

Thermal Degradation of Resins

G. S. LEARMONTH, *Chemistry Department, College of Advanced Technology, Gosta Green, Birmingham, England*, and T. WILSON, *Research Division, Formica, Ltd., Maidenhead, Berks., England*

Synopsis

Differential thermal analysis and thermogravimetric analysis techniques were investigated with a view to prediction of the thermal behavior and flammability of plastics materials. Paper-reinforced phenolic and epoxide resins were used. It was found that with phenolic laminates the pattern of the thermograms was characteristic of the paper, while with epoxide laminates (and melamine) it was characteristic of the resin used. This cannot be correlated with fireproofness or flammability, and further work is necessary to establish better techniques and to study the thermal behavior of the laminates by service testing.

INTRODUCTION

The thermal degradation of resins and moldings made from them is of importance in the use of plastics at high temperatures. There is therefore interest, not only in the mechanism of the degradation, but also in the conditions under which it occurs in practice.

Holmes¹ has studied the breakdown of cotton into low boiling fragments, high boiling tar, and carbonaceous residue, and has related this to the degree of flammability. Our paper is concerned with studying the degradation of resins by thermal analysis and if possible, relating it to the release of fragments as described by Holmes.

There are recent reviews of thermal analysis by McKenzie,² Manley,³ and Smothers and Chiang⁴ which give an extensive set of references. Differential thermal analysis (DTA) was used initially for studying phase changes and chemical reactions in minerals and ceramics. It has been used in studying polymers,³ e.g., by Tolchinskii⁵ on polypropylene, Bhannick⁶ on hard rubber, and Anderson⁷⁻⁹ on polyesters. Baker¹⁰ and Varma¹¹ also refer to polymers. Thermal degradation of epoxide resins has been studied and some products identified by Neiman^{12,13} and Anderson,⁸ and these papers were concerned mainly with the mechanism of the reaction. Pyrolysis of phenolic resins has been reported by Heron¹⁴ and Runavot.¹⁵

Our object was to use thermal analysis as a tool to study the properties of molded materials, and DTA was chosen as a screening test to find out the temperatures at which various fragments are evolved. The simple equipment of Roberts and Grimshaw¹⁶ was used, as it was readily available, and

TABLE I

No.	Resinification catalyst	Additive	Analysis of resins		Analysis of laminate	
			Type ^a	Peak, °C. ^b	Type ^a	Peak, °C. ^b
Differential Thermal Analysis						
Phenol resins R ₁	0.075% NH ₃	nil	2	600-700	1	450
	0.030% Ba(OH) ₂	nil	2	450-800	1	400
	0.025% NaOH	nil	1	5/800	1	400
	0.025% NaOH	5% Al ₂ O ₃	1	450/800	1	400
	"	5% NaBO ₂	1	550/900	1	400
	"	12.5% TD CPP	2	560-750	1	250-500
	"	12.5% Phosgard	2	500	1	320-450
	"	12.5% Aroclor	2	570	1	320-430
	"	nil	3	650	3	550
	"	nil	3	450	—	—
Thermogravimetric Analysis						
Phenol resins R ₁	0.025% NaOH	nil	2	400-750	1	230/580
	"	12.5% TD CPP	1	420-690	1	200-600
	"	12.5% Phosgard	2	400-700	—	—
	"	12.5% Aroclor	2	400-800	1	240-570
Melamine resin R ₂						
Paper alone						

^a Type 1: two distinct major peaks; type 2: one complex major peak; type 3: one sharply defined narrow peak.

^b Solidus (/) denotes two separate peaks; dash (-) gives width of a complex peak.

no other technique seemed to be especially standardized. This seemed justified because we required only empirical information about the effect of variations of the resin upon properties of the moldings made from it. In addition, thermogravimetric analysis (TGA) was used to follow the rate of degradation, as well as vacuum pyrolysis,¹ which we hoped would relate to plastics materials.

It was known that resins containing aromatic rings¹⁷ with methylene or ether bridges break down at ca. 200°C. in presence of oxygen, but otherwise only at 500–600°C. A preliminary experiment in presence of nitrogen unexpectedly showed a slight exotherm, perhaps due to traces of oxygen.

Most of the work was done in presence of air or oxygen (150 cc./min. were passed through the furnace), the rate of temperature increase was 10°/min., and the reference material was silica of 30–85 mesh B.S. grist.

PHENOLIC RESINS

Experimental

This section is concerned with DTA and TGA of phenolic resin, kraft paper, and laminates made from them. At first, a standard phenolic resin and paper were used, and in later experiments various inorganic materials, phosphate esters, or chlorinated organic compounds were added. Some work was done with melamine resin, for comparison. R1 was a phenol/formaldehyde resin with a molar ratio of 1:1.3 and catalyzed as indicated in Table 1. R2 was BL 49 supplied by B.I.P. Chemicals, Ltd. Paper used was kraft, 75 g./m.², supplied by Wiggins Teape, Ltd.

Tris(dichloropropyl) phosphate (TDCPP), tritolyl phosphate (TTP), Phosgard ClCH₂CH₂[PO(OCH₂CH₂Cl)OCH(CH₃)₃]Cl (Monsanto Chemicals Ltd.), and Aroclor chlorinated diphenyl (Monsanto Chemicals Ltd.), were used as additives.

Samples of resin for analysis were prepared by heating 5 g. resin in a shallow dish at 135°C. till fully cured then grinding to pass 30 mesh but retained on 85 mesh.

Laminates were prepared by hand dipping the paper in the resin to give a resin content of 35–40%, drying, and pressing at 1400 psi and 135–145°C. till fully cured. The degree of cure was assessed from previous experience of these systems. The samples were ground and sieved and the fraction between 30 and 85 mesh used for analysis.

The paper was prepared for analysis by grinding and compressing to the same volume as it would occupy in a laminate.

The thermal analysis cell and furnace¹⁶ were obtained from Gallenkamps, Ltd. London. The reference temperature was determined by a potentiometer (Forster 3154X/1532) and the differential by a galvanometer (Scalamp 7901/5).

Thermogravimetric analysis was made using a Stanton recording balance with a cell similar to that for DTA, and again the work was done in presence of oxygen or air.

Results

The results of DTA were plotted on a curve showing the relation of differential to reference temperature. TGA was shown as a curve of rate of weight loss against temperature, and is therefore directly comparable with the DTA curves.⁸ The position of the peaks is given in Table I and typical peaks in Figure 1.

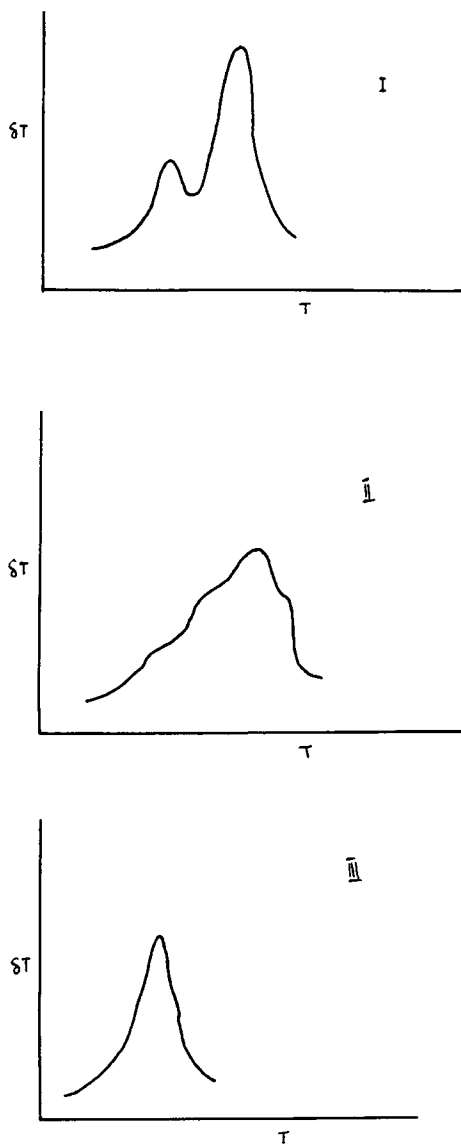


Fig. 1. Typical DTA curves: (*I*) two distinct major peaks; (*II*) one complex major peak; (*III*) one sharply defined narrow peak.

TABLE II
DTA, TGA, and VP of Epoxide Resins

No.	Resin	Resinification catalyst	Resin alone			Paper laminate			Glass laminate				
			DTA peak, °C.*	TGA peak, °C.	VP I, II, %	DTA peak, °C.*	TGA peak, °C.	VP I, II, %	DTA peak, °C.	VP I, II, %	VP I, II, %		
15	R ₃	None	300/400/530		20	64	350		22	49	460	93	8
16	"	12.5% TDOPP	360/600	410	28	45	290/650		31	30	450	69	19
17	"	12.5% TTP	360/575	400	25	29	330/600		28	42	480	88	8
18	"	12.5% Arochlor	390/500	410	23	62	300/600		32	42	450	65	30
19	"	12.5% Phosgard	330/600	410	31	42	310/600		33	26	450	67	18
20	"	Brom. DDS	360/590	550	20	56			23	51			
21	"	HET acid	290/460	610	24	63	440/670	500	22	47			
22	R ₄ (Brom. resin)		400/560	450	27	53	330/500	450	28	50	400	83	14

* Solidus (/) denotes two separate peaks.

EPOXIDE RESINS

The work was extended to epoxide resins and laminates made from them. In addition to DTA and TGA, vacuum pyrolysis (VP) was carried out and the amount of tar (VP I) and charred residue (VP II) were estimated.

A standard epoxide resin was used alone and with additives, and later, brominated or chlorinated hardeners and brominated resin were used.

R3 was resin MY750 supplied by CIBA (ARL) Ltd. with diaminodiphenyl sulfone (DDS) as hardener and benzyldimethylamine (BDMA) as catalyst.

R4 was made by brominating bisphenol A by the addition of liquid bromine to a 20% solution in aqueous alcohol. The resin was formed as described in the literature.¹⁸

Diaminodiphenylsulfone was brominated by the addition of liquid bromine to an alcohol solution. Bromine content was 24.6% (theory for monobromo compound 25.8%).

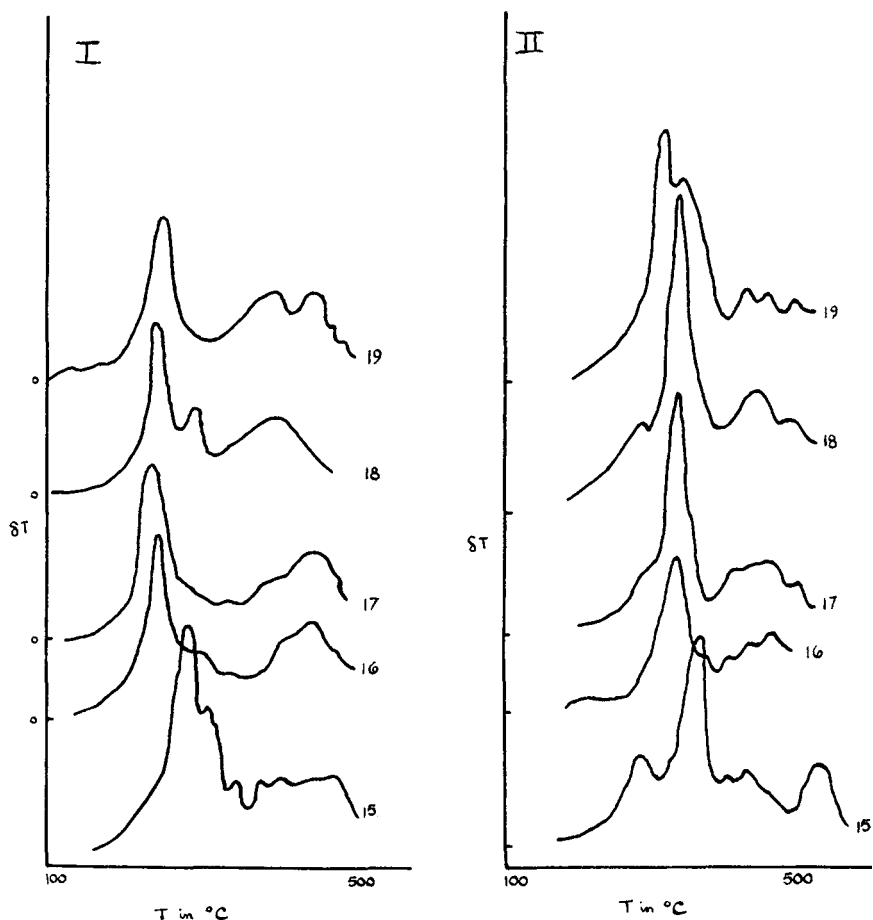


Fig. 2. DTA curves: (I) epoxide resins; (II) epoxide laminates.

HET-acid, (hexachloroendomethylenetetrahydrophthalic acid) was supplied by M. W. Hardy & Co. Ltd.

Samples of resin for analysis were prepared as described above. Laminates were made with cotton paper (150 g./m.²) from Wiggins Teape, Ltd., with 55–60% resin content, and with glass cloth (Y101/T5) from Fothergill & Harvey, Ltd., with 35–40% resin content. Laminates were pressed at 700 psi and 160–165°C. The thermal analyses were as described for the phenolic resins, except that the temperatures in the DTA were recorded by a Cambridge sixpoint potentiometric recorder (1 mv. full-scale deflection for reference and $\pm 1/2$ mv. for differential temperature). Vacuum pyrolysis was done exactly as described by Holmes.¹

Results

The results of DTA, TGA, and VP were expressed as described previously and the results are given in Table II. Typical curves are shown in Figure 2.

DISCUSSION

We found that under the conditions of the work described, the results of DTA were qualitative only. The positions of the events recorded could be reproduced, but the area under the curve varied. This must mean that more refined techniques and equipment are necessary. This feature of DTA was commented upon recently,⁹ and our results confirm that DTA is best used in conjunction with other methods.

Three different types of curve were obtained with different number or shape of peaks; these were type 1: two distinct major peaks; type 2: one complex major peak; type 3: one sharply defined narrow peak.

When phenolic resins were tested alone, the results were strongly affected by the catalyst used in the condensation. When NaOH was used the curve was type 1 with a marked peak at about 500°C. and a second one at 750–800°C. With Ba(OH)₂ there was a single type 2 peak showing maxima at about the same temperatures. When the catalyst was ammonia or an amine there was a fairly simple peak at 750°C.

When the same resins were tested in the form of laminates there was a type 3 curve showing a single sharp peak at about 400–550°C. and identical with that given by paper alone.

The addition of inorganic materials to the resin does not have a great deal of effect. Alumina obscures the dip between the two peaks, and sodium borate gives a first peak distinctly lower and about 50°C. later, and the second peak is delayed almost 100°C. The laminates from these resins give a normal type 3 curve.

In the DTA curves effects of aromatic phosphates (tolyl and xylenyl) are slight and similar, chloroethyl phosphate has rather more effect and tris-(dichloropropyl) phosphate and Phosgard markedly decrease the height of the peaks while Aroclor gives a characteristic plot peak at 650°C., which is 50–70°C. higher than all the others (Table II).

Both melamine resins and laminates made from them give a single very sharp peak at 550°C. This appears to indicate complete suppression of the effect of the paper, perhaps indicating chemical reaction between the resin and the paper.

When DTA was carried out in the presence of nitrogen very little exotherm was found up to 900°C. This was taken to indicate that the system of aromatic rings linked by methylene bridges is inherently stable, except under oxidative conditions. Later, results of TGA on other resins indicated that this is only partly true, and that in fact part of the DTA curve is missing.

The degradation of all epoxide resins systems followed a single pattern. This is unlike phenolic resins, but like melamine resins, and again the resins and paper laminates give similar curves. When the curves for DTA and TGA of resin samples are compared, a considerable loss in weight is found, which does not correspond to any thermal indication. With laminates there is more overlap, but the loss in weight is still well in advance of the exotherm. These observations may mean that a part of the pyrolysis products escaped from the cell and was oxidized in the furnace where the exotherm was not picked up by the differential thermocouple. This would mean that the first part of the DTA curve which is formed from two factors, an endothermic reaction due to bond breaking, and an exothermic one due to oxidation, will have a variable form according to the amount of material escaping from the cell. This would mean that the exotherm actually recorded represents oxidation of carbon and nonvolatile fragments within the cell. This part of the curve was considerably altered by halogenated additives and may correspond to the "after-glow" mentioned by Holmes.¹ More work on analysis of the volatile products at this stage is necessary to clarify this point.

Vacuum pyrolysis results show considerable correlation between the quantities of tar (VP I) and char (VP II), high tar being associated with low char. The variation of results is not very high and does not correspond to any features of the DTA and TGA results.

CONCLUSIONS

(1) Phenolic resins give DTA results depending on the catalyst used. There is a complex of peaks between 200 and 750°C.

(2) Laminates from phenolic resins give a single sharp peak at 450°C. which is identical with that from paper alone.

(3) Melamine resins and paper laminates from them given a single sharp peak at 550°C.

(4) Epoxide resins and laminates from them have similar curves irrespective of added material.

(5) There are insufficient TGA results to enable general conclusions to be drawn.

(6) Direct application of the results to problems of thermal stability of plastics was not found possible.

(7) Better experimental techniques are required. This is at present being investigated.

Acknowledgments are made to the Director and personnel of the Research Department of Formica, Ltd., for help in this work, and to the Directors for permission to publish.

References

1. Holmes, J. C., *J. Appl. Chem. (London)*, **5**, 21 (1961).
2. McKenzie, R. C., *Analyst*, **87**, 420 (1962).
3. Manley, T. R., "Techniques of Polymer Science," *Soc. Chem. Ind.*, Monograph No. 7, London, 1962.
4. Smothers, W. J., and Y. Chiang, *Differential Thermal Analysis*, Chemical Publishing Co., New York, 1958.
5. Tolchinskiĭ, I. M., *Soviet Plastics*, **1**, 6 (1960).
6. Bhaumik, M. L., *J. Appl. Polymer Sci.*, **4**, 366 (1960).
7. Anderson, H. C., *Anal. Chem.*, **31**, 1697 (1959).
8. Anderson, H. C., *Anal. Chem.*, **32**, 1592 (1960).
9. Anderson, H. C., *Nature*, **191**, 1088 (1961).
10. Ke, B., and B. Ke, in *Organic Analysis*, Vol. 4, Interscience, New York, 1960.
11. Varma, M. C. P., *J. Appl. Chem. (London)*, **8**, 117 (1958).
12. Neiman, M. B., *J. Polymer Sci.*, **56**, 383 (1962).
13. Neiman, M. B., *Vysokomol. Soedin.*, **1**, 1531 (1959); *ibid.*, **3**, 602 (1961); *Dokl. Akad. Nauk SSSR*, **135**, 1147 (1960).
14. Heron, G. F., "Thermal Degradation of Polymers," *Soc. Chem. Ind.*, Monograph No. 13, London, 1961.
15. Runavot, Y., and P. Schneebeli, *Recherche Aeronautique*, **80**, 13 (1961).
16. Roberts, R. W., and A. L. Grimshaw, *Trans. Brit. Ceramics*, **52**, 50 (1953).
17. Newkirk, A. E., *Anal. Chem.*, **32**, 1559 (1960).
18. Brit. Pat. 681,108, example 2 (Bataafsche Petroleum Maatschappij), October 15, 1952.

Résumé

Des analyses thermiques différentielles et des analyses chermogravimétriques ont été effectuées en vue de prédire le comportement thermique et l'inflammabilité de matières plastiques. On a employé du papier renforcé par des résines phénoliques et époxydes. On a trouvé que, avec des lamelles de résines phénoliques, le diagramme des thermogrammes était caractéristique du papier tandis que avec des lamelles d'époxyde (et de mélamine) il était caractéristique de la résine utilisée. Ceci ne peut être mis en rapport avec l'incombustibilité ou l'inflammabilité, et dès lors un travail ultérieur est nécessaire pour établir de meilleures techniques et pour étudier le comportement thermique des lamelles par des essais de service.

Zusammenfassung

Die Differentialthermal- und die thermogravimetrische Analyse wurde in Hinblick auf die Vorhersage des thermischen Verhaltens und der Entflammbarkeit von plastischen Stoffen untersucht. Mit Phenol und Epoxydharzen verstärktes Papier wurde verwendet. Bei Phenolbeschichtung erwies sich der Verlauf des Thermogramms für das verwendete Papier, bei Epoxyd- (und Melamin-)beschichtung für das verwendete Harz charakteristisch. Es besteht keine Beziehung zur Feuerfestigkeit oder Entflammbarkeit, daher ist eine weitere Untersuchung für bessere Methoden und zum Verständnis des thermischen Verhaltens der Beschichtungsmaterialien notwendig.

Received December 26, 1963