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Low Temperature Rearrangement of Amine Cured Epoxy Resins

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ABSTRACT

Studies are reported on the rearrangements which occur in epoxy resins when heated above 497 K. The nature of the processes which occur in the resin and in model compounds is discussed with reference to changes in the ultraviolet, infra-red and ^{13}C *and* ^{1}H *NMR spectra. Chain scission is preceded by dehydration of the glycidyl segment and occurs at the C—N and O—C bonds, generating phenoxy radicals in the latter case. The observed coloration of the resin at high temperatures is associated with the formation of a polyenyl structure and the possible generation of quinoid and cyclic conjugated nitrogen-containing aromatic ring structures.*

INTRODUCTION

Epoxy resins are widely used as structural adhesives in the aerospace industry and they have, as a consequence, been studied extensively from the point of view of thermal stability.[1-19] In a recent paper,[18] we indicated that increases in the strength of lap joints post cured above 497 K can be correlated with changes in the colour of the resin. In this

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paper, we attempt to identify the nature of the chemical changes which are occurring within the resin and lead to increased adhesion to the substrate.

Review of low temperature rearrangement and degradation in epoxy resins

The majority of the investigations on epoxy resins have been performed at temperatures of 573 K and higher. It has, however, been recognised that rearrangement of the resin can occur at much lower temperatures. The previous paper[18] indicated that visible colour changes can be detected as low as 497 K. Before presenting the data obtained on thermally induced changes we will consider the present state of understanding of thermal and thermal oxidative degradation of epoxy resins alone and cured with amine hardeners.

Four possible degradation schemes for uncured expoxy resins have been proposed by Lee:[1]

(1) Isomerisation of the uncured epoxy group to the aldehyde followed by cleavage with the formation of phenol derivatives and volatile products.
(2) Ether cleavage followed by various scission reactions leading to volatile products.
(3) Homopolymerised epoxy cleavage.
(4) Various oxidative routes.

These processes are summarised in Fig. 1 and will occur to some extent at high temperatures, 823 K, where most aliphatic bonds can undergo chain scission. However, typical resin systems contain a curing agent, usually a bi- or tetra-functional amine.

The degradation of amine cured epoxy resins has been explored by Keenan and Smith.[2] They observed that the degradation processes can be sub-divided into two groups: low temperature processes occurring below 498 K and high temperature processes above. The lower temperature process is preceded by a degradation reaction (Fig. 2). Much of the data upon which this scheme is based has been questioned. However, strong evidence appears to exist for the initial step involving a dehydration reaction.

Infra-red studies by Dante and Conley[5] on the degradation of amine cured epoxy resins at 373, 448 and 498 K indicate that, as degradation proceeds, two new bands at 5·8 and 6·0 μm are observed assigned to the generation of carbonyl and N-substituted oximes, respectively. Chain scission is believed to occur at the weakest bond, the 1,2-amino alcohol

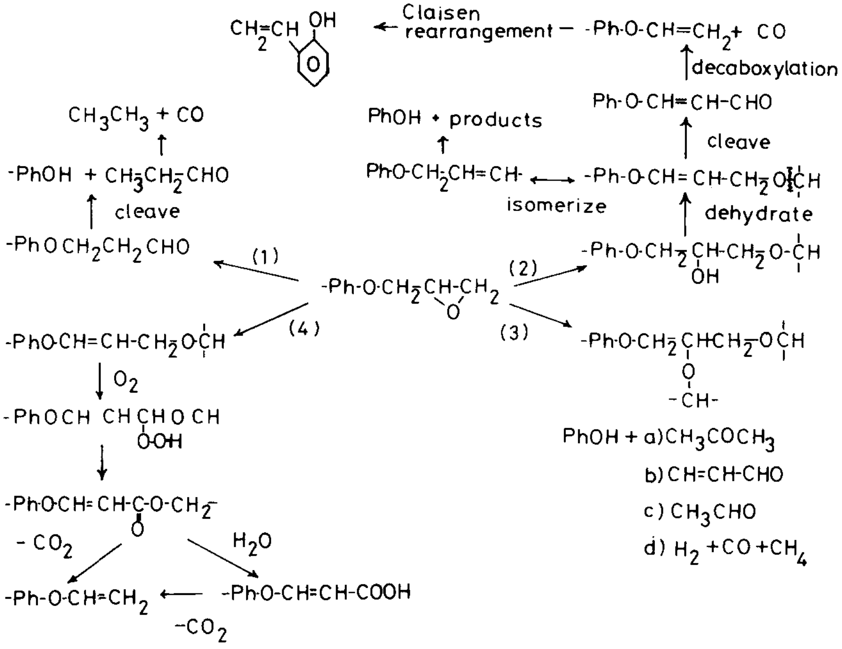


Fig. 1. Degradation scheme proposed by Lee[1] for amine cured epoxy resins (for simplicity certain details of the mechanism, i.e. hydrogen abstraction processes, have been omitted in this and subsequent schemes).

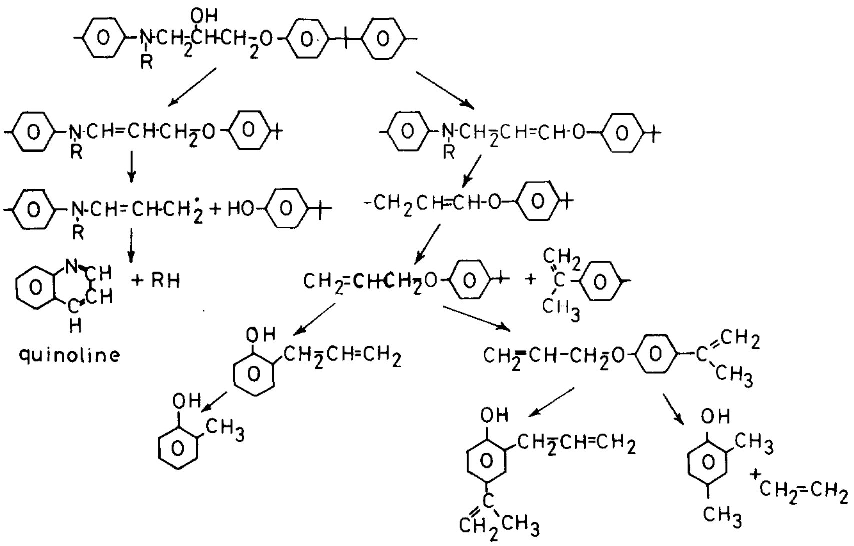


Fig. 2. Degradation scheme proposed by Keenan and Smith[2] for amine cured epoxy resins.

sequence, and would be expected, as is in fact observed, to be sensitive to the type of curing agent used. Additional evidence for this proposition is gained from a lack of change in the infra-red spectrum on heating anhydride cured epoxy resins to 498 K.

A possible mechanism based on the infra-red evidence described above is presented in Fig. 3. The N-oxime formed initially undergoes chain scission to form various carbonyl-containing compounds. Evidence for the generation of hydroxylamine and N-oxime comes from the infra-red studies. However, the detection and identification of the aldehyde and its various oxidation products is far less conclusive. Other schemes have been proposed in which direct oxidation occurs at either the secondary hydroxyl or the bisphenol moiety. However, their validity has not so far been substantiated.

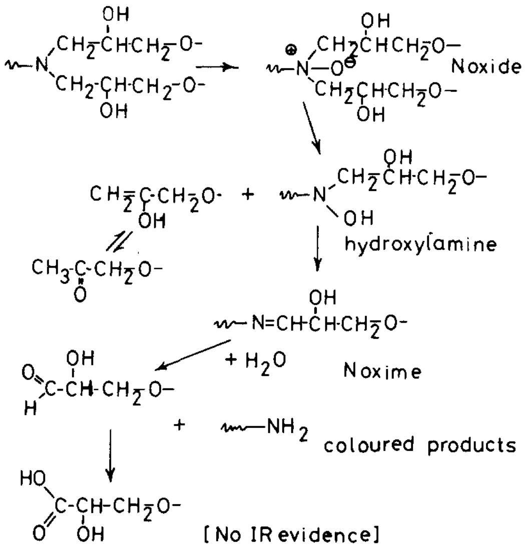


Fig. 3. Degradation scheme proposed by Dante and Conley[5] for amine cured epoxy resins.

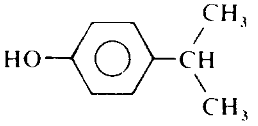
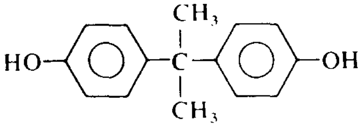
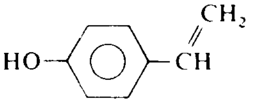
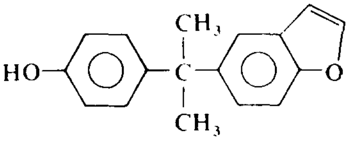
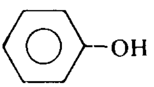
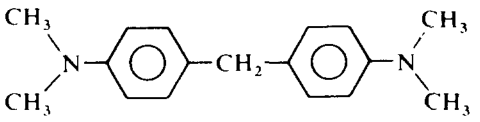
Thermal degradation of epoxy resins has been observed to generate 'long lived' free radicals, which exist for up to 5 months after their generation.[7,8] Similar species have been reported by Conley[11] and are associated with the appearance of infra-red absorptions at 1650–1680 cm^{-1} ascribed to quinoid type structures.

Studies of epoxy resins containing novalak resins indicate that thermal oxidative degradation at 438 K is associated with changes in the structure of the bisphenol moiety.[11] The appearance of infra-red absorption at 1665 and 1735 cm^{-1} is characteristic of the hydroxy substituted benzophenone structure. This process does not occur in vacuum and occurs more readily with the methylene bridge of the novalak resin than with the *iso*-propylene bridge of the bis-phenol A.

A comprehensive study of amine cured epoxy resins has been performed by Patterson-Jones and his co-workers on a resin formed from the diglycidyl ether of bisphenol-A (DGEBA) and diamino diphenyl methane.[13-16] Two degradation processes have been identified based on studies performed *in vacuo* at 577 K. The products of degradation were analysed using HPLC, infra-red and NMR and the major and minor products of degradation are listed in Table 1. Scheme (I) in Fig. 4 involves

TABLE 1

Degradation Products Observed with Amine Cured Epoxy Resins

Major degradation products	*Minor Products*
H_2O	
	
	
	
	

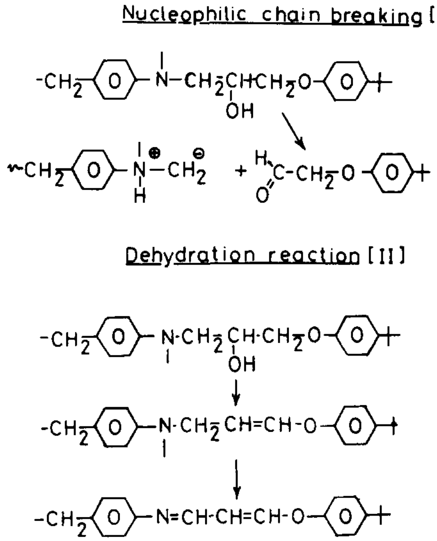


Fig. 4. Degradation scheme proposed by Patterson-Jones and his co-workers[12-16] for amine cured epoxy resins.

nucleophilic chain breaking whereas Scheme (II) is initiated by a dehydration reaction. All the major products, except for benzofuran, can be found as a consequence of chain scission of the least stable bond in the dehydrated structure. The fact that benzofuran and methyl amine structures are amongst the major products indicates that alkyl C—N fission is largely superseded by reaction (I). Therefore it would appear that reaction (I) occurs at lower temperatures than reaction (II). Related studies on 1,3 diphenoxypropane-2-ol have indicated that it is relatively stable and dehydration is a minor degradation reaction, whereas 1,3 diphenoxypropane degrades rapidly. The presence of a nitrogen atom modifies the stability of the glycerol segment catalysing the dehydration to form a 1,3 diphenoxypropane structure which degrades readily and has been demonstrated in studies of 1(N-ethyl anilino)-3-phenoxy propen-2-ol. Whether or not the same mechanisms operate in atmospheric conditions is not clear.

In summary, amine cured epoxy resins are heat sensitive as a consequence of the presence of the nucleophilic nitrogen in the backbone. Use of anhydride and catalysed cures eliminates the nitrogen and also reduces the number of pendant hydroxyl groups and therefore the possibility of dehydration is reduced and degradation is suppressed.

A recent study of three epoxy systems cured with trimethoxy borazine (TMB)[10] has shown that degradation involves the epoxy resin chain. Unfortunately, the reference used in this Fourier transform infra-red study was DGEBA, which itself may be subject to oxidation during its cure which was performed at 493 K. It was suggested that isomerisation of the epoxide group occurs to the aldehyde which subsequently forms a per ester. This study is complicated by the author's use of acetone as a solvent in the formation of the films used in these studies and this could possibly be retained in the crosslinked matrix. On the basis of the analysis of the infra-red spectra it was concluded that the order of functional group stability to thermal degradation is methyl-benzyl > methylene > *p*-phenylene > ether > *iso*-propylidene linkages. This implies that the weakest element in the homopolymerised structure is the *iso*-propylidene bridge group. Bowen[19] has shown, using ^{14}C labels, that the glycidyl group is less stable than the *iso*-propylidene group in both oxidative and non-oxidative conditions.

The instability of the *p*-phenylene linkages compared with the total substituted benzene ring has been discussed by Lin.[9] Claisen rearrangement of the aryl alkyl ether to form the more heat stable 1,2,4 trisubstituted benzene as in Fig. 5, has been proposed. Evidence for the generation of these species is based on the appearance of absorptions at 815, 1425, 1480 and 1600 cm^{-1}.

Under thermoxidative conditions it is found that the degradation rate is enhanced by the formation of carbonyl groups, as evidenced by the appearance of absorptions at 1620–1800 cm^{-1} and a specific peroxide

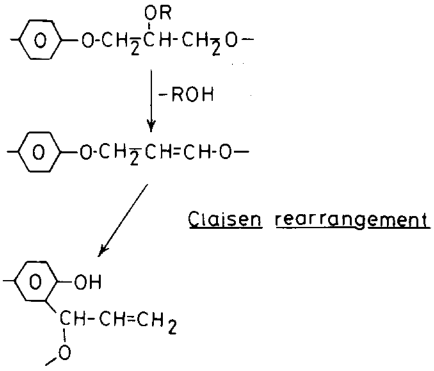


Fig. 5. Degradation scheme proposed by Lin[9] involving Claison rearrangement of the aryl alkyl ether.

band at 885 cm^{-1}, implying that the thermoxidative degradation is a radical autocatalytic process. A similar conclusion has been put forward by Neimann on the basis of studies of induction times for degradation as a function of oxygen pressure.[3,20]

The observation by Lin of carbonyl bands at 1808, 1784, 1765, 1732 and 1665 cm^{-1} has been explained on the basis of attack at the α position of ethers and subsequent scission and rearrangement to form esters, acids, aldehydes and acid anhydrides. The precursor for these reactions is the loss of a methyl group in the *iso*-propylidene bridge, followed by subsequent peroxide formation and Wieland rearrangement (Fig. 6).

Although the studies performed to date indicate the complexity of the possible degradation routes in the decomposition of epoxy resins, they do not indicate the origin of the colour generated when samples are heated above 493 K. In this study we report a systematic investigation of the degradation of an amine cured epoxy resin and of its model compound, the study being directed towards understanding the changes which occur on post curing and which lead to the improved adhesion[18] and peel strength.

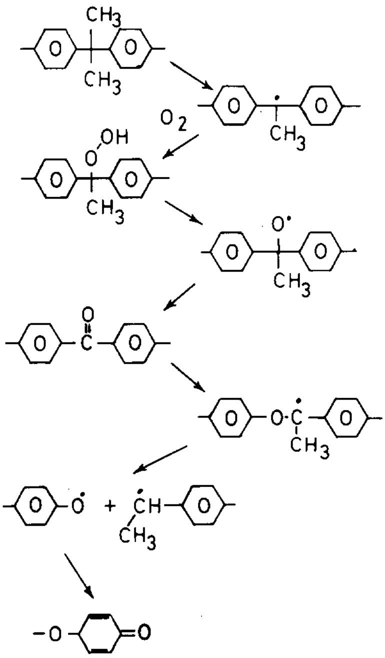


Fig. 6. Generation of semiquinone structures due to Sidyakin.[20]

EXPERIMENTAL

Materials

The samples used in this study were obtained by curing the diglycidyl ether of bisphenol-A (DGEBA) with triethyl tetramine (TETA). The DGEBA was obtained as a commercial sample from Ciba Geigy and has a code MY 790; the TETA was obtained from BDH. The resin was cured at 333 K, the ratio of TETA to DGEBA being 14:100. The cure was allowed to proceed for 2 h, whereupon a solid matrix is formed. Subsequent cure was performed for a further 16 h at 373 K. The cure of the resin was monitored by the disappearance of the epoxide ring absorption at $915\,cm^{-1}$. A model system was also studied; this was the result of the reaction of diethyl amine (DEA) with DGEBA.

It was prepared by refluxing DGEBA with an excess of DEA at 308 K, the boiling point of DEA being 328 K. The excess of DEA was removed after cure was complete.

Methods of analysis

Infra-red spectroscopy
Epoxy films cast directly on to KBr discs and cured at 373 K were explored over the frequency range 4000–$400\,cm^{-1}$ using a Perkin Elmer 397 infra-red spectrophotometer. The films were approximately 0·01 mm thick. The resin, DGEBA/TETA, was post cured for 1 h at each of the following temperatures—428, 448, 463, 483, 503, 518, 533 and 558 K—and the infra-red spectra were recorded.

Ultraviolet spectra
Epoxy resin films were deposited on quartz slides and their ultraviolet spectra examined using a Perkin Elmer 402 spectrophotometer. The films were prepared using chloroform as a solvent and were subjected to the same cure and post cure schedule as that described for the infra-red study. Spectra were recorded over the range 190–830 nm.

Carbon-13 NMR spectra
Solutions of DGEBA/DEA in $CDCl_3$ were investigated using a Jeol PS-100 PFT-100 spectrometer operating at 25·15 MHz with a deuterium lock and proton noise decoupling. The degradative changes were followed by

infra-red and spectra were obtained until definitive changes were detected in the ^{13}C spectrum.

Studies of the solid DGEBA/TETA were performed using a Bruker CXP-300 spectrometer at 75·46 MHz. Both 'magic angle' rotation and 'proton enhanced' techniques were employed. Machined cylindrical samples (diameter 7 mm) were spun at speeds of up to 3250 Hz. All the spectra were obtained using identical conditions for spectrum width, carrier frequency offset and are referenced to adamantane. Samples were post cured to 373, 423, 473 and 523 K.

Electron spin resonance measurements

These were performed using a Jeol JES-FE spectrometer. Samples of DGEBA/TETA were cured in a glass ESR tube and subsequently degraded at 498 K before being placed in the resonance cavity. The spectrometer was calibrated using Mn^{2+} dispersed in MgO.

RESULTS AND DISCUSSION

In a previous paper we reported that the colour of epoxy resin films changed dramatically when heated above 473 K. An increase in the tensile strength of lap joints was also observed to occur as a consequence of the post cure. In this study we attempt to define the nature of the rearrangements of the epoxy structure which lead to this colour change. Since DGEBA/TETA is a highly crosslinked resin, a model compound, DGEBA/DEA, was considered for the initial investigations. In all these studies particular care was taken to ensure that full cure had been achieved as determined by the disappearance of the epoxy group absorption at 915 cm^{-1}.

Thermoxidative degradation of model compound DGEBA/DEA

Infra-red spectra

The changes in the infra-red spectrum which occur on curing the above system are shown in Fig. 7 and assigned in Table 2. The principal changes which occur are associated with the loss of the N–H stretching vibration with the generation of an O—H stretch and the disappearance of the epoxy ring vibrations. Degradation is more difficult to achieve in this model system; heating for 12 h at 473 K being required to achieve the

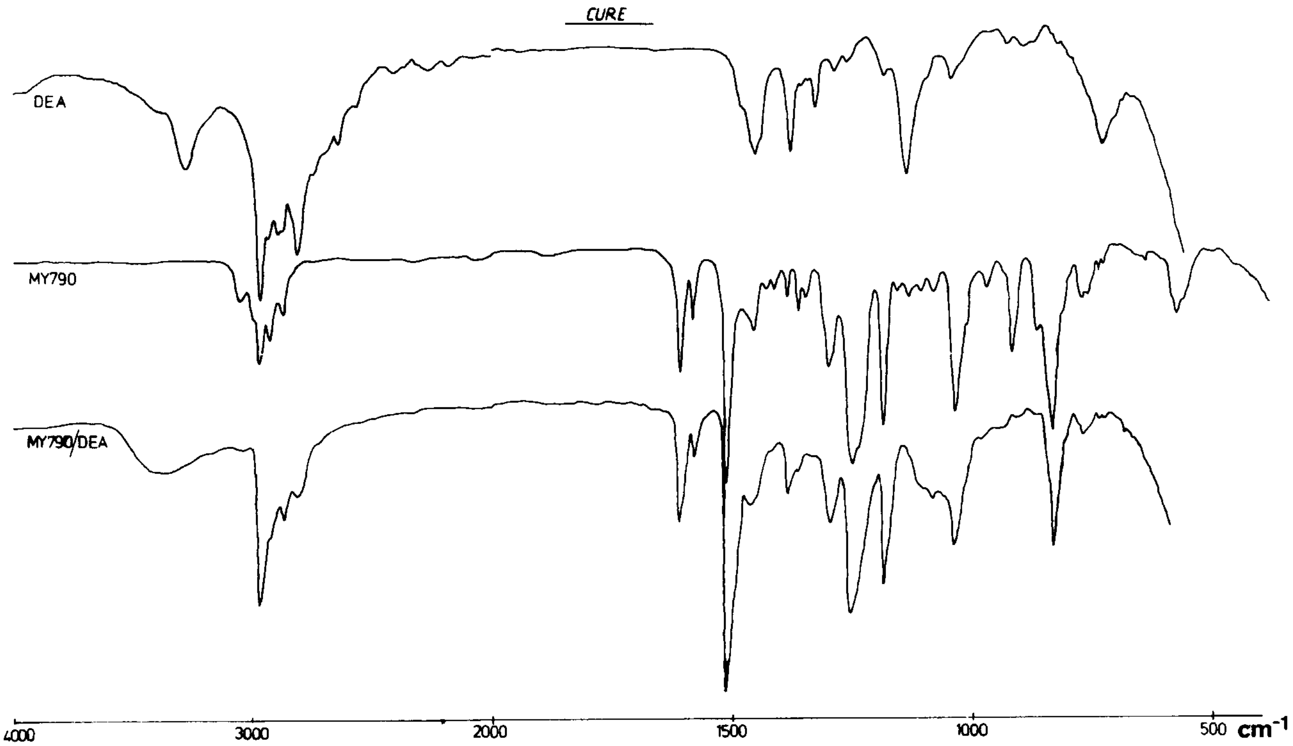
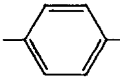


Fig. 7. Cure of DGEBA with DEA—infra-red spectra.

TABLE 2
Assignment of Infra-red Spectra of DGEBA/DEA

Spectra at 333 K		*Spectra at 473 K*	
Peak *(cm^{-1})*	*Assignment*	*Peak* *(cm^{-1})*	*Assignment*
3 100–3 600	OH/NH stretching	3 100–3 600	OH/NH stretching
3 052	Arylene C—H stretch	3 052	Arylene C—H stretch
3 034	Methyl stretch	3 034	Methyl C—H stretch
2 970	Methyl stretch	2 970	Methyl C—H stretch
2 935	$-CH_2-(CH_2)-CH_3$ stretch	2 935	$-CH_2-(CH_2)-$ stretch
2 876	$-CH_2-(CH_2)-CH_3$ stretch	2 876	$-CH_2-(CH_2)-$ stretch
2 820–2 800	$N-(CH_2)-CH_3$ stretch	2 820–2 800	$N-(CH_2)-CH_3$ stretch
		1 710–1 800	$C{=}O$ stretch
		1 655	$C{=}O$ or $C{=}C$ stretch
1 610	Aromatic $C{=}C$ stretch	1 610	Aromatic $C{=}C$ stretch
		1 580	Aromatic $C{=}C$ stretch
1 503	Aromatic $C{=}C$ stretch	1 503	Aromatic $C{=}C$ stretch
1 480	Deformation vibrations of CH_2, CH_3	1 480	CH_2, CH_3 deformation vibrations
1 385	Methyl $C-(CH_3)_2$ band	1 385	Methyl $C-(CH_3)_2$ band
1 360	Methyl $C-(CH_3)_2$ band	1 360	Methyl $C-(CH_3)_2$ band
1 250	$=C-O$ band	1 250	$=C-O$ band
1 188	$=C-O$ band	1 188	$=C-O$ band
1 135	Secondary OH band	1 135	Secondary OH band
1 110	Aliphatic C—O—C band	1 110	Aliphatic C—O—C band
1 040	Ph—(O—C)— band	1 040	Ph—(O—C)— band
915	Epoxide ring deformation	915	Epoxide ring deformation
830	*Para* disubstituted benzene	830	*Para* disubstituted benzene
		815	1,2,4 trisubstituted benzene

same degree of change as occurs with heating DGEBA/TETA for 3 h. The infra-red spectra of the degraded material show additional absorptions at 1665 and 1720 cm^{-1} (Fig. 8). Similar changes have been reported in the DGEBA/TETA system and assigned to a rearrangement of unreacted epoxy groups. However, this is highly unlikely since the disappearance of the oxirane band at 915 cm^{-1} had been carefully checked. A reduction in the absorption at 1503 cm^{-1} is associated with changes in the structure of the phenyl rings. Similar changes in bands at 1040, 1188 and 1250 cm^{-1} are associated with the —O—C structure. These observations

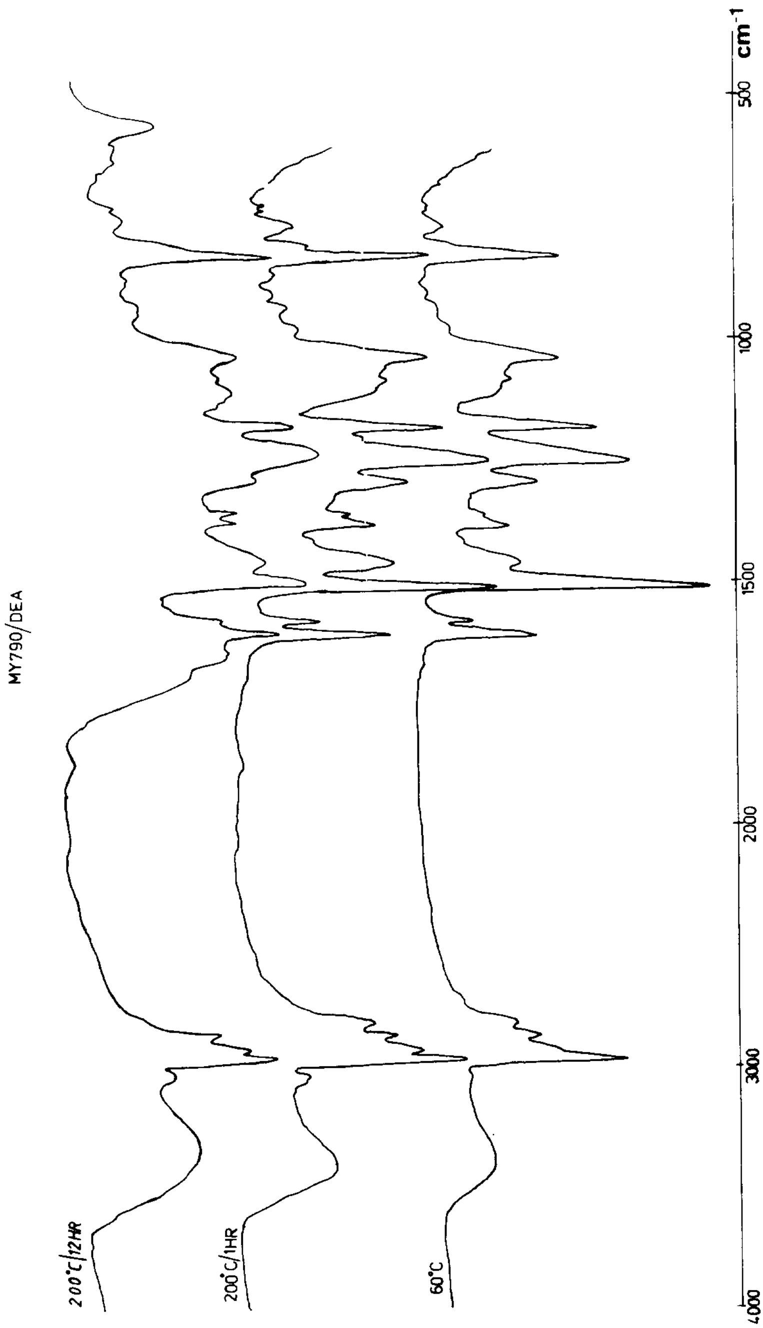


Fig. 8. Degradation of the model compound DGEBA/DEA—infra-red spectra.

indicate that chain scission is taking place at both sides of the ether linkage, with the more severe scission occurring at the alkyl ether. The appearance of a band at 815 cm^{-1} is associated with the generation of a 1,2,4 trisubstituted aromatic. A further notable change is the loss of a band at 2820–2800 cm^{-1} corresponding to the C—H stretch of diethyl amine. A general loss of intensity in the aliphatic C—H stretch region is observed by an increase in the aromatic C—H stretch at 3060 cm^{-1} and similarly an increase in the O—H band.

Evidence for the generation of phenol compounds, in the form of bisphenol-A, would be associated with the collapse of a doublet at 1390 and 1368 cm^{-1} into a singlet. This is, in fact, not observed; neither are absorptions in the region 1200–1300 cm^{-1} associated with phenol compounds.

Loss of one of the gem methyls from the bridge *iso*-propylidene group would involve a shift of the $C—CH_3$ stretch at 1184 to 1174 cm^{-1}. No evidence for this can be obtained from these infra-red studies.

^{13}C NMR spectra of the model compound

The ^{13}C NMR spectra of DGEBA/DEA and the cured material are shown in Fig. 9. The assignment of the spectrum is summarised in Table 3. The spectrum of the material degraded at 473 K reflects the changes which occur (Fig. 10), a general loss of intensity in the aliphatic region occurs with only the shifts at 31·2 and 41·8 ppm being unaffected. This is supported by the observation that the intensities of the C_3, C_5 and C_6 are unchanged between 333 and 473 K. The inference which can be drawn from this observation is that the bisphenol A moiety remains intact. Poranski[21] has shown that substitution of the gem methyls on the bridge carbon produces a shift of 9 ppm on the aromatic carbon atom and there is a concurrent loss of intensity at the gem methyl peak (31·5 ppm).

All the aliphatic peaks show a loss of intensity with respect to C_6 and this is in accord with the i.r. observations. Another effect is that there is a change in intensity of the aromatic shifts relative to C_3 and also a new shift appears at 115·3 ppm. Poranski and Moniz[21] produced evidence that substitution of Br at C_2 and C_6 causes shifts at all the aromatic carbons, Table 4. However, this will obviously have a different effect from an alkyl substitution at C_2. A paper by Sojka *et al.*[22] on phenol model compounds shows an assignment for C_2 in *p*-methyl phenol at 115·2 ppm. Similarly, Schilling *et al.* have shown[23] that C_2 in dihydroxydiphenyl propane has a

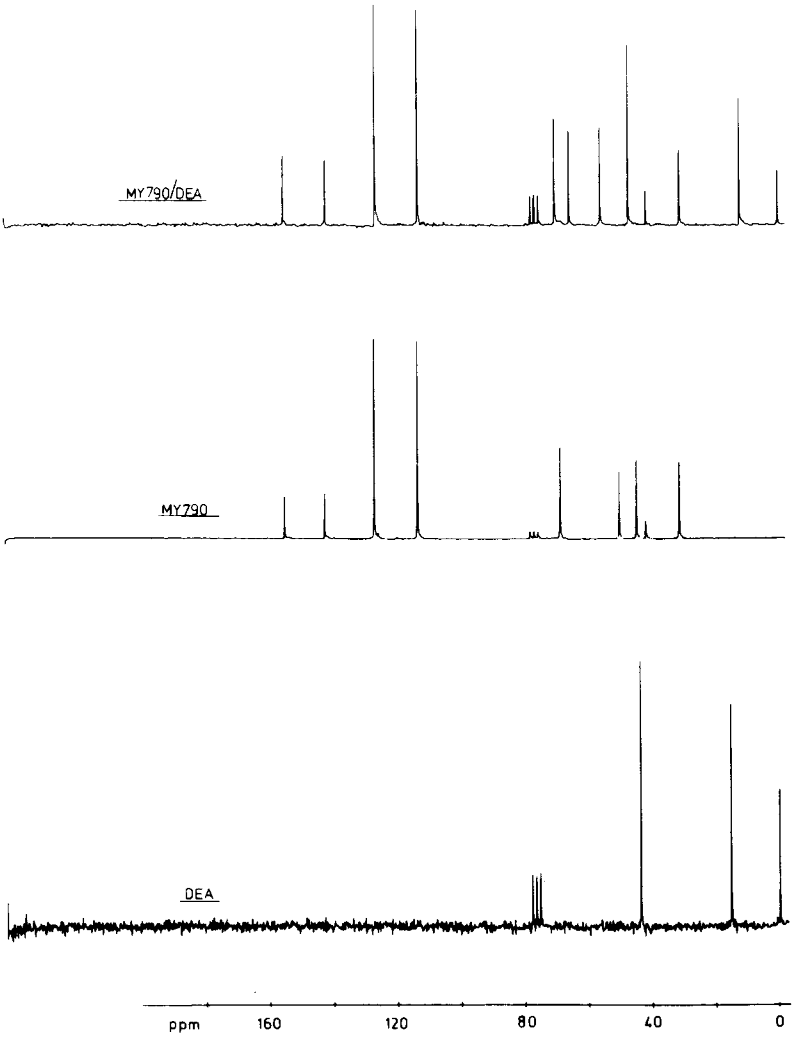
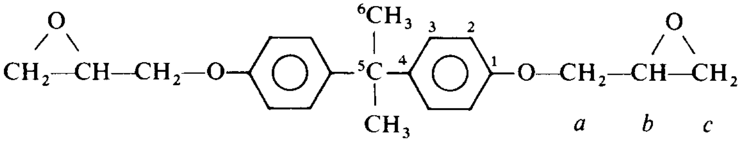


Fig. 9. ^{13}C NMR of the model compounds DGEBA and DEA.

shift of 114·9 ppm and therefore it would seem that phenol compounds are being formed, which is also explained by the loss of aliphatic carbons. These data confirm the assignment placed in Table 3. However, this does not account for the infra-red changes at 1665 and 1720 cm^{-1}. One possible explanation is that the infra-red technique, being more sensitive, is showing carbonyl and unsaturated species at a concentration which ^{13}C cannot detect. Carbonyls will be expected to show weak resonances in ^{13}C

TABLE 3
^{13}C NMR of the Model Compounds

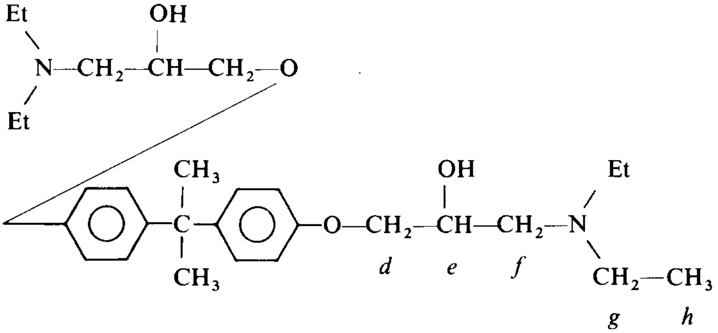
Structures



DGEBA


$\underset{}{CH_3}\underset{i}{CH_2}NH\underset{j}{CH_2}CH_3$

DEA



DGBE/DEA

Molecule	*Carbon atom*					
	1	2	3	4	5	6
DGEBA	156·4	114·0	127·7	143·6	41·4	30·9
DEA	—	—	—	—	—	—
DGEBA/DEA	157·3	114·4	128·0	143·7	41·9	31·2

Molecule	*Carbon atom*						
	a	*b*	*c*	*d*	*e*	*f*	*g*
DGEBA	68·6	49·9	44·4	—	—	—	—
DEA	—	—	—	—	—	—	—
DGEBA/DEA	—	—	—	70·9	66·4	56·4	47·6

Molecule	*Carbon atom*		
	h	*i*	*j*
DGEBA	—	—	—
DEA	—	44·2	15·4
DGEBA/DEA	12·1	—	—

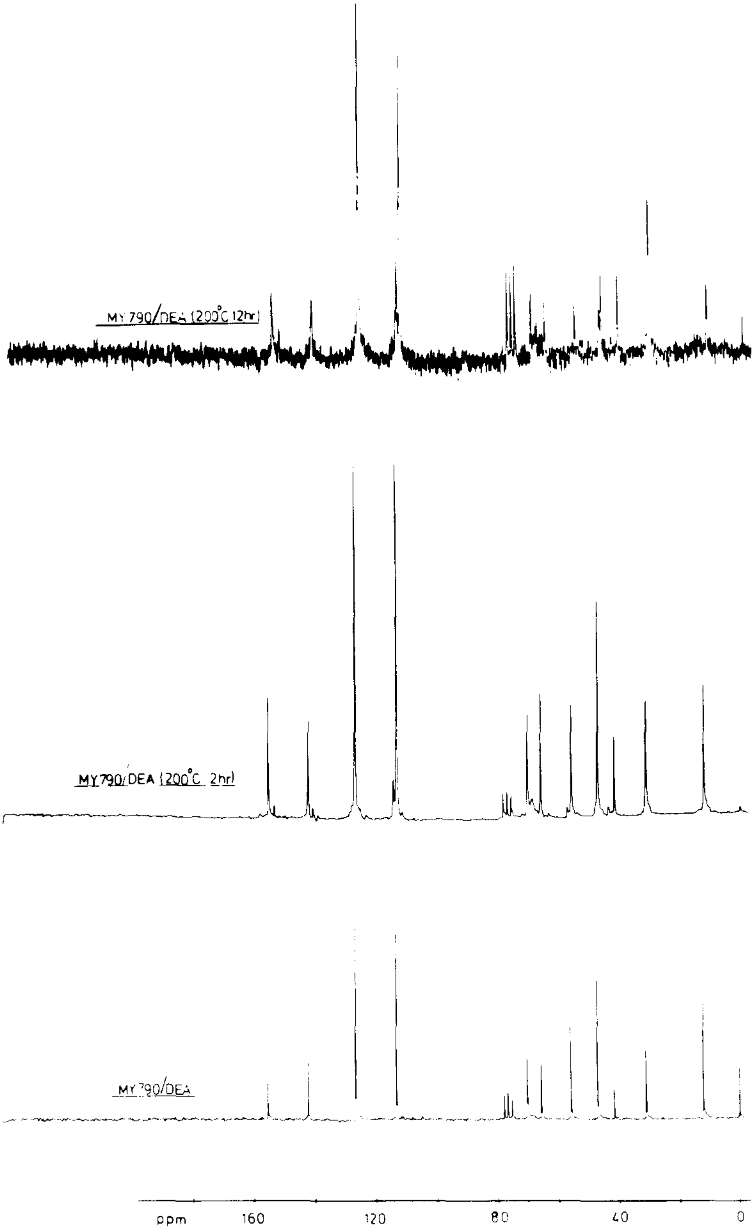
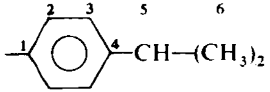
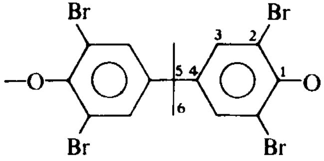
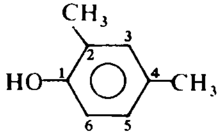
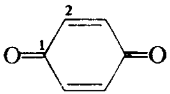
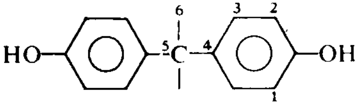
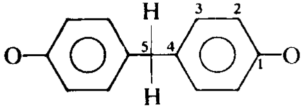
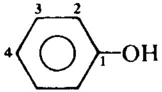
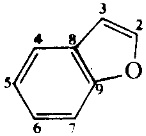


Fig. 10. Degradation of the model compound DGEBA/DEA—^{13}C NMR spectra.

TABLE 4
^{13}C Shifts for Model Compounds

Compound	*Shifts (ppm)* *Carbon atom* 1	2	3	4	5	6	*Reference*
	125·7	128·2	126·3	148·7	34·2	23·9	26
	150·4	117·5	130·4	147·3	41·7	30·0	21
	151·2	123·6	127·2	129·4	116·9	131·5	22

	187·2	136·2							27
	153·4	114·4	128·1	143·2	41·8	31·2			23
	156·7	114·3	127·3	133·9	39·1				21
	155·5	115·4	129·7	120·7					22
	2 145·9	3 107·3	4 123·6	5 125·1	6 122·0	7 112·1	8 128·5	9 155·9	28

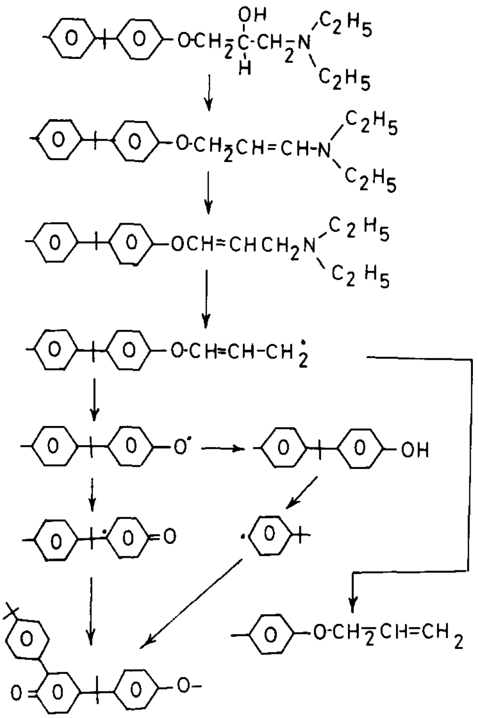


Fig. 11. Degradation scheme for DGEBA/DEA.

due to long T_1 values. Carbonyls could be formed by the Patterson-Jones nucleophilic chain-breaking mechanism or by formation of quinoid, rather than phenol.

A scheme for the degradation in the model compound is presented in Fig. 11.

Thermoxidative degradation of DGEBA/TETA

Infra-red studies

The changes which occur in the infra-red spectrum on heating the resin in the range 375–558 K are shown in Fig. 12. The changes can be sub-divided into two distinct temperature regions—(i) 443–503 K and (ii) above 503 K. In region (i) the in-growth at 1665 cm^{-1} increases gradually to a maximum and a small in-growth appears at 1725 cm^{-1}. The general slope of the rest of the spectrum is unaltered. Above 503 K the in-growth at 1725 cm^{-1} increases until it is equal to the 1665 cm^{-1} in intensity. There is

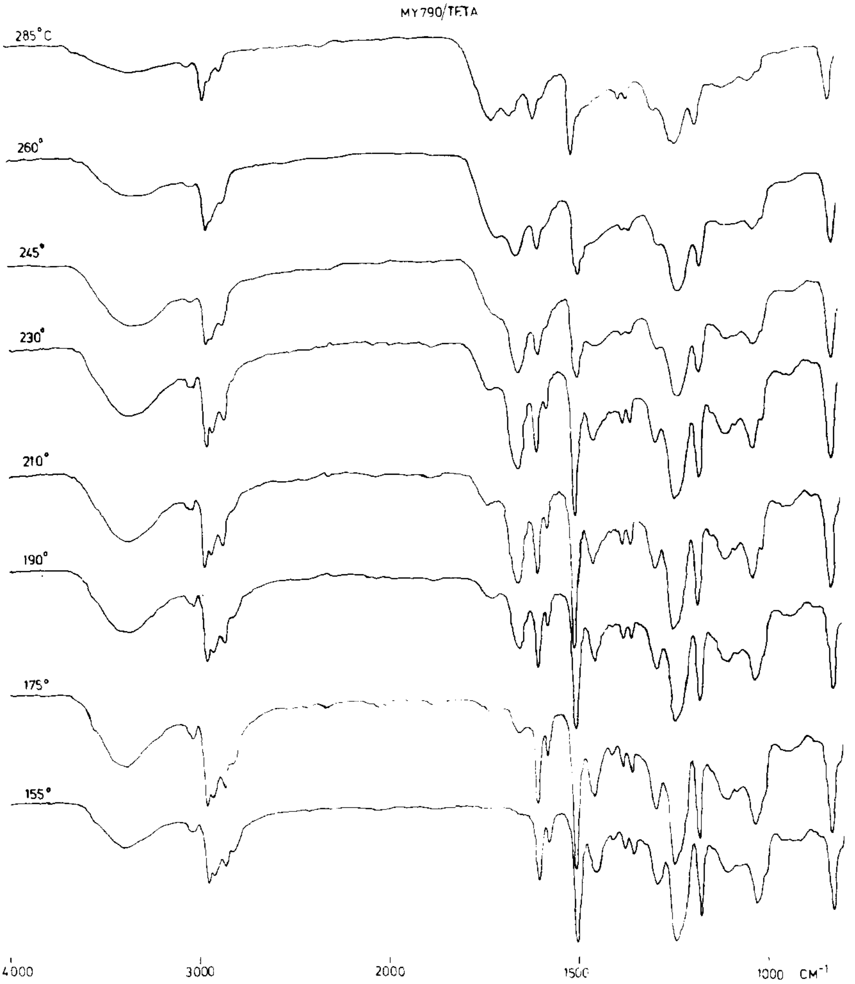
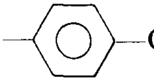


Fig. 12. Degradation of DGEBA/TETA, infra-red spectra.

a fall of intensity of the 1040 cm^{-1} band with respect to the 1250 and 1188 cm^{-1} bands which indicates scission at the alkyl ether section of the —O—C structural unit. Support for this proposition by a reduction of 1110 cm^{-1} (alkyl ether) is difficult to substantiate due to general broadening of the spectra at 1135–1100 cm^{-1} at higher temperatures. A reduction in the O—H stretching intensity (3100–3600 cm^{-1}) is observed, consistent with the idea that dehydration is a prerequisite for degradation. The absorptions at 1503 and 830 cm^{-1} show a decrease with a corresponding increase in the region 1480–1425 cm^{-1} and 815 cm^{-1}. These changes are indicative of the formation of a 1, 2, 4 trisubstituted benzene from a 1,4 *para* disubstituted phenyl. A small increase at 730–770 cm^{-1} is indicative of the formation of mono-substituted benzene.

The changes observed below 503 K are consistent with the Patterson-Jones mechanism (Fig. 4). The band at 1665 cm^{-1} can be attributed to the olefinic structure and the smaller peak at 1725 cm^{-1} to the carbonyl in the nucleophilic chain-breaking mechanism. There appears to be no evidence for changes in the *iso*-propylidene linkage.

Changes above 503 K are consistent with bond scission at the alkyl ether linkage with subsequent formation of a 1, 2, 4-trisubstituted aromatic structure. The doublet at 1390 and 1365 cm^{-1} is sensitive to the packing of the dimethyl diphenyl structure of bisphenol A.

ESR studies

The ESR spectrum of the DGEBA/TETA sample degraded at 473 K is shown in Fig. 13. The g value of 2·004 for the singlet and the absence of hyperfine structure indicate that the spectrum is due to phenoxy type radicals rather than a radical associated with aliphatic carbons, e.g. the *iso*-propylidene bridge group.

Ultraviolet spectroscopic studies

The results of heating the DGEBA/TETA are shown in Fig. 14. The lower temperature spectrum has been assigned to the presence of *para*

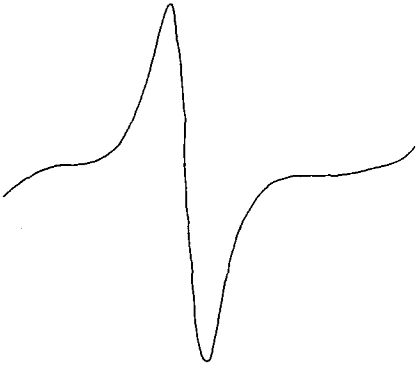


Fig. 13. ESR spectrum of degraded DGEBA/TETA.

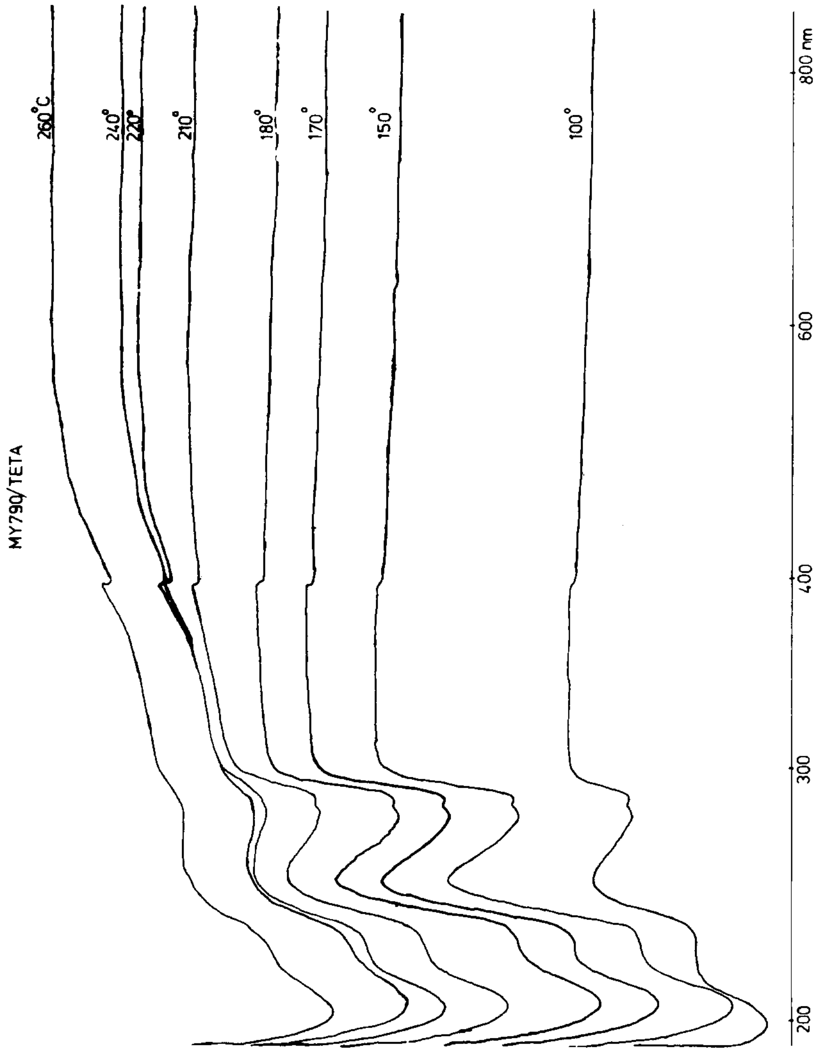


Fig. 14. Ultraviolet spectrum of degradation in DGEBA/TETA.

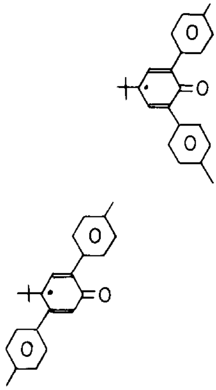


Fig. 15. Possible cyclic structures generated during rearrangement.

disubstituted benzenes. At temperatures above 473 K a tail is observed in the region 300–450 nm associated with the generation of colour in the films. No absorption maxima are detectable in this region so it seems reasonable to assume that varying lengths of conjugation are being produced in the oxidised matrix. It is unlikely that this increased conjugation is situated in the aliphatic sections because of chain scission. However, rearrangement to form conjugated cyclic structures is expected as degradation proceeds (Fig. 15).

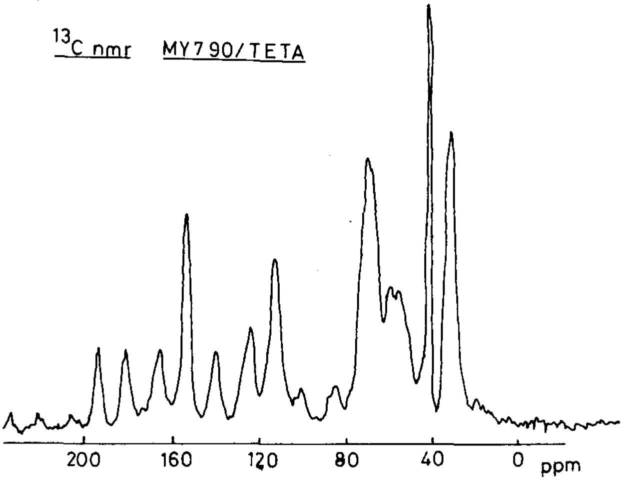
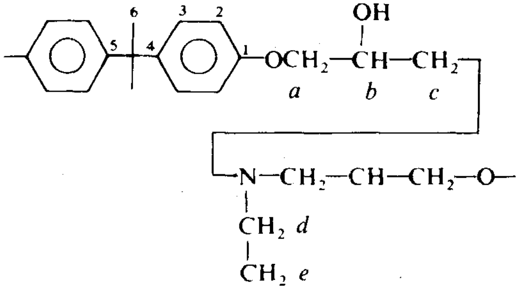
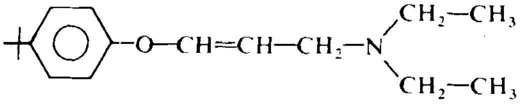
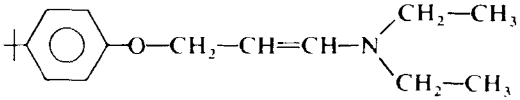
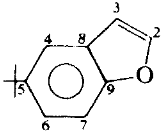
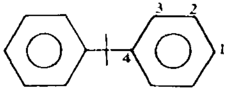
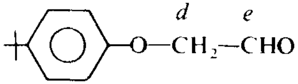


Fig. 16. ^{13}C NMR of solid epoxy resin.

TABLE 5

^{13}C Shifts of the DGEBA/TETA Cured System

Structures	*Carbon shifts (ppm)*								
	1 157·3 *a* 70·7	2 114·4 *b* 69·5	3 128·0 *c* 60·3	4 143·8 *d* 52·5	5 41·9 *e* 52·9	6 31·2			
	*d* 163·5	*e* 124·1	*f* 52·1	*g* 48·9	*h* 12·2				
	67·0	131·2	149·0	50·3	13·2				
	2 143·6	3 106·9	4 122·5	5 148·6	6 120·9	7 111·7	8 128·1	9 153·6	
	1 126·4	2 128·3	3 127·3	4 152·6					
	*d* 90·2	*e* 201·1							

^{13}C spectra of the solid epoxy

The ^{13}C spectra of the solid resin (Fig. 16) is complicated by the presence of bands arising from the perspex rotor and also spinning side bands. The analysis of the spectrum is presented in Table 5, together with the spectra of model compounds. It was not possible to detect significant changes in the spectrum of the degraded material associated with possible structures generated in degradation because of overlapping side bands.

CONCLUSIONS

Before summarising the mechanism of thermoxidative degradation of amine cured resins, one additional factor should be noted. Several years ago Ericksen[24] reported the rapid diffusion of polyamines in epoxy resins. Patrick[25] has since stated that because of the rapid gelation as curing proceeds in epoxy/polyamine systems, a certain amount of polyamine is available in the unbound form and can diffuse out of the cured resin over a period of time. This is especially true if the epoxy is cured in contact with a high surface energy substrate such as a metal. These observations suggest that amine cured epoxies tend to have excess amine surfaces and this will lead to enhanced degradation at the surface by the Patterson-Jones mechanism.

The low temperature changes may be considered to be a consequence of (i) dehydration of glycidyl segment and (ii) nucleophilic chain breaking of glycidyl segment and oxidation of alcohol. As a consequence of the dehydration, chain scission occurs at the weakest bonds in the network, $(\mathrm{N} \wr \mathrm{CH_2{-}CH{=}})$ and $(\mathrm{O{-}CH_2{-}CH{=}C})$, resulting in the formation of phenoxy type radicals. The development of colour is due to the formation of polyenyl structures with the possible formation of quinoid or cyclised conjugated nitrogen compounds. These reactive species may form chemical bonds with the surface which explains the previous observations of an increase in the lap strength of post-cure bonds.

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