

Combined Pyrolysis and Radiochemical Gas Chromatography for Studying the Thermal Degradation of Epoxy Resins and Polyimides.

I. The Degradation of Epoxy Resins in Nitrogen Between 400°C and 700°C

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Synopsis

The thermal degradation of a bisphenol A-based epoxy resin (EP 274) cured with 4,4'-diaminodiphenyl methane (DDM) and with phthalic anhydride (PA) was studied using a radiochemical pyrolysis gas chromatography technique. Conclusive evidence for some of the degradation mechanisms of these resins was obtained by pyrolyzing samples containing various ^{14}C -labelled groups and analyzing the products using this method.

INTRODUCTION

In a review of work on the thermal degradation of epoxy resins carried out before mid-1966,¹ the authors concluded that despite the considerable amount of work that had been done in this field, there was still relatively little known about the mechanisms of the thermal breakdown of this important class of polymers.

Since that time a number of papers have been published that contribute to the understanding of the thermal degradation of these resins.²⁻⁶ Probably the most significant of these is the paper by Bowen² which describes the use of a combination of thermogravimetric and radioisotope techniques to study the thermal breakdown of a variety of ^{14}C -labelled epoxy resins.

The aim of the present work was to establish the principle degradation mechanisms of aromatic amine- and anhydride-cured resins using a combination of pyrolysis gas chromatography and ^{14}C tracer techniques. The ^{14}C -labelled resin-hardener systems studied were similar to those used by Bowen, and consequently it has proved possible to interpret some of his findings in more detail and pinpoint the origin in the molecular network of some of the breakdown products.

EXPERIMENTAL

Pyrolysis gas chromatography techniques have been comprehensively reviewed by Levy.^{7,8} The pyrolysis unit used for the present work consisted of an electrically heated nichrome filament housed in a Pyrex glass tube. This tube was built into a Perkin-Elmer 452 gas chromatograph so that degradation products volatile at the chromatograph oven temperature were swept into the column and separated. This apparatus and techniques for its use are described in detail elsewhere.^{3,9} Pyrolysis temperatures were measured using a Chromel/Alumel thermocouple attached to the midpoint of the filament and the filament temperature was correlated with the supply voltage for various carrier gas flow rates and oven temperatures. The detector was a cathetometer and positive and negative peaks thus appear on the pyrograms. The carrier gas was oxygen-free nitrogen.

The sample size was varied between 5 and 50 mg, depending on the specific activity of the resin and on the degradation products being studied. It was found that varying the sample size in this range did not significantly alter the relative amounts of the degradation products formed at a given pyrolysis temperature. Probably this is because no radical change in the geometry of the system was involved. It has been shown that results for this type of work are highly dependent on the heating method used, and in some cases catalytic degradation is a complicating factor.^{8,10}

The separated degradation products were identified by comparing their retention times with model compounds under varied conditions, and also by trapping them on KBr crystals, recording their infrared spectra, and comparing these with the spectra of known compounds.

The methods available for detecting and measuring radioactivity in the effluent of a gas chromatograph have been reviewed by Karmen.¹¹ There are continuous methods in which radioactivity is detected and measured in the gas stream, and discontinuous methods in which the labelled compounds are condensed in a scintillator solution (or on scintillator crystals) and then counted by conventional counting techniques. Continuous methods have the advantage of speed and convenience, but the time taken for an active compound to pass the radioactivity detector must be limited in order to preserve resolution of the various compounds. It is therefore impossible to count low levels of activity with accuracy when using continuous techniques.

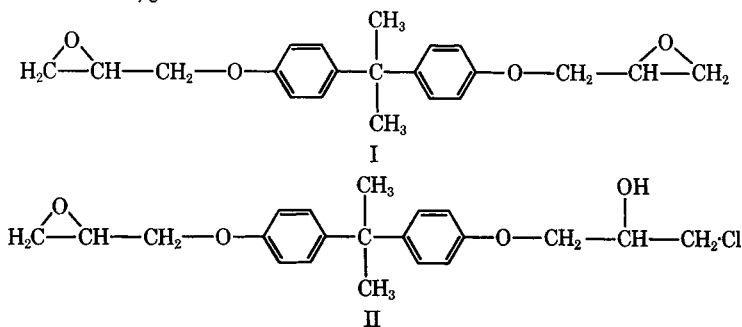
The tendency for high-boiling compounds to condense in the radioactivity detector was overcome by burning the separated products from the gas chromatograph to CO₂ and water by passing them through cupric oxide heated in a tube to 650°–700°C. The radioactivity detector was a modified Nuclear Enterprises NE 5504 shielded scintillation head unit. Essentially this consisted of a glass spiral packed with scintillation-grade anthracene crystals which were viewed by a photomultiplier tube. When a radioactive compound passed through the spiral, the weak β -emission from the ¹⁴C caused scintillations in the anthracene which were detected by the

photomultiplier. Events per second data from the photomultiplier tube were amplified and passed to an integrator unit which was designed to drive a chart recorder and to integrate each radioactive peak and display the total digitally.

Pyrolysis of a ^{14}C -labelled sample gave the usual pyrogram and also a "radiopyrogram," where the activity of labelled breakdown products was recorded. The system detected ^{14}C -labelled compounds with about 20% efficiency, which was adequate for the detection of major degradation products. The method was not adequate to record the activity of minor degradation products, however. Consequently the separated products from these resin pyrolyses were condensed and collected separately in a suitable scintillator solution (0.5% butyl P.B.D. in redistilled A.R. toluene) contained in counting bottles. These samples were then counted using normal liquid scintillation counting techniques. It was estimated that the process used for minor products had a 65% efficiency.

Materials

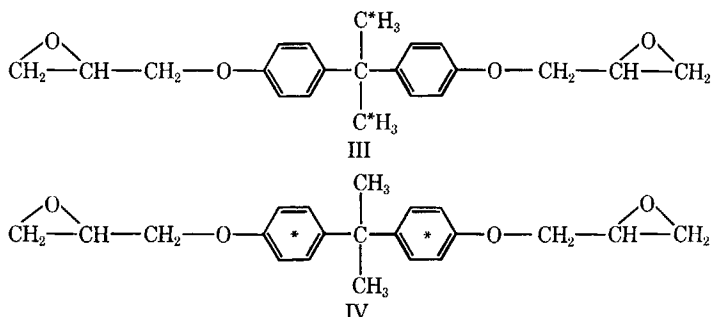
EP274. An epoxy resin known as EP274 was used throughout this work. It was supplied by Ciba (A. R. L.) Ltd. as "almost pure" diglycidyl ether of bisphenol A (I), a white waxy solid melting at 42°C . It was recrystallized from absolute alcohol and vacuum dried before use. Elemental analysis for I requires: C, 74.1%; H, 7.1%; O, 18.8%; found for EP274: C, 73.9%; H, 7.0%; Cl, 0.23%; O, by difference, 18.9%. Assuming that chlorine occurs as shown in structure II, the amount found in EP274 (0.23%) suggests that the sample of EP274 consisted of 98% structure I and 2% structure II.



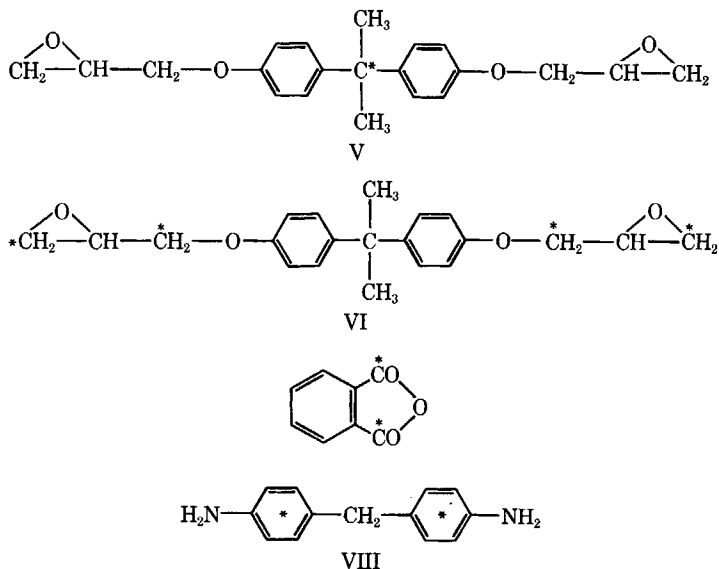
4,4'-Diaminodiphenylmethane (DDM) was obtained in a "pure" form from Koch-Light Laboratories Ltd. This material (mp $88^\circ\text{--}89^\circ\text{C}$) was recrystallized from benzene and vacuum dried to mp $90^\circ\text{--}91^\circ\text{C}$. It was kept in well-sealed bottles in the dark to minimize the discoloration which occurs on exposure to light and oxygen.

Phthalic anhydride (PA) was obtained from May and Baker Ltd. in a pure form (mp 132°C). Further purification was considered to be unnecessary. The sample was stored in a desiccator over phosphorous pentoxide to minimize reaction with atmospheric moisture.

^{14}C -labelled Compounds. The ^{14}C -labelled epoxides III and IV were prepared in these laboratories from appropriately labelled acetone and phenol, respectively, supplied by the Radiochemical Centre, Amersham, Bucks. Experimental details appear in the literature.^{12,13} Specific activities of III and IV were 1.1 and 1.2 $\mu\text{c/g}$, respectively. C* denotes ^{14}C .



The labelled epoxides V and VI and the labelled phthalic anhydride VII were obtained from Dr. D. O. Bowen of The Dow Chemical Co., Freeport, Texas. The labelled DDM, VIII, was prepared by Yarsley Research Laboratories, Chessington, Surrey. Specific activities of V, VI, VII, and VIII were 4.0, 20, 4.9, and 3.8 $\mu\text{c/g}$, respectively.



Preparation of Cured Resins

EP274/DDM. The resin EP274 and hardener DDM were mixed together in stoichiometric proportions at 100°C. When a homogeneous solution had been obtained it was placed in a vacuum desiccator for 3 hr for degassing. The resin was then cured for 16 hr at 55°C, 2 hr at 125°C,

and 2 hr at 175°C. Cured resins were prepared from III, IV, V, and VI and DDM, and from EP274 and VIII in the same way.

EP274/PA. The resin EP274 and hardener PA were mixed together at 130°–140°C using 85% of the stoichiometric amount of anhydride. When a homogeneous solution had been obtained it was cured at 130°C for 24 hr and then at 175°C for 5 hr. Cured resins were prepared from III, IV, V, and VI and PA, and from EP274 and VII in the same way.

RESULTS

The volatile degradation products identified on pyrolysis of the cured resins EP274/DDM and EP 274/PA (at temperatures between 400 and 700°C in nitrogen) are listed in Tables I, II, and III, and some typical pyrograms are shown in Figures 1–5.

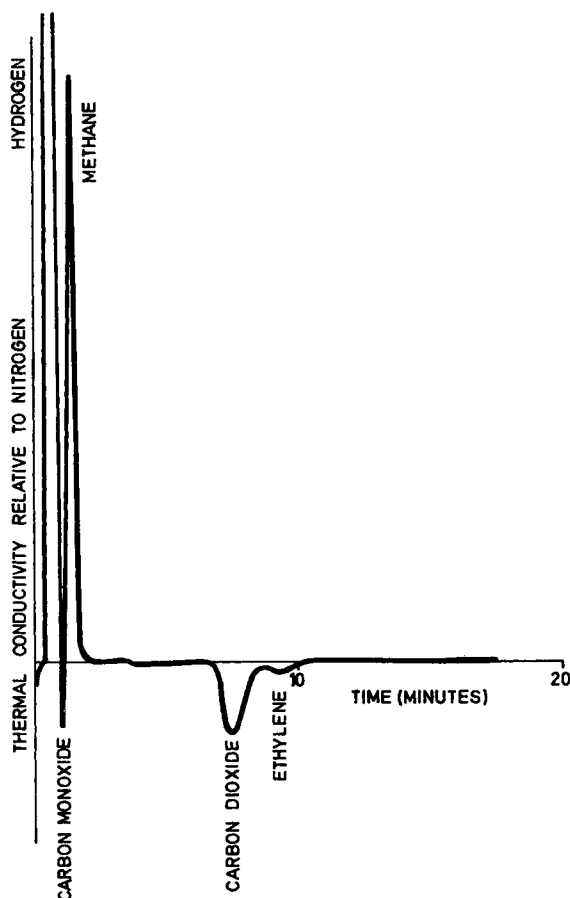


Fig. 1. Pyrogram of EP274/PA: pyrolysis temp 700°C, column: silica gel, oven temp 50°C, carrier gas N₂, 40 ml/min.

It should be noted that although degradation products are assigned to the pyrolysis temperatures, it does not mean that these are the only degradation products formed at those temperatures, but that these were the products formed in sufficient quantities during the pyrolysis time of 30 sec to be

TABLE I
Degradation Products of EP274/DDM at Pyrolysis Temperatures
Between 400° and 700°C in Nitrogen

Pyrolysis temperature			
400°C	500°C	600°C	700°C
Hydrogen	Hydrogen	Hydrogen	Hydrogen
Methane	Carbon monoxide	Carbon monoxide	Carbon monoxide
Water	Methane	Methane	Methane
	Carbon dioxide	Carbon dioxide	Carbon dioxide
	Acetaldehyde	Formaldehyde?	Formaldehyde?
	Water	Acetaldehyde	Acetaldehyde
	Phenol	Water	Unknown
		Phenol	Acetone
		<i>o</i> -Cresol	Water
			Benzene
			Toluene
			Unknown
			Phenol
			<i>o</i> -Cresol
			<i>p</i> -Cresol
			Higher phenols

TABLE II
Degradation Products of EP274/PA at Pyrolysis Temperatures
Between 400° and 700°C in Nitrogen

Pyrolysis temperature			
400°C	500°C	600°C	700°C
Hydrogen	Hydrogen	Hydrogen	Hydrogen
Methane	Carbon monoxide	Carbon monoxide	Carbon monoxide
Carbon dioxide	Methane	Methane	Methane
Water	Carbon dioxide	Carbon dioxide	Carbon dioxide
	Acetone	Acetaldehyde	Formaldehyde?
	Water	Acetone	Acetaldehyde
	Phthalic anhydride	Water	Unknown
		Phenol	Acetone
		Phthalic anhydride	Water
			Benzene
			Toluene
			Unknown
			Unknown
			Phenol
			<i>o</i> -Cresol
			Unknown
			Phthalic anhydride

TABLE III
Volatile Radioactive Degradation Products of ^{14}C -Labelled Resins

Resin	Volatile radioactive degradation products at 700°C
III/DM } III/PA }	Methane
IV/DDM	Phenol, <i>o</i> -cresol, <i>p</i> -cresol (benzene, toluene?)
V/DDM } V/PA }	Methane, higher phenols
VI/DDM } VI/PA }	Methane, ethylene, acetaldehyde, acetone
EP274/VII	Carbon monoxide, carbon dioxide, phthalic anhydride
EP274/VIII	None (benzene, toluene?)

detected by our equipment. For example, no degradation products were detected after pyrolysis for 30 sec at 350°C, but it is well known that if an epoxy resin is maintained at 350°C in an inert atmosphere, considerable degradation does occur.⁴

The results of the work with ^{14}C -labelled resins are summarized in Table III and some typical pyrograms and radiopyrograms are shown in Figures 6-9.

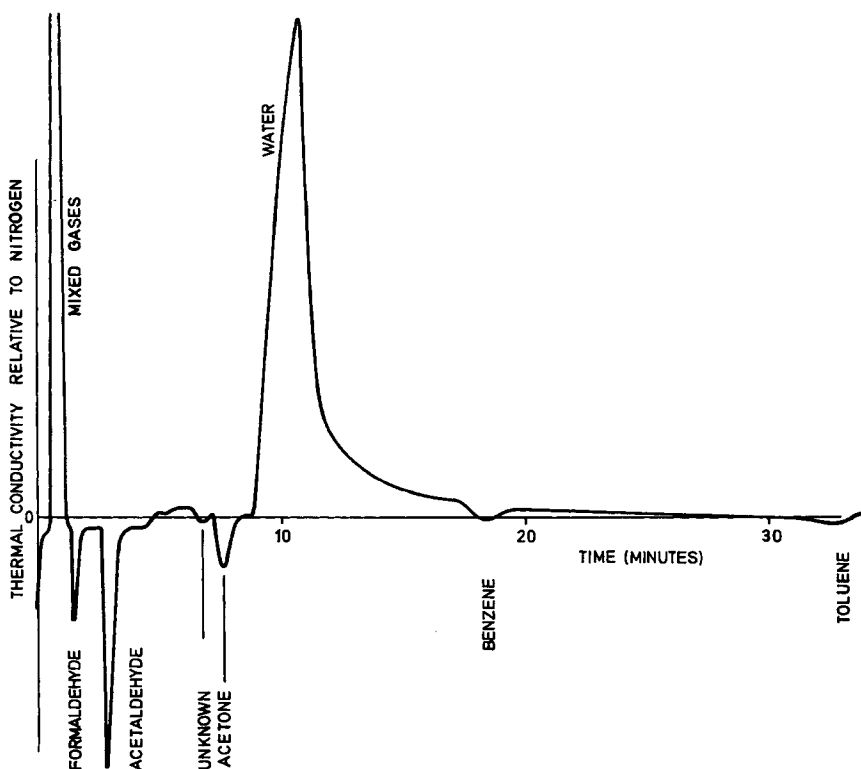


Fig. 2. Pyrogram of EP274/DDM: pyrolysis temp 700°C, column: 7,8-benzoquinoline/Chromosorb P, 15/85, oven temp 50°C, carrier gas N_2 , 40 ml/min.

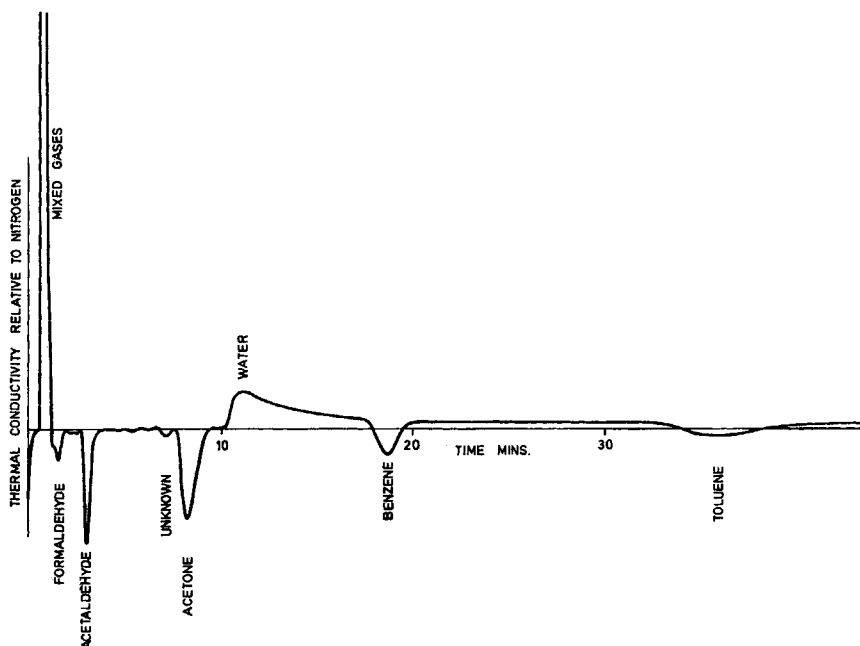


Fig. 3. Pyrogram of EP274/PA: pyrolysis temp 700°C, column: 7,8-benzoquinoline/Chromosorb P, 15/85, oven temp 50°C, carrier gas N₂, 40 ml/min.

DISCUSSION

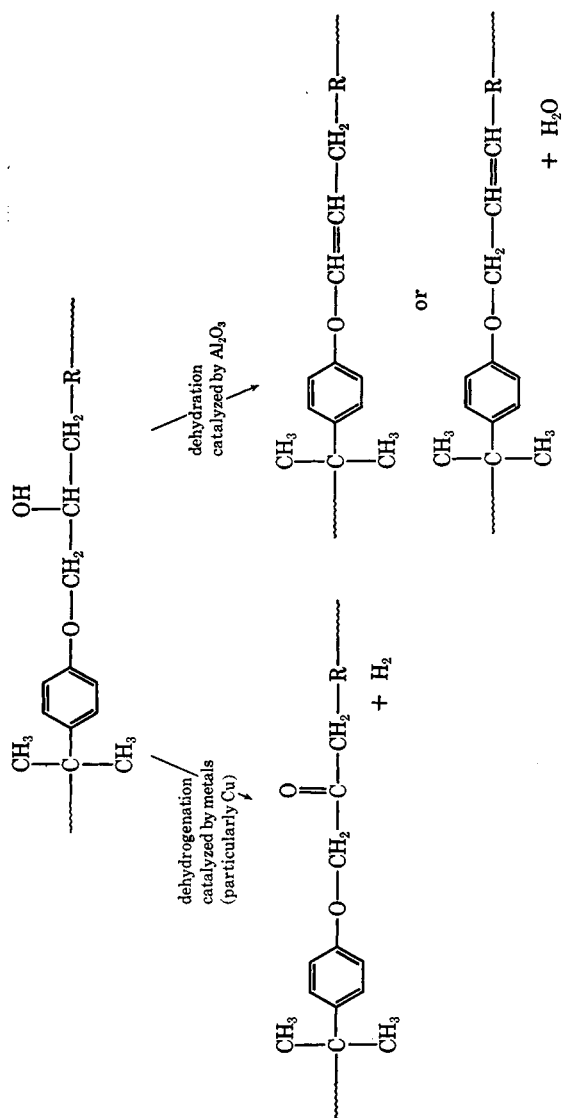
The results of this work provide sufficient information for a fairly detailed picture of the thermal breakdown of these aromatic amine- and anhydride-cured epoxy resins to be given.

In the early stages of degradation, at the lowest temperature studied, the predominant breakdown mechanisms are clearly "non-chain-scission" reactions leading to the formation of hydrogen, methane, and water. At higher temperatures degradation products resulting from the breakdown of the aliphatic part of the resins appear in large quantities together with some primary breakdown products of the aromatic entities. At the highest pyrolysis temperatures studied secondary breakdown products of the aromatic parts of the resins are formed in addition to all the other products. The mechanisms of the various stages of degradation may be discussed in some detail.

Non-Chain-Scission Reactions

Dehydration and Dehydrogenation

The most important nonscission reactions occurring in these resins are the competing dehydration and dehydrogenation reactions associated with the secondary alcohol groups in the cured resin structures. The cured resin structures are shown in Figs. 10 and 11). The relative extents to which these reactions occur are dependent on the pyrolysis technique; as follows:



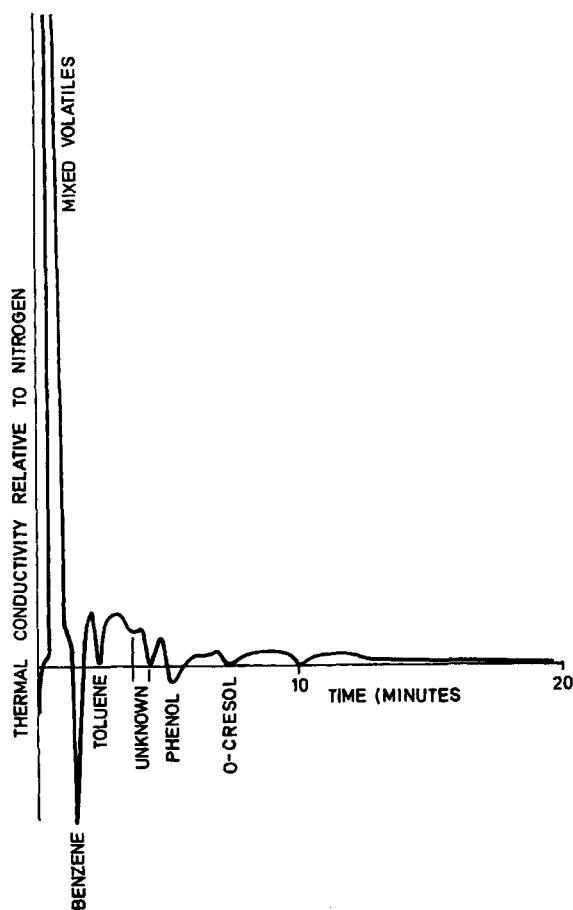


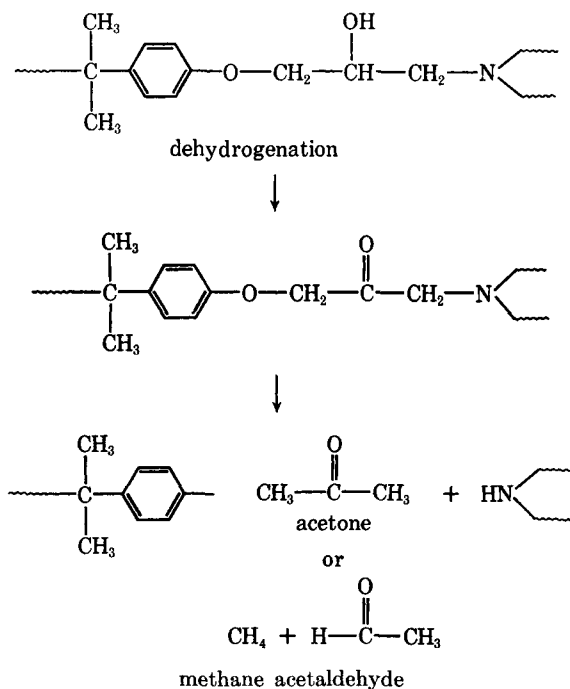
Fig. 4. Pyrogram of EP274/PA: pyrolysis temp 700°C, column: Apiezon L/Chromosorb P, 10/90, oven temp 150°C, carrier gas N₂, 40 ml/min.

When hot-wire pyrolysis is used, it is likely that the dehydrogenation reaction is catalyzed; pyrolysis in a porcelain boat, on the other hand, would favor the dehydration reaction.

TABLE IV
Comparison of "hot wire" and "porcelain boat"
pyrolyses of EP274/DDM at 700°C in N₂

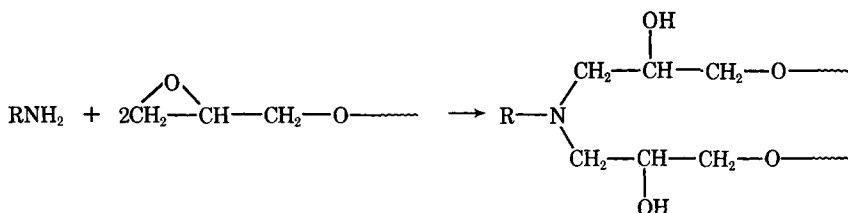
	Nichrome filament	Porcelain boat
Sample wt	19.65 mg	1.9 mg
CH ₃ CHO wt	0.226 mg	0.14 × 10 ⁻³ mg
CH ₃ CHO wt-%	1.15%	0.01%
(CH ₃) ₂ CO wt	0.039 mg	0.13 × 10 ⁻³ mg
(CH ₃) ₂ CO wt-%	0.20%	0.01%
Ratio $\frac{\text{CH}_3\text{CHO}}{(\text{CH}_3)_2\text{CO}}$	5.8	1.1

This effect has been demonstrated by comparing the quantities of acetone and acetaldehyde liberated on complete pyrolysis of samples of EP274/DDM (a) on the nichrome filament and (b) in a porcelain boat. The quantities of acetone and acetaldehyde represent the extent of dehydrogenation, because:



The pyrolysis results are listed in Table IV. They show that the hot wire technique yields about 100 times more acetaldehyde and 20 times more acetone than the porcelain boat method, and thus underline the fact that degradation mechanisms are sometimes a function of pyrolysis technique.

Quantitative measurements of the water formed on complete pyrolysis of EP274/DDM samples on the nichrome filament indicate that about 50% of all the secondary alcohol groups undergo dehydration. This result was obtained by assuming that the curing reaction



is stoichiometric. (In fact, about 90% of the epoxy groups react in this way.) Most of the other secondary alcohol groups are probably dehydrogenated; at least 25% of these yield acetone or acetaldehyde and methane

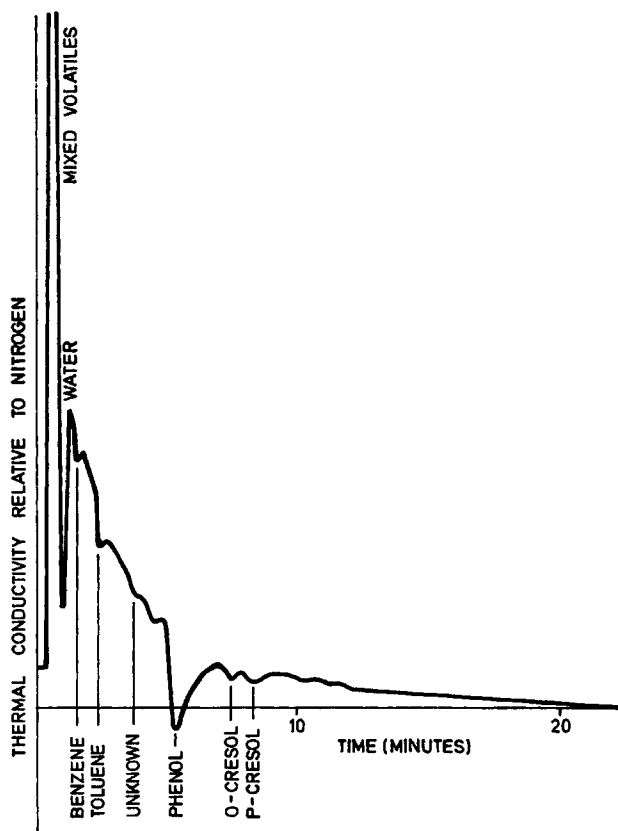
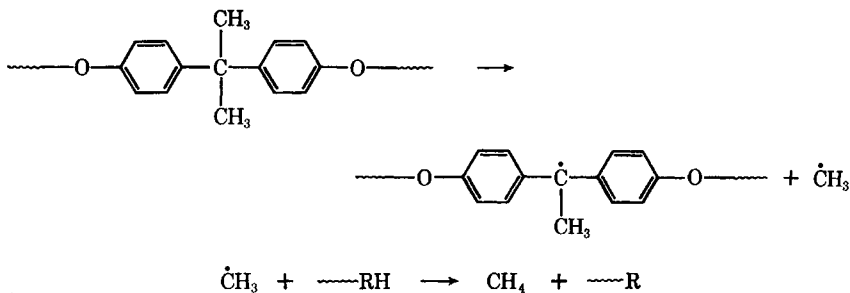


Fig. 5. Pyrogram of EP274/DDM: pyrolysis temp 700°C, column: Apiezon I./Chromosorb P, 10/90, oven temp 150°C, carrier gas N₂, 40 ml/min.

and others probably give methane and carbon monoxide or formaldehyde; but these products are discussed in more detail under chain scission reactions.

Other Non-Chain-Scission Reactions

Methane. It has already been noted that methane is a product of the breakdown of the aliphatic parts of the cured resin; but since relatively large quantities of methane are liberated before any other chain scission products, it seems likely that the following mechanism is responsible for the formation of methane at the lower degradation temperatures:



The fact that the cured resins III/DDM and III/PA both gave $^{14}\text{CH}_4$ confirmed that this reaction does occur.

Carbon Dioxide. In the early stages of the degradation of anhydride cured resins, some CO_2 may result from decarboxylation of unreacted carboxyl groups.

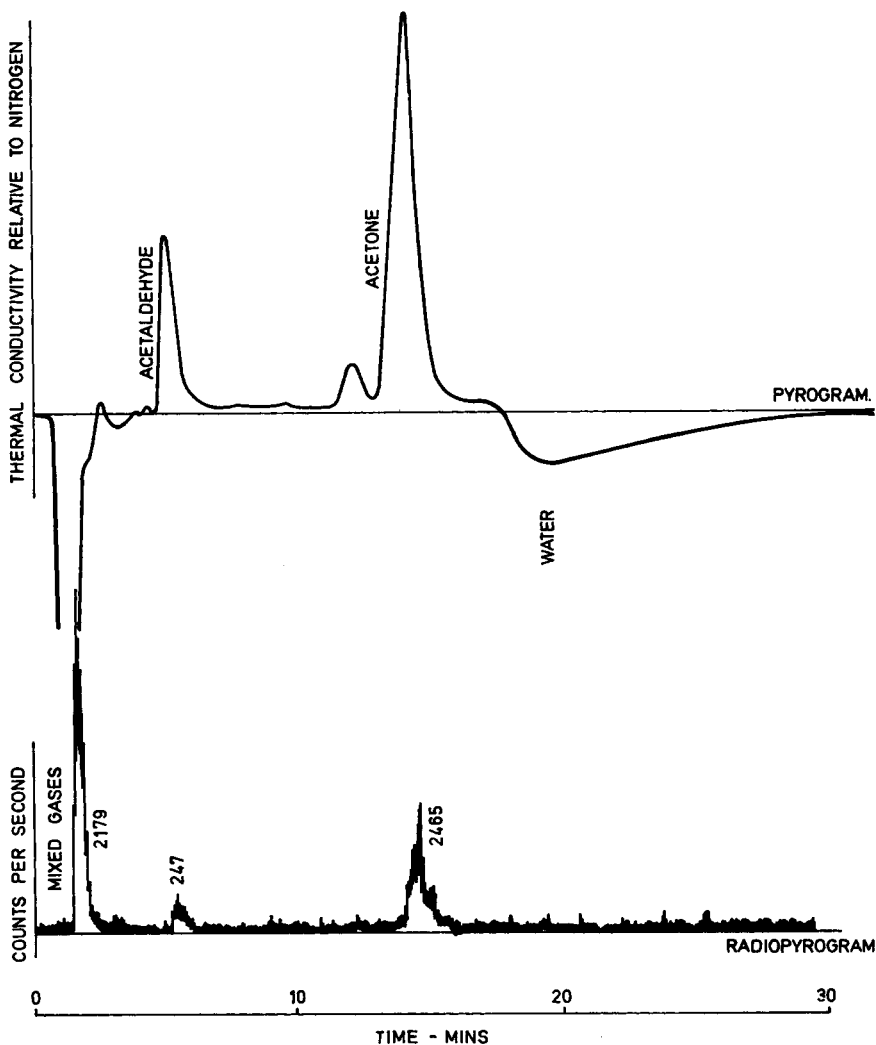


Fig. 6. Radiopyrogram of VI/PA: pyrolysis temp 700°C , column: 7,8-benzoquinoline/Chromosorb P, 15/85, oven temp 50°C , carrier gas N_2 , 20 ml/min.

Hydrogen. In addition to the dehydrogenation reaction discussed above, hydrogen may also be stripped from aromatic nuclei at temperatures above 600°C .

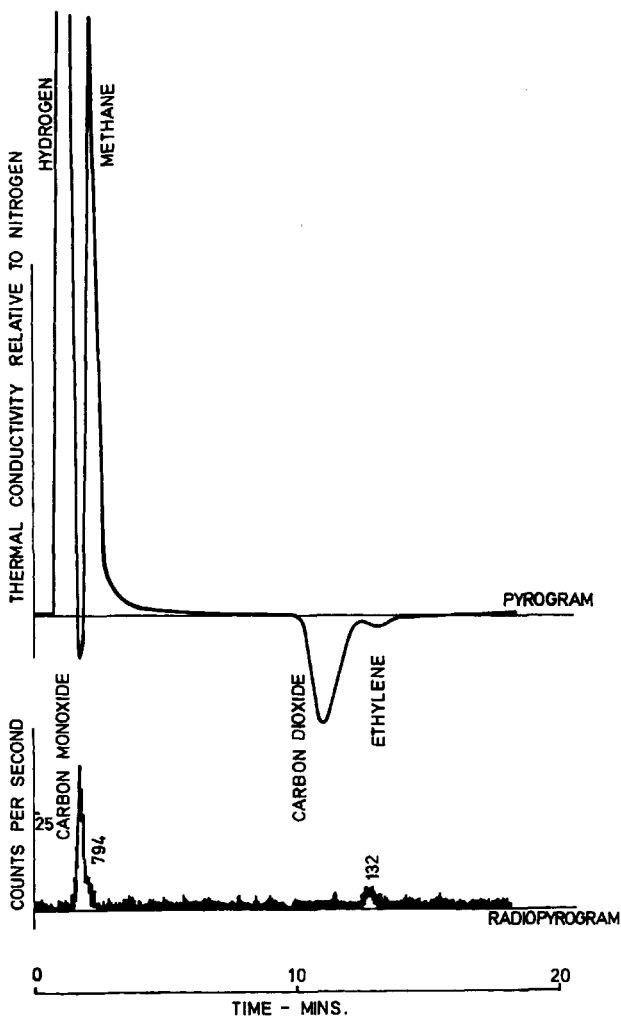


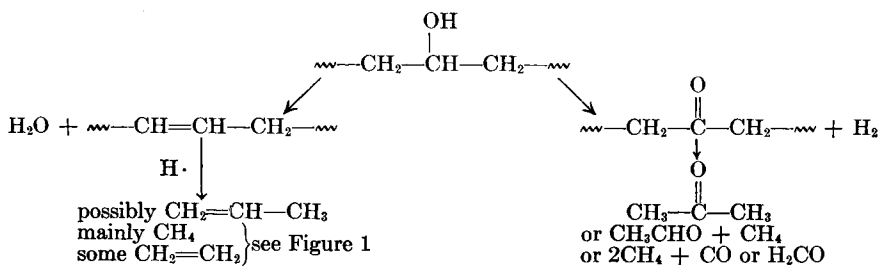
Fig. 7. Radiopyrogram of VI/PA: pyrolysis temp 700°C, column: silica gel, oven temp 50°C, carrier gas N₂, 30 ml/min.

Chain Scission Reactions

Primary Chain Scission Products

The primary chain scission products result from the breakdown of the aliphatic segments of the cured resin structures and from the initial stages of breakdown of the aromatic segments.

Following dehydration or dehydrogenation, the aliphatic segments break down into methane and ethylene (and possibly propylene) or acetone, acetaldehyde, and methane (and probably carbon monoxide and formaldehyde):



These mechanisms were confirmed by the fact that pyrolysis of the cured resins VI/DDM and VI/PA yielded ^{14}C -labelled methane, ethylene, acetaldehyde, and acetone (Figs. 6 and 7).

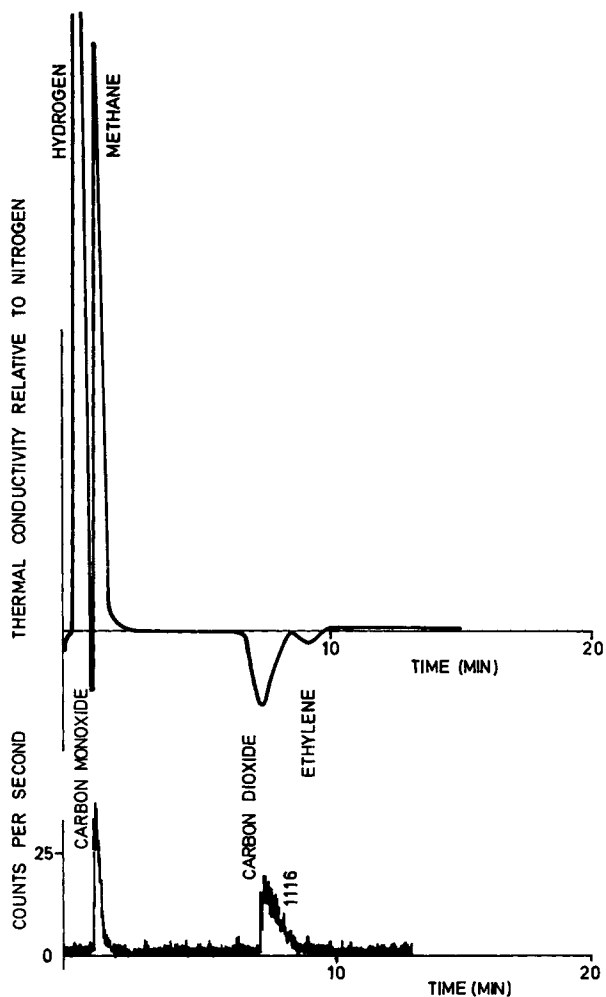


Fig. 8. Radiopyrogram of EP274/VII: pyrolysis temp 700°C , column: silica gel, oven temp 50°C , carrier gas N_2 , 40 ml/min.

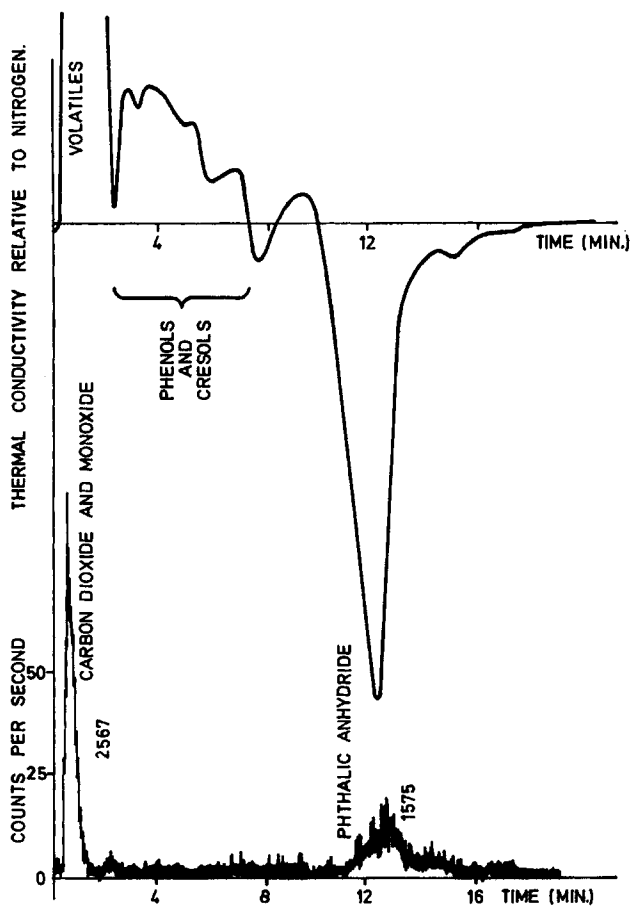
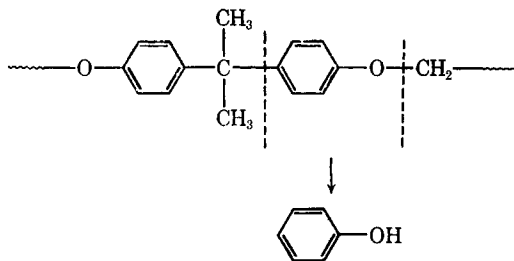


Fig. 9. Radiopyrogram of EP274/VII: pyrolysis temp 700°C, column: Apiezon L/Chromosorb P, 10/90, oven temp 200°C, carrier gas N₂, 30 ml/min.

The initial stage of the breakdown of the aromatic segments of these resins produces phenol which originates from the bisphenol A structures:



This was confirmed by the identification of ¹⁴C-labelled phenol in the pyrolysis products of the resin IV/DDM.

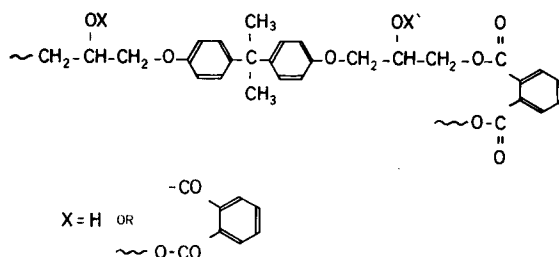


Fig. 10. Structure of cured EP274/PA.

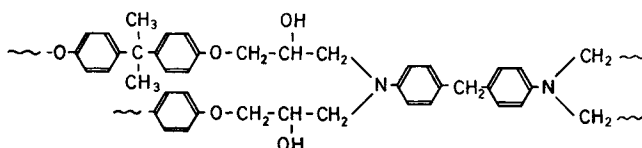
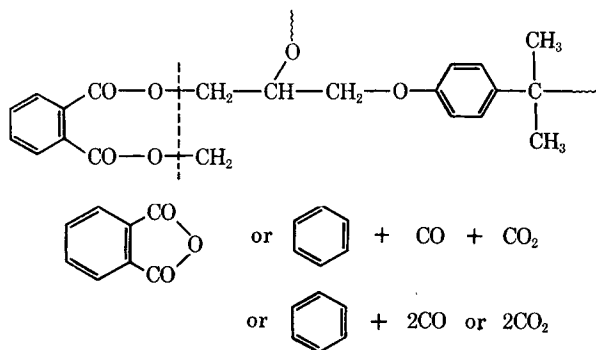


Fig. 11. Structure of cured EP274/DDM.

Phthalic anhydride was regenerated in large quantities on pyrolysis of EP274/PA at temperatures of 500°C and above, together with carbon monoxide and carbon dioxide. The PA-cured resins also gave off larger quantities of benzene than the DDM-cured resins. The following mechanisms account for these findings:



Pyrolysis of EP274/VII gave ¹⁴C-labelled CO, CO₂ and phthalic anhydride as would be expected (Figs. 8 and 9).

Further Chain Scission Products

The degradation products which only occur in detectable quantities at the higher pyrolysis temperatures are benzene, toluene, *o*- and *p*-cresols, higher phenols, and some unidentified products. In general these may be accounted for by further breakdown or rearrangement of the aromatic segments of the resins. The cresols and higher phenols originate from the bisphenol A structures, but benzene and toluene may originate from any of the aromatic nuclei. Pyrolysis of EP274/VIII did not give any positive

evidence on the fate of the DDM; slight activity was noted in the benzene and toluene from this resin but clearly the bulk of the DDM remained in the high-boiling tars.

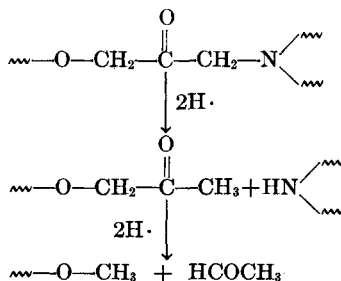
Differences Between Aromatic Amine- and Anhydride-Cured Resins

The principal differences in the thermal degradation patterns of the anhydride- and amine-cured resins are:

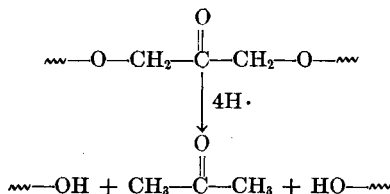
(1) Amine-cured resins contain many more $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$ groupings (Figs. 10 and 11) than the anhydride-cured resins and consequently yield more water and hydrogen. Since the dehydration and dehydrogenation reactions occur at relatively low temperatures, the amine-cured resins show more weight loss at these temperatures and therefore appear to have inferior thermal stability to the anhydride resins.

(2) When chain scission occurs, the anhydride-cured resins tend to regenerate the hardener and CO and CO_2 in large quantities. The amine hardeners do not appear to be regenerated, but their fate has not been clearly established.

(3) The aliphatic segments of the amine-cured resins yield more acetaldehyde than acetone, whereas the reverse is true for the anhydride-cured resins. This may be due to a preferential rupture of the C—N bond in the case of the amine-cured resins leading to acetaldehyde:



The anhydride system is symmetrical and may tend to break symmetrically:



CONCLUSION

The number of degradation products of a hardened epoxy resin is sufficiently large for the origin of particular fragments to be in doubt. The use of ^{14}C -labelling techniques has made it possible to pinpoint the origin of most of these degradation products.

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