

Thermal Degradation of Epoxide Polymers

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INTRODUCTION

Investigation of the thermal degradation of cross-linked epoxide polymers by differential thermal analysis is not satisfactory because they usually contain residual epoxy groups. Since the heat and temperature of degradation are the main parameters involved in differential thermal analysis, concomitant exothermic isomerization¹ and/or polymerization of the residual epoxy groups and endothermic bond scission and volatilization of the polymer would complicate the picture.^{2,3} A better dynamic technique for studying the pyrolysis of epoxide polymers is differential thermogravimetry, which was used in this investigation. This consisted of electronically recording weight loss of a decomposing sample as a function of temperature and time, while sample temperature was continuously raised at a rate of 5°C./min. from 25 to 925°C. Resulting weight loss curves were graphically differentiated with respect to time, and these differentials were then plotted versus temperature of sample. Experiments were run *in vacuo* to avoid complications that would be caused by oxidation reactions in air and slow diffusion of decomposition products from the samples under atmospheric pressure. The differential thermogravimetric curves show how the chemical structures of both the epoxide monomer and polymerizing agent can influence the mode and rate of decomposition of the resulting polymer. Polymers containing methyl nadic anhydride had two chief modes of decomposition, whereas those containing maleic anhydride or *m*-phenylenediamine had only one. This difference in behavior is attributed to the tendency of the dicarboxylic structure in methyl nadic anhydride to decarboxylate.

EXPERIMENTAL

Materials

The materials were used as received without further purification, and their suppliers were as

follows: D.E.R. 332 (diglycidyl ether of bisphenol-A), The Dow Chemical Co.; resorcinol diglycidyl ether, Koppers Company, Inc.; maleic anhydride, Fisher Scientific Co.; methyl nadic anhydride, Allied Chemical Corp., National Aniline Division; *m*-phenylenediamine (purified), General Aniline and Film Corp. Each of the two epoxide monomers was polymerized with stoichiometric amounts (based on epoxy equivalents of monomers) of methyl nadic anhydride and *m*-phenylenediamine. D.E.R. 332 epoxide monomer was also polymerized with maleic anhydride. *N,N*-dimethylbenzylamine (1% of the weight of epoxide) was used as a catalyst in the anhydride polymerizations. All five of the reaction mixtures were subjected to the following cumulative polymerization schedule: 24 hr. at 60°C.; 24 hr. at 100°C.; 4 hr. at 150°C.; 2 hr. at 175°C.; 1 hr. at 200°C. Resulting polymers were pulverized, carbon dioxide snow being used as a coolant to prevent premature pyrolysis. Air-dried particles collected between a 60 and 100 mesh screen were used for pyrolysis studies.

Apparatus and Procedure

The thermogravimetric apparatus was built around an Ainsworth Model RU-AU-2 semimicro vacuum recording balance, as shown photographically in Figure 1 and schematically in Figure 2. A Marshall furnace was used to heat the sample, and a West Instrument Corp. Model JSBG-2 stepless programming and controlling pyrometer was used to maintain the heating rate. Interruption of the current in the cam-motor circuit with an Eagle Signal Corp. 60-sec. timer permitted the selection of any heating rate from 0° to 20°C./min. over the range of from 25 to 1000°C. The heating rate of the furnace was monitored with a Brown recorder. Both the sample and furnace temperatures were measured with B and S No. 28 Gage chromel-alumel thermocouples. The sample thermocouple was located 1/4 in. above the crucible

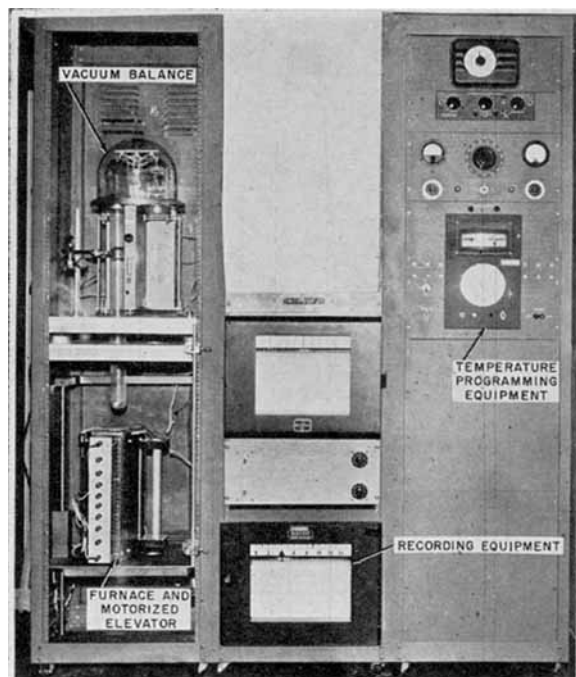


Fig. 1. Thermogravimetric apparatus.

and 1/4 in. from the platinum-quartz chain that supported the crucible. Quartz was used in the upper part of the chain to minimize heat conduction to the balance; it was not used for the entire chain because it sublimates at high temperatures.

Ten-milligram samples (weighed to 0.1 milligram on an ordinary semimicro balance) were heated in No. 0000 Coors glazed porcelain crucibles at a rate of $5 \pm 0.5^\circ\text{C./min.}$ over the temperature range from 25 to 925°C. Loss of sample weight as a function of temperature and time was followed by means of a Bristol two-pen recorder. All of the experiments were performed at a pressure of approximately 0.05 mm. Hg. The weight-loss curves were converted to percentage weight-loss curves and then graphically differentiated with respect to time. These rate-of-weight-loss values were then plotted versus temperature.

RESULTS

The thermogravimetric curves in Figure 3 show that polymers prepared by reacting maleic anhy-

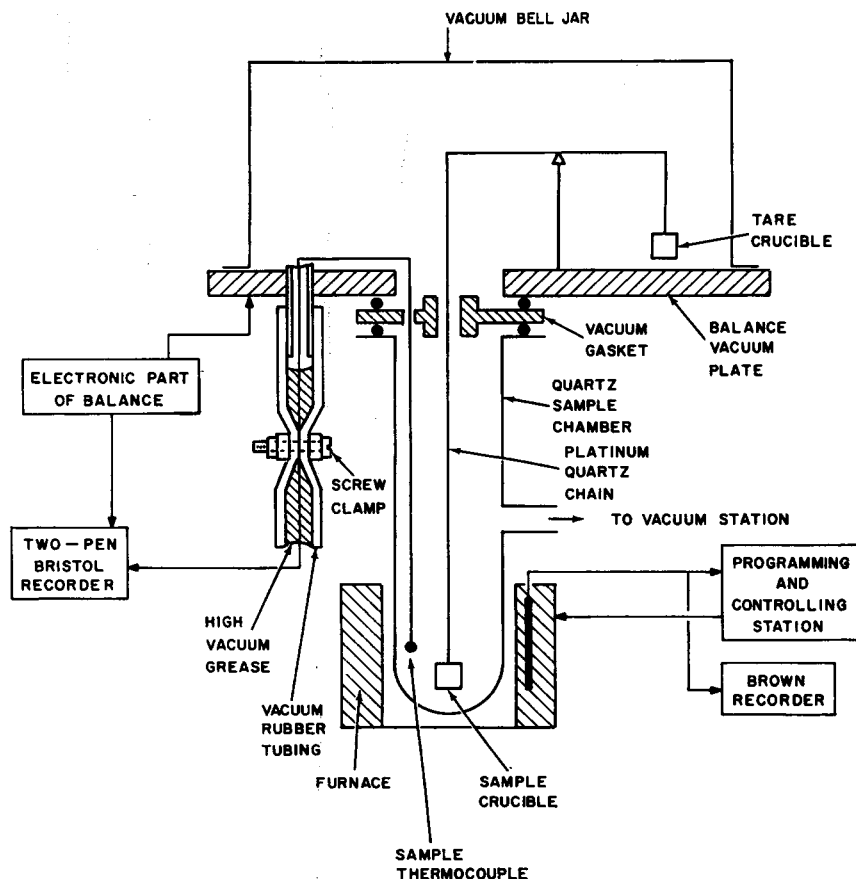


Fig. 2. Thermogravimetric experimental arrangement.

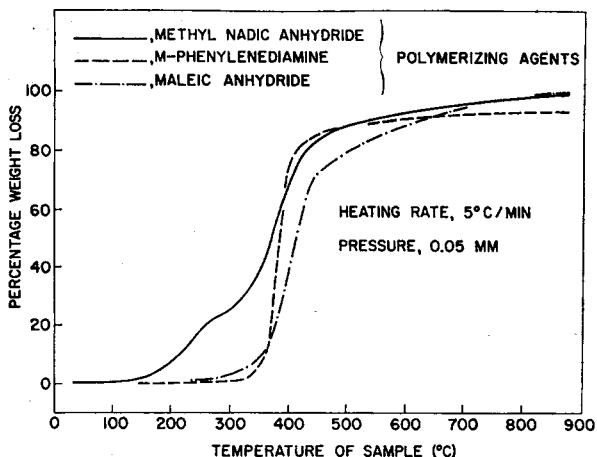


Fig. 3. Thermogravimetric curves for polymers of diglycidyl ether of bisphenol-A.

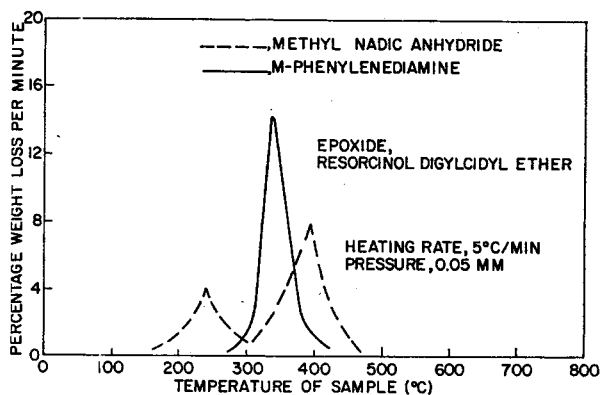


Fig. 6. Differential thermogravimetric curves for epoxide polymers.

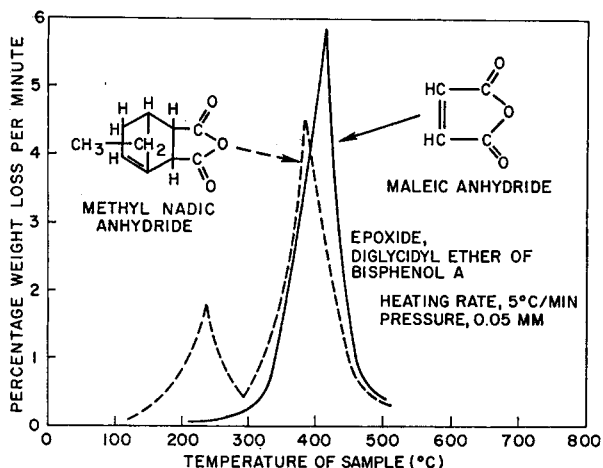


Fig. 4. Differential thermogravimetric curves for epoxide polymers.

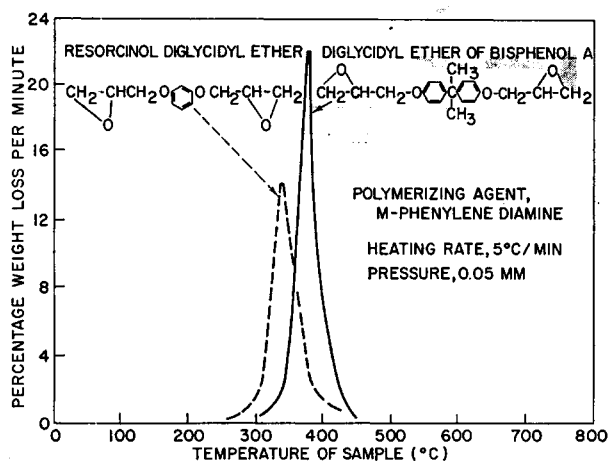


Fig. 7. Differential thermogravimetric curves for epoxide polymers.

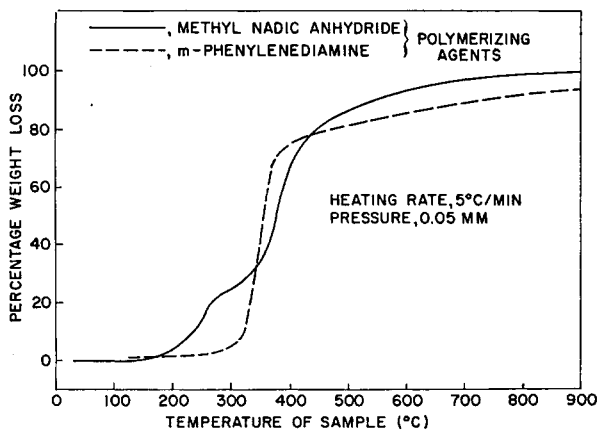


Fig. 5. Thermogravimetric curves for polymers of resorcinol diglycidyl ether.

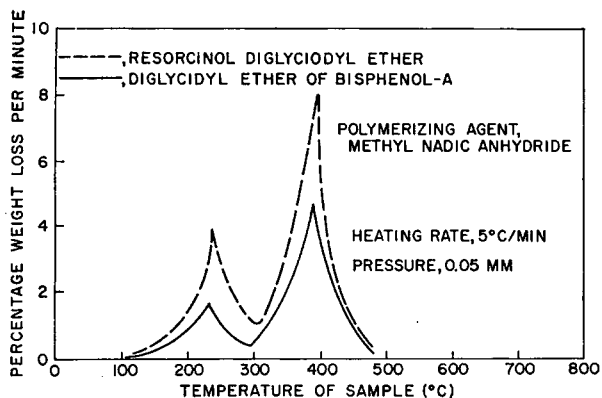


Fig. 8. Differential thermogravimetric curves for epoxide polymers.

dride or *m*-phenylenediamine with diglycidyl ether of bisphenol-A decomposed in one stage, whereas the polymer incorporating methyl nadic anhydride decomposed in two stages. This difference in pyrolytic behavior is better demonstrated by the differential thermogravimetric curves in Figure 4. This same difference in behavior was observed for polymers prepared by reacting resorcinol diglycidyl ether with methyl nadic anhydride or *m*-phenylenediamine, as shown by the thermogravimetric and differential thermogravimetric curves in Figures 5 and 6, respectively.

Comparison of the thermogravimetric curves for polymers prepared by reacting two different epoxide monomers, resorcinol diglycidyl ether and diglycidyl ether of bisphenol-A, with the same polymerizing agent shows that the maximum rates of weight loss were distinctly different. This is shown more clearly in Figures 7 and 8.

DISCUSSION

The first stage (Figures 3 and 5) of the two-stage mechanism of degradation of epoxide polymers incorporating methyl nadic anhydride is attributed to decarboxylation of ester groups. This assumption seems reasonable since methyl nadic anhydride itself decarboxylates, as was shown by heating it to about 200°C. in a stream of nitrogen and precipitating the carbon dioxide evolved in barium hydroxide solution. Although the exact location of the double bond in methyl nadic anhydride (Fig. 4) has not been established, this ease of decarboxylation suggests that it may be in the β - γ position.⁴ At any rate, the methyl nadic dicarboxylic structure would be present in the ester groups, which could have been formed by either or both of the following reactions: (a) direct addition of the ionic form of the anhydride to the ionic form of the epoxy, both ionic forms being catalyzed by *N,N*-dimethylbenzylamine,⁵ and/or (b) reaction of the anhydride with a hydroxyl group to form a monoester containing an acid group if the hydroxyl group is contained in an alcohol or phenol, or two acid groups if the hydroxyl group is derived from water. These acids can react with epoxy linkages to form diesters and new hydroxyl groups.⁶ Both of the epoxide monomers used were shown to contain hydroxyl groups by infrared spectroscopy. The hydroxyl groups could have originated from traces of water or, more likely, from unreacted phenolic groups in the resorcinol or bisphenol-A derivative.

On the basis of stoichiometric relationships, evolution of carbon dioxide could not account for

all of the weight loss in the first stage of decomposition. Nevertheless, decarboxylation could certainly be responsible by generating free radicals capable of initiating other degradative reactions, in addition to further crosslinking reactions.

Chemical structures of the epoxide monomers, as well as those of the polymerizing agents, can influence the pyrolysis characteristics of the resulting polymers. For example, Figure 7 shows that the replacement of the phenyl group between two glycidyl ether groups in resorcinol diglycidyl ether by a 2,2-diphenylpropyl group increases appreciably the maximum rate of decomposition of the polymer when *m*-phenylenediamine is the polymerizing agent. This maximum is also shifted to a higher temperature. When methyl nadic anhydride was used to polymerize the same two epoxide monomers, the maximum rates of decomposition for the two polymers were also appreciably different. However, in this case, the polymer derived from resorcinol diglycidyl ether had the higher maximum rate of degradation. These observations demonstrate the importance of the overall chemical structure of the final polymer, as well as those of the epoxide monomers and polymerizing agent, in affecting its mode of thermal degradation.

References

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Synopsis

The thermal degradation of five crosslinked epoxide polymers were studied *in vacuo* by differential thermogravimetry. Three of the polymers were prepared by reacting methyl nadic anhydride, maleic anhydride, and *m*-phenylenediamine with diglycidyl ether of bisphenol-A; the other two were obtained by reacting methyl nadic anhydride and *m*-phenylenediamine with resorcinol diglycidyl ether. Ten-milligram powdered samples were heated over the temperature range from 25° to 925°C. at a rate of 5°C./min. Differential thermogravimetric curves showed that the polymers incorporating methyl nadic anhydride decomposed in two distinct stages, whereas those based on *m*-phenylenediamine or maleic anhydride degraded in only one stage. This difference in mechanism of decomposition is attributed to decarboxylation of ester groups having the methyl nadic

dicarboxylic structure in the polymers. Substitution of a 2,2-diphenylpropyl group for a phenyl group in resorcinol diglycidyl ether, to give diglycidyl ether of bisphenol-A, influenced appreciably the maximum rates of decomposition of the corresponding polymers. In the case of the polymer based on *m*-phenylenediamine, the rate was increased by this substitution, but for the polymer derived from methyl nadic anhydride the rate was decreased.

Résumé

On a étudié la dégradation thermique de cinq polymères époxydés pontés par thermogravimétrie différentielle sous vide. On a préparé trois de ces polymères par réaction de l'anhydride méthyl-nadique, de l'anhydride maléique et de la métaphénylènediamine avec l'éther diglycidyl du A-bisphénol; on a obtenu les deux autres par réaction de l'anhydride méthyl-nadique et de la métaphénylènediamine avec l'éther diglycidyl résorcinol. On a chauffé dix milligrammes d'échantillons poudreux de 25°C. à 925°C à une vitesse de 5°C/min. Les courbes thermogravimétriques différentielles ont montré que les polymères, contenant l'anhydride méthyl-nadique, se décomposent en deux étapes distinctes, tandis que ceux basés sur la métaphénylènediamine ou l'anhydride maléique se décomposent en une seule étape. On attribue cette différence de mécanisme de décomposition à la décarboxylation des groupes esters ayant la structure méthyl-nadique carboxylique dans le polymère. La substitution d'un groupe, 2,2-diphényl-propyl par un groupe phényl dans l'éther diglycidyl résorcinol, qui donne l'éther diglycidyl du bisphénol A, a fortement influencé les vitesses maximales de décomposition des polymères correspondants. Dans le cas des polymères à base de métaphénylènediamine, la vitesse est accrue par cette

substitution tandis que la vitesse décroît pour les polymères dérivés de l'anhydride méthyl-nadique.

Zusammenfassung

Es wurde der thermische Abbau von fünf vernetzten Epoxydpolymeren im Vakuum durch Differential thermogravimetrie untersucht. Drei der Polymeren wurden durch Reaktion von "methyl nadic"-Anhydrid, Maleinsäureanhydrid und meta-Phenylen-diamin mit dem Diglycidyl-äther des Bisphenol-A dargestellt; die anderen zwei wurden durch Reaktion von "methyl nadic"-Anhydrid und meta-Phenylen-diamin mit Resorcinoldiglycidyläther erhalten. Zehn Milligramm der gepulverten Proben wurden von 25 auf 925°C mit einer Geschwindigkeit von 5°C/min. erhitzt. Die differential thermogravimetrischen Kurven zeigten, dass die Zersetzung der Polymeren mit "methyl nadic"-Anhydrid zwei unterscheidbare Stufen aufweist, während die Polymeren auf Grundlage von meta-Phenylen-diamin und Maleinsäureanhydrid sich in einer Stufe zersetzen. Dieser Unterschied im Zersetzungsmechanismus wird der Decarboxylierung der Estergruppen zugeschrieben, welche die "methyl nadic"-Dicarbonsäurestruktur in den Polymeren besitzen. Durch Substitution der Phenylgruppe im Resorcinol durch eine 2,2-Diphenylpropylgruppe erhält man den Diglycidyläther von Bisphenol-A; diese Substitution hat einen beträchtlichen Einfluss auf die maximale Zersetzungsgeschwindigkeit der entsprechenden Polymeren. Im Falle des von meta-Phenylen-diamin abgeleiteten Polymeren stieg die Geschwindigkeit durch diese Substitution an, für das von "methyl nadic"-Anhydrid abgeleitete nahm die Geschwindigkeit ab.

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