weight loss, 27.6%; linear shrinkage, 3%. Products in the reaction vessel, foretube, and −12.2°C trap were dissolved in diethyl ether and the solutions were combined. Products in the −77°C trap were dissolved in diethyl ether and this solution was separated from the water present in the trap.

After degradation the resin bars in both experiments were a uniform red-brown color. Shrinkage occurred but the bars were not appreciably distorted. The bars retained little strength and were brittle. No reaction products collected in the portion of the reaction vessel covered by the heater.

Reaction Products

Gaseous Products in −196°C Trap. In both experiments samples were removed for determination of mass and infrared spectra. In addition, a sample of the gases was distilled into a trap containing methanol at −196°C. The trap was stoppered and warmed to room temperature. On treatment of a portion of the solution with Brady's reagent, a copious orange precipitate, identified as acetaldehyde 2,4-dinitrophenylhydrazone, was formed. The mass and infrared spectra of the gaseous products showed the presence (in order of abundance) of acetaldehyde, chloromethane, carbon dioxide, ethene, carbon monoxide, ethane, methane, nitrogen (trace), and water (trace).

Water. In experiment I, aliquots from the methanol solutions of the products from the −12.2°C and −77°C traps were titrated against previously standardized Karl Fischer reagent. The total water content of these traps was 809.9 mg (−77°C trap, 792 mg). Assuming that the resin is completely cured and that the only reaction of hydroxyl groups is to form water (neither assumption being strictly correct), the total possible water production is 1241 mg.

Products in −77°C Trap. In experiment I, the remaining methanol solution was dried over anhydrous sodium sulfate and chromatographed on a 15 ft × $^3/_8$ in. diam. glass preparative column packed with 25% PEG 20M poly(ethylene glycol) on 60–72 mesh silanized Celite. A temperature program of 66°C held for 10 min after injection, then increased at a rate of 12°C/min to 173°C, was used. Repeated injections showed that both the position and heights of the peaks showed wide variations over a period of a few hours and it was evident that the methanol solution was un-
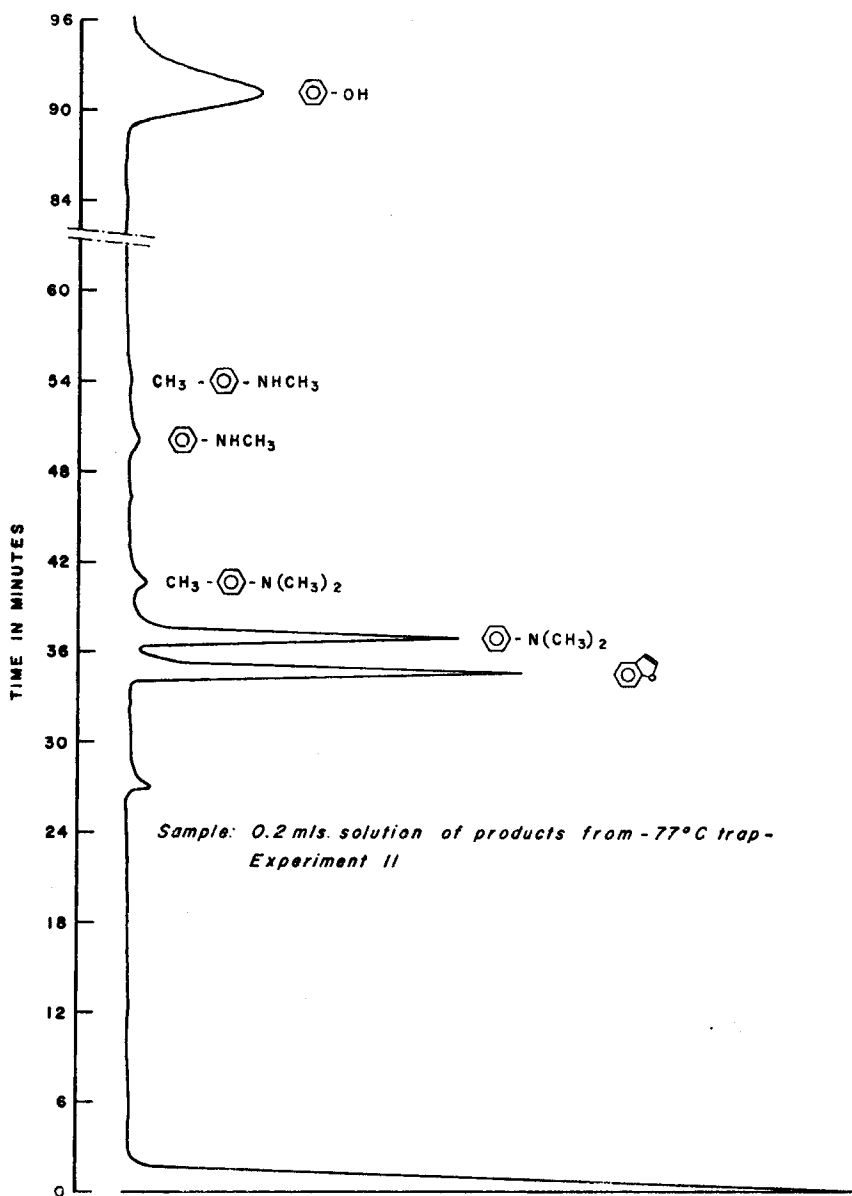
Fig. 2.

stable. Its analysis was not pursued. In experiment II, water in this trap was discarded since a quantitive analysis was obtained in experiment I and the diethyl ether solution, which proved completely stable, was analyzed (Fig. 2). Fairly large quantities of phenol, benzofuran, and N,N-dimethylaniline, small quantities of N-methylaniline and N,N-dimethyl-*p*-toluidine, and a trace of N-methyl-*p*-toluidine were present.
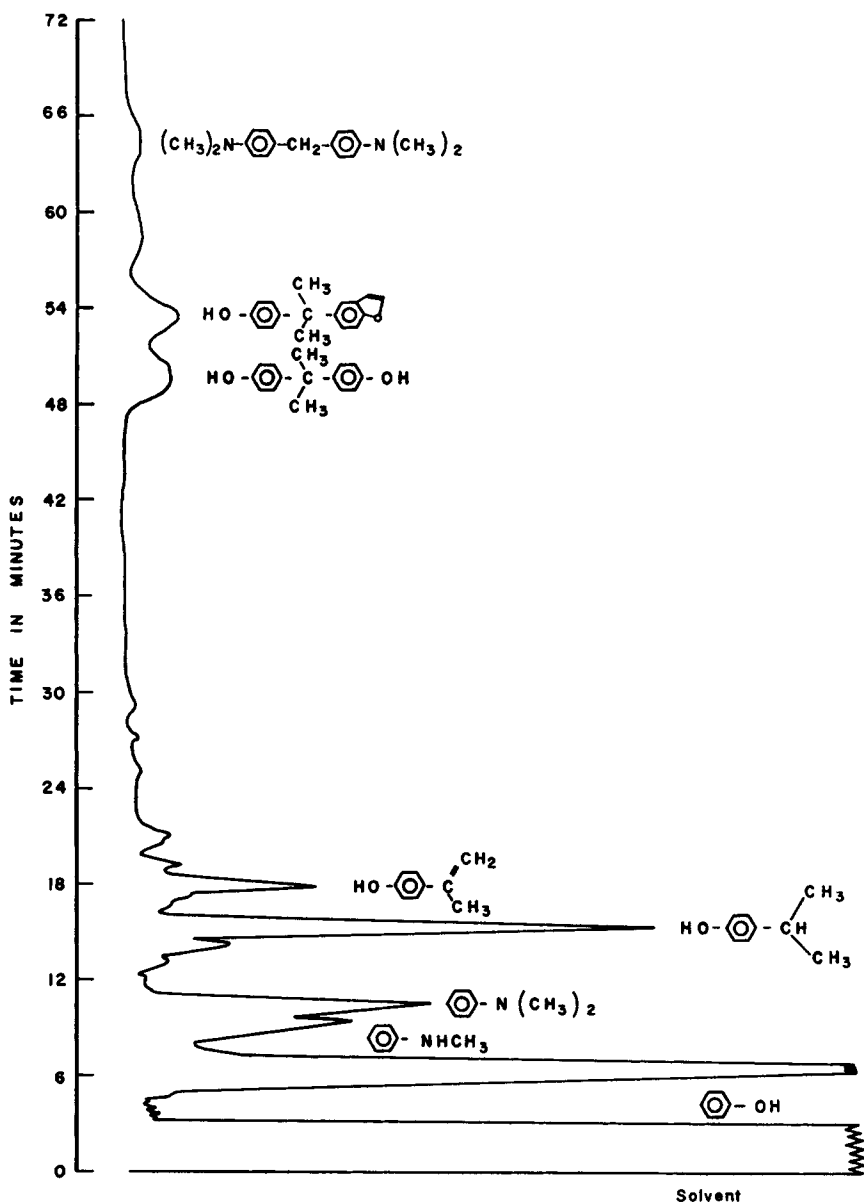
Fig. 3.

Products in −12.2°C Trap, Foretube, and Reaction Vessel. In experiment I, the methanol solution of −12.2°C trap products showed slight precipitation. The clear solution was chromatographed (Fig. 3) on a 7 ft × ³/₈ in. diam. glass preparative column packed with 25% E30 methyl silicone gum on 60–72 mesh silanized Celite. A temperature program of 131°C held for 10 min after injection, then increased at a rate of 6°C/min
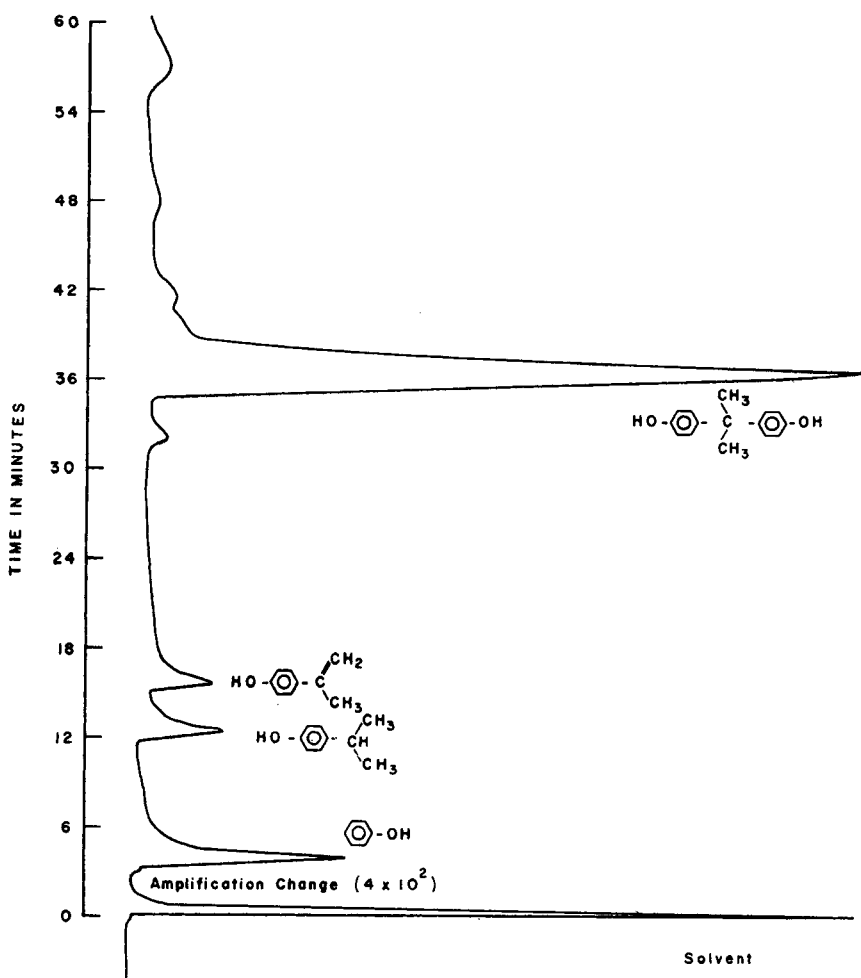
Fig. 4.

to 230°C, was used. Phenol, N-methylaniline, N,N-dimethylaniline, p-isopropylphenol, p-isopropenylphenol, bisphenol A, and 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane were isolated, collected, and identified. The presence of N,N,N′,N′-tetramethyl-p,p′-diaminodiphenylmethane was suspected. The chloroform solution of the products from the foretube and reaction vessel of experiment I showed extensive precipitation. The clear solution was chromatographed. Because of the precipitation in the solution and because the chromatogram showed that essentially the same products were present in this solution as in the −12.2°C trap solution (though in differing quantities), the analysis was not pursued. In experiment II, the ethereal solution showed no precipitation.

Since experiment I had shown the presence of acidic and basic products, in experiment II the products in diethyl ether solution from the foretube,
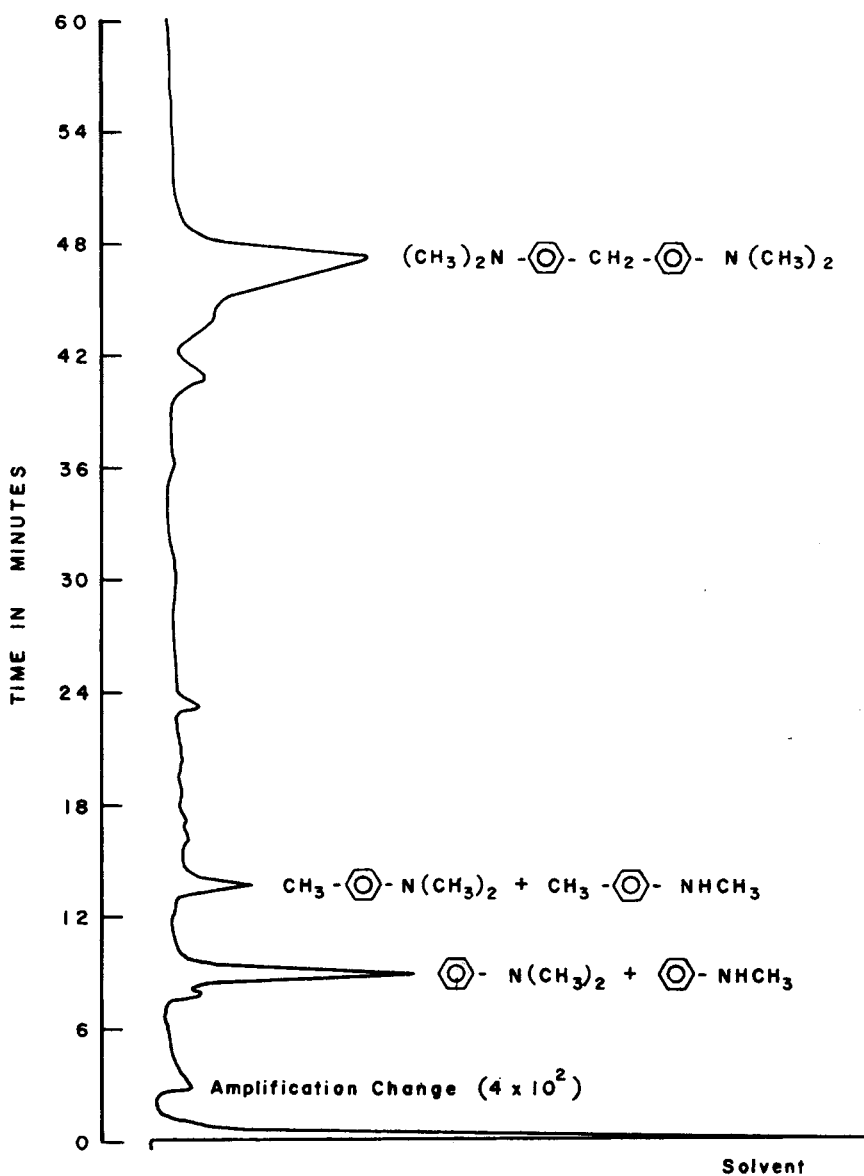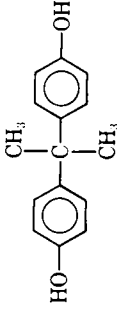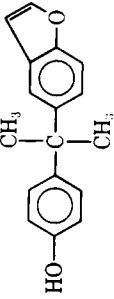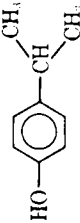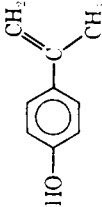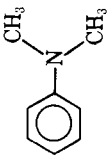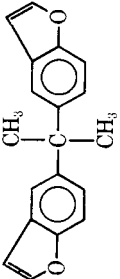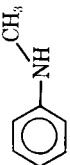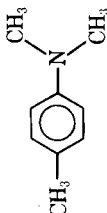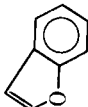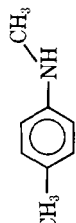
Fig. 5.

reaction vessel, and $-12.2°C$ trap were subjected to a conventional separa-
tion of acidic, basic, and neutral components.   The ethereal solution was
extracted with 10% sodium hydroxide solution.   The aqueous layer was
titrated to pH 7 with hydrochloric acid and the phenolic components were
extracted with diethyl ether.   The remaining solution was extracted with
7% hydrochloric acid.   The aqueous layer was basified and the basic com-

TABLE II

Degradation Products in Order of Abundance

Compound	Formula	Abundance	Identification methods[a] Karl Fischer assay
Water	H_2O	major product	
Bisphenol A		major product	t, i, m
2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)pro-pane		major product	t, i, m, n, s
N,N,N',N'-Tetramethyl-p,p'-diaminodiphenyl-methane		major product	t, i
Phenol		major product	g, i
p-Isopropylphenol		smaller quantities	t, i, n, d
p-Isopropenylphenol		smaller quantities	t, i, d

Compound	Structure	Quantity	Method
N,N-Dimethylaniline		smaller quantities	g, i
2,2-Bis(benzofur-5-yl)-propane		smaller quantities	i, m
N-Methylaniline		smaller quantities	g, i
N,N-Dimethyl-p-toluidine		smaller quantities	g, i
Benzofuran		smaller quantities	g, t, i, n
N-Methyl-p-toluidine		smaller quantities	g, i
Acetaldehyde	CH_3CHO	minor product	i, m, d
Chloromethane	CH_3Cl	minor product	i, m
Carbon dioxide	CO_2	minor product	i, m
Ethene	C_2H_4	minor product	m
Carbon monoxide	CO	minor product	m
Ethane	C_2H_6	minor product	m
Methane	CH_4	minor product	m
Nitrogen	N_2	trace	m

a g: GLC retention volume data; d: derivative formation; t: R_{F}, TLC; i: infrared spectrum; m: mass spectrum; n: NMR spectrum; s: synthesis.
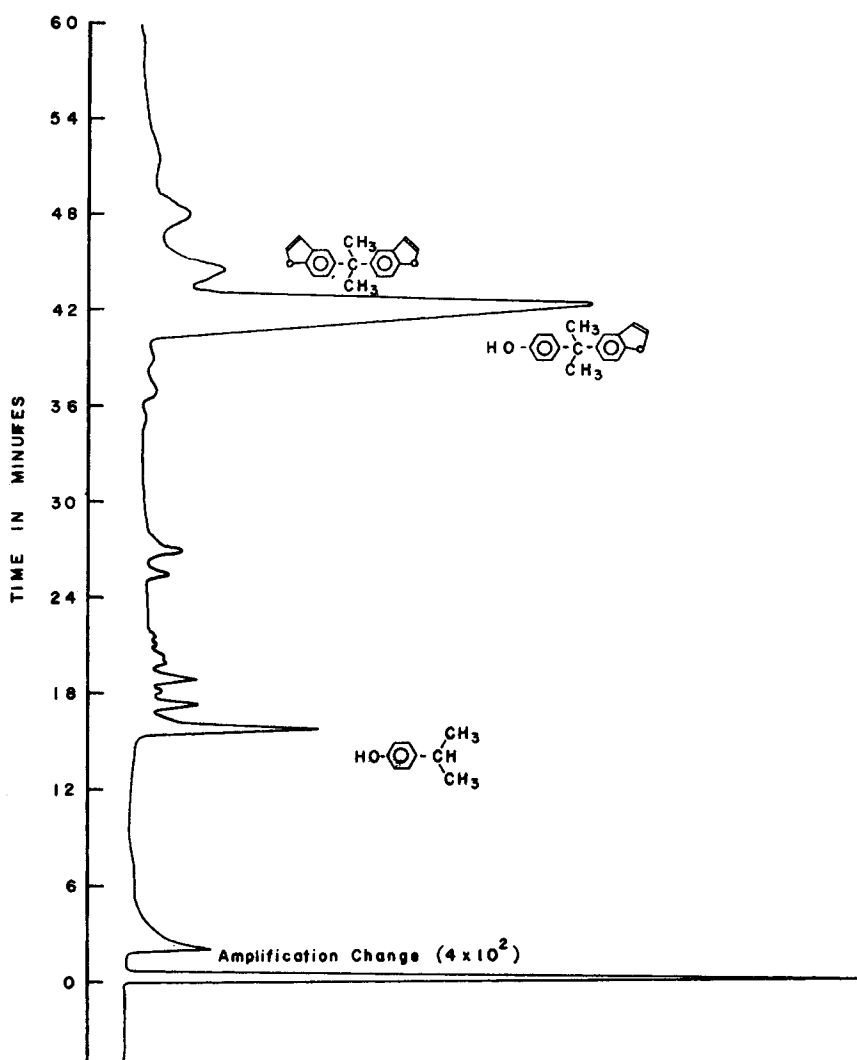
Fig. 6.

ponents were extracted with diethyl ether. The order of separations and the pH of the solutions were critical, since p-isopropenylphenol polymerizes readily in the presence of dilute acid. The benzofuryl structure polymerizes in the presence of concentrated mineral acids. The three ethereal solutions of phenolic, basic, and neutral components were each chromatographed (Figs. 4, 5, and 6) on a 7 ft $\times$ $^3/_8$ in. diam. glass preparative column packed with 15% E30 methylsilicone gum on 60–72 mesh silanized Celite. A temperature program of 105°C held for 10 min after injection, then increased at a rate of 8°C/min to 238°C, was employed. The major phenolic products were isolated, collected, and identified as bisphenol A, phenol,

p-isopropylphenol, and p-isopropenylphenol. The major basic products present were N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane, N,N-dimethylaniline, N-methylaniline, N,N-dimethyl-p-toluidine, and N-methyl-p-toluidine. The solution of neutral materials contained 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane, 2,2-bis(benzofur-5-yl)propane, and p-isopropylphenol. The presence in this solution of p-isopropylphenol showed that the initial separation of phenolic components was not clear-cut. 2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)propane is not appreciably soluble in 10% sodium hydroxide solution despite its phenolic hydroxyl. Large numbers of minor unidentified products were present.

Identification of Individual Products

The identification of the gaseous products was made from their mass spectra and infrared spectra and 2,4-dinitrophenylhydrazone formation. These methods provided the conclusive identification of individual components because of their simple chemical nature. The condensible products identified were in each case collected as pure compounds from the chromatograph, the exception being 2,2-bis(benzofur-5-yl)propane, which contained as impurities small quantities of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane and a compound of molecular weight 266 which was possibly 2-(1,4-benzopyran-6-yl)-2-(p-hydroxyphenyl)propane. Their identification was made in every case (except that of 2,2-bis(benzofur-5-yl)propane) by a comparison of their infrared spectra with those of standards obtained commercially or by synthesis, together with at least one supplementary analytical method.

Table II lists the degradation products identified, in order of abundance, together with the analytical methods used for their identification. Infrared, mass, and NMR spectra, GLC retention volume data, and TLC R_F value data for these compounds have been published.[11]

The syntheses of p-isopropenylphenol, benzofuran, and 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane have been described elsewhere.[11] Since the 2,2-bis(benzofur-5-yl)propane isolated from the reaction products was contaminated and since its infrared and mass spectra were not compared with those of a synthetic compound, its identification is not conclusive.

DISCUSSION

The Resin Structure

The resin, after the initial and postcures, is relatively well cured. In addition, further cure reactions will occur as the bars are heated in the reaction vessel and the temperature exceeds 165°C. This effect has been discussed in previous papers.[8,9] The resin which undergoes degradation is, therefore, well cured. That complete cure can never be achieved has been discussed.[8] The cure reactions for this resin–hardener system are relatively simple. The normal ring-opening reaction of the epoxide group (which initially requires traces of a proton-donating species[12,13,14]),

$$R_2N{-}H \;+\; \overset{O}{\overset{\triangle}{CH_2{-}CH}}{-}R^1 \;\longrightarrow\; R_2N{-}CH_2{-}\overset{OH}{\underset{}{CH}}{-}R^1$$
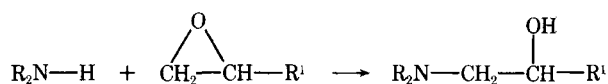
is not accompanied to any appreciable extent by the abnormal ring opening reaction

$$R_2NH \;+\; \overset{O}{\overset{\triangle}{CH_2{-}CH}}{-}R^1 \;\longrightarrow\; \overset{OH}{\underset{NR_2}{\overset{}{CH_2{-}CH{-}R^1}}}$$
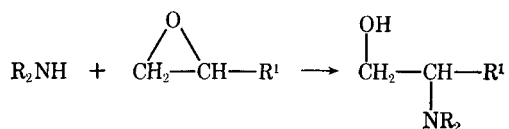
or by etherification of hydroxyl groups:

$$R_2N{-}CH_2{-}\overset{OH}{\overset{}{CH}}{-}R^1 \;+\; \overset{O}{\overset{\triangle}{CH_2{-}CH}}{-}R^1 \;\longrightarrow\; R_2N{-}CH_2{-}CH{-}R^1$$
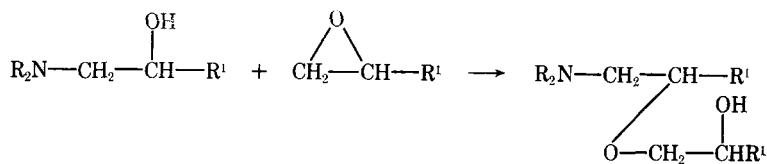
In view of this and the relative completeness of the cure, an idealized network (partstructures I and II) can be considered:

I

II
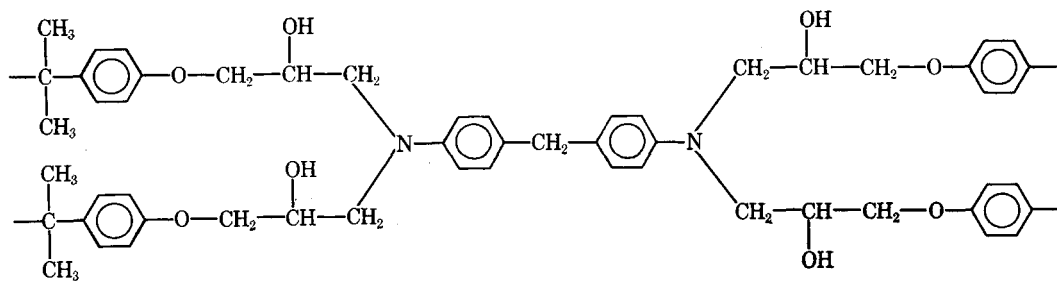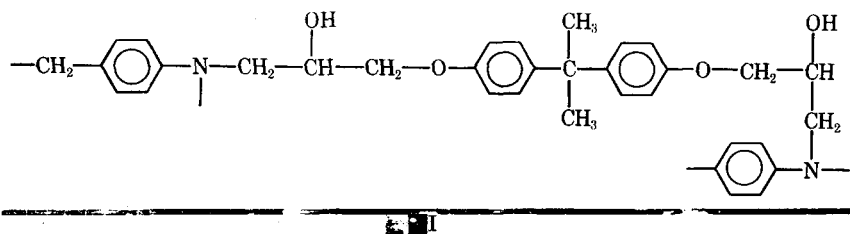
The structure is amorphous, highly crosslinked, and random, so that the number of pairs of bisphenol A residues linked to the same two nitrogen atoms is small.[8,11]   Partstructures III and IV,
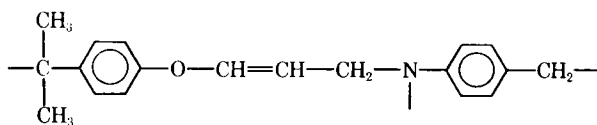
III
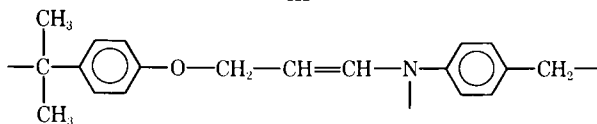
IV

show the most probable structures for the glyceryl portion of the network which are formed by its dehydration.

Chemical Bond Strengths

Keenan and Smith[7] discussed the stabilities of the bonds in the network and a comprehensive discussion extending these authors' conclusions has been published.[11] The results are summarized in Table III.

TABLE III
Bond Dissociation Energies

Approximate bond dissociation energy	
Bond	kcal/mole
ϕ—O	100
ϕ—N	95
(CH=CH)—O and (CH=CH)—N	>90
(CH=CH)—C	90
C—O	90
C—C and C—N	80
CH$_2$—ϕ	<76.5
((CH$_3$)$_2$—C)—ϕ	≪76.5
(CH=CH—H$_2$C)—O	70
(CH=CH—H$_2$C)—N	65

Reaction Mechanisms

The reactions outlined below illustrate possible routes to the formation of the products identified. The postulated schemes are speculative.

The chemical and dielectric results of previous investigations[5−9] showed that the network must degrade, in part at least, by the scission of chemical bonds in the network. In the absence of agents likely to catalyze an ionic scission (heterolytic fission), it appears probable that homolytic scission of chemical bonds occurs preferentially since, in general, such a process requires less energy than heterolytic fission. There is evidence for free radical formation.[7]

During degradation, the network is above its glass transition temperature.[11] Despite this, because of its highly crosslinked structure, the move-

ment of any part of the network relative to another is severely hindered. Because of this, the tentative degradation schemes proposed are largely limited to a consideration of the scission of chemical bonds in the network and to how such reactions lead to the production of small molecules. An exceptional reaction is the dehydration of the network.

Dehydration Reaction

The formation of water from the ether oxygen is not reasonable because of the stability of the aryl-oxygen bond. The formation of water from the aliphatic hydroxyl group can occur in several ways. Elimination of water from the network can lead to structures III and IV. In addition, elimination of water from two neighboring hydroxyl groups may lead to an ether structure:

V
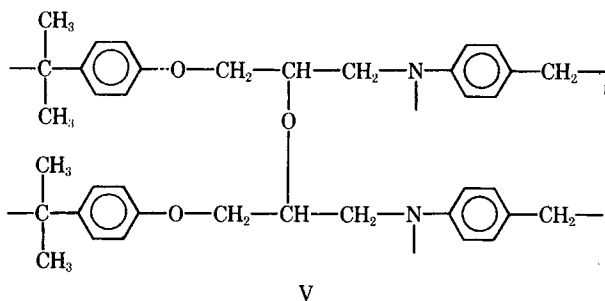
In the case where a common nitrogen atom joins the chains, a morpholine-type structure may be produced:

Va
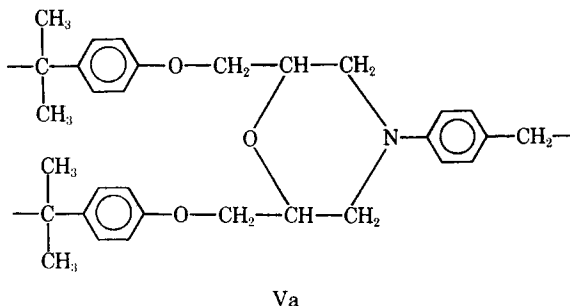
Structures V and Va are not likely to be found in large numbers. This is because, on account of the random structure of the network, the number of pairs of hydroxyl groups which at any time are close enough to react is small. It is postulated, therefore, that degradation largely results in the formation of structures III and IV. The driving force behind the reaction is the large increase in stability of the system which follows double bond formation. This is especially true because the double bonds so formed are pseudo-conjugated via an oxygen or nitrogen atom with an aromatic ring.[7]

The available evidence[8,9,11] indicates that dehydration probably precedes to a large extent any further degradation of the network.

Formation of Major Condensible Products

The formation of a small molecule from the network requires at least two scissions of its chemical bonds.   The formation of all the condensible products can be explained on this basis.   It is not necessary to assume reaction between neighboring chains which, in any event, would not lead to large quantities of any one product because the random nature of the network and the restrictions on its internal mobility would preclude such specific interactions.

The reactions outlined below are classified according to the scission of particular chemical bonds.   In all cases, except the reaction to form benzo-furyl and methylamino structures, which is exceptional, the nature of the products formed is a direct result of the scission of the less stable bonds in the network.

Aryl—Isopropyl Scission

The scission of this bond may be followed by either of two processes. The free radicals produced may abstract hydrogen from neighboring portions of the network being saturated, or may disproportionate:

p-isopropylphenol
phenol
benzofuran

phenol
p-isopropenylphenol
benzofuran

The isopropyl radical is stabilized by resonance with the benzene ring and by hyperconjugative effects.[11]

Aryl—Methylene Scission

N,N-dimethylaniline
N-methylaniline

N,N-dimethyl-p-toluidine
N-methyl-p-toluidine

Allyl—Oxygen Scission[5,6]

phenol, bisphenol A,
2-(benzofur-5-yl)-2-
(p-hydroxyphenyl) propane

(substituted propenyl radical is
resonance stabilised[11])

p-isopropylphenol
p-isopropenylphenol
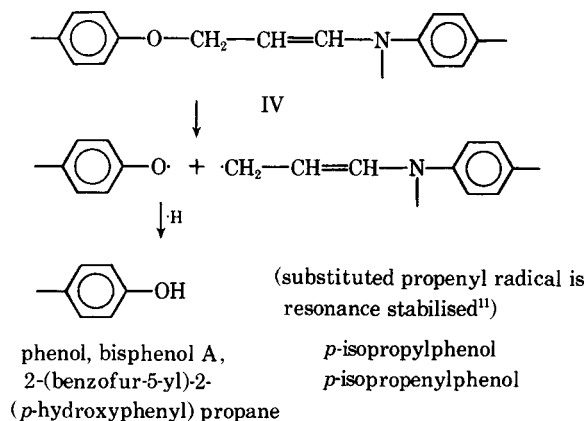
Allyl—Nitrogen Scission

(propenyl radical is
resonance stabilised[11])

N-methylaniline
N-methyl-p-toluidine
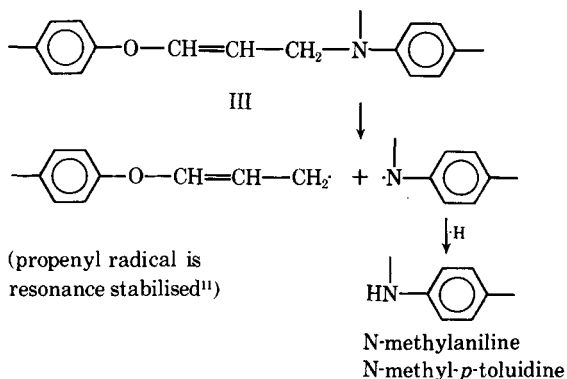
It is possible that the secondary amines are formed also from an incompletely cured dehydrated structure:
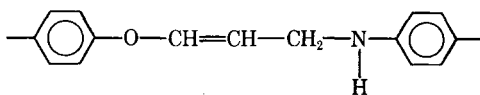
but the percentage of such structures in the resin is small.[11]

Benzofuryl and Methylamino Structures

The formation of only small quantities of secondary amines and the fact that primary amines were not among the major degradation products suggests that the above reaction occurs only to a limited extent. The presence of benzofuryl and methylamino structures among the major products indicates that allyl C—N fission is largely superceded by a reaction in which these products are formed preferentially. The precise nature of the reaction is not known, although cyclization of partstructure III has been proposed[11] to account for their formation.

Gaseous Products

The gaseous products were all minor products of the degradation.

The formation of acetaldehyde has been postulated to occur via a scission of the network before its dehydration.[11]   The pyrolysis of acetaldehyde[15] leads to the formation of carbon monoxide, methane, and traces of ethane. The formation of ethane and ethene has been explained[11] from degradation of the isopropyl moiety.   Chloromethane is formed from chlorinated molecules originally present as an impurity in the diglycidyl ether of bisphenol A.   Carbon dioxide probably arises from oxidation reactions from adsorbed oxygen from the air.   The traces of nitrogen present are probably from absorbed air.   Nitrogen is not formed from the network.   (The aryl-nitrogen bond is extremely stable.)

Possible Nature of Minor Condensible Products

The gas–liquid chromatograms showed the presence of large numbers of minor condensible products.   The nature of some of these can be predicted on the basis of the knowledge gained about the degradation.

5-Isopropylbenzofuran, 5-isopropenylbenzofuran, N,N,N'-trimethyl-p,p'-diaminodiphenylmethane, and N,N'-dimethyl-p,p'-diaminodiphenylmethane are likely products.   In addition, products containing the primary amine structure (aniline, p-toluidine, N,N-dimethyl-p,p'-diaminodiphenylmethane, N-methyl-p,p'-diaminodiphenylmethane, and p,p'-diaminodiphenylmethane) are likely to be formed in small quantities via two allylic-nitrogen bond scissions involving the same nitrogen atom.

So far, no mention has been made of the fate of the propenyl radicals remaining in the network following allylic-nitrogen and allylic-oxygen bond scissions, viz.:
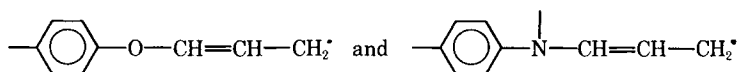
Lee[6] postulated the formation of 1,4-benzopyranyl structures from the degradation at 470°C of an uncured low molecular weight bisphenol A-type epoxide resin.   Mass peaks 132, 146, 160, and 174 in the mass spectrum of the degradation products were attributed by Lee to 1,4-benzopyran and methyl-, ethyl-, and propyl-substituted 1,4-benzopyran, respectively.   A mass peak 132 was also present in the mass spectrum of the products from degradation[5] at 475°C of a low molecular weight bisphenol A-type resin cured with p,p'-diaminodiphenylmethane.   There is no concrete evidence for the formation of benzopyranyl structures during degradation of epoxide resins, but a possible reaction of the phenoxypropenyl radical is cyclization to form 1,4-benzopyrans.

An interesting product found by Lee[5] for the degradation of this resin–hardener system at 450°C was methylcyclopentadiene.   This product may be formed[11] from reactions of propenyl structures left in the resin.   Such

structures are probably present in large quantities following the initial degradation reactions.

The Residual Resin

It is clear that the loss from the network of saturated degradation products must lead to the formation in the resin of a highly unsaturated structure. The term "unsaturated" implies the presence of both double bonds and unpaired electrons. The structure of the resin remaining in the latter stages of degradation bears little resemblance to its original structure. The coloration of the resin bars after degradation is consistent with their highly unsaturated structure. It is probable that further crosslinking reactions involving both double bonds and radical recombination occur in the later stages of degradation. The extent of this is not, however, such that the resin retains its original good mechanical and electrical properties. The resin bars after degradation were brittle, a property typically associated with rigid polymers of low molecular weight.

CONCLUSION

The degradation of the adduct of DGEBPA and DDM may be considered as occurring in four stages:

1. At low temperatures (220°C to 240°C), appreciable scission of the least stable bonds (viz., the aryl-methylene and aryl-isopropyl bonds) occurs.[8] The radicals formed may recombine, disproportionate, or abstract hydrogen.

2. At higher temperatures (above 250°C or thereabouts), a dehydration reaction modifies and weakens the network structure and paves the way for its further degradation.

3. At temperatures above 280°C or 290°C, the weakened structure breaks down and small fragments of the network appear as phenolic, benzofuryl, and basic compounds together with large numbers of minor products.

4. At higher temperatures the remaining structure, which is highly unsaturated, may react to form further products, e.g., methylcyclopentadiene.

The degradation of amine-cured epoxides of higher molecular weight may be expected to yield similar products, except that in this case larger quantities of phenolic and possibly benzopyranyl structures would be expected from the unit

$$\text{—}\langle\bigcirc\rangle\text{—O—CH}_2\text{—}\overset{\displaystyle \overset{\text{OH}}{|}}{\text{CH}}\text{—CH}_2\text{—O—}\langle\bigcirc\rangle\text{—}$$
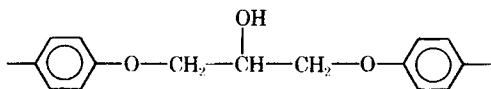
The degradation of anhydride-cured or catalyst-cured epoxide resins is likely to differ markedly because of the appreciable etherification and esterification of the hydroxyl groups in the network which occur during cure. The extra thermal stability of anhydride-cured epoxide resins over that of amine-cured resins is probably a direct consequence of the reduction in the

number of pendant hydroxyl groups present in their structure.   The possibility of dehydration of the network is thus greatly reduced and the formation of the weakened dehydrated structure is precluded to some extent.

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