

Thermal Analysis of Nitro-Substituted Epoxide Polymers

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Synopsis

The thermal properties of a number of nitro-substituted and analogous nonnitro-substituted epoxide polymers were investigated. Dramatic increases in char yield and decreases in maximum rate of weight loss were observed for the nitro-substituted systems compared to their nonnitrated analogs. These effects were enhanced when highly functional and highly aromatic epoxide resins were used. The sample size and heating rate employed had pronounced effects upon the amount of char formed during thermal degradation. Analysis of char residues indicates heteroring formation for the nitro-substituted systems during pyrolysis.

INTRODUCTION

In an earlier paper¹ the relationship between the chemical structure of epoxide polymers and their char yield upon pyrolysis was discussed. The effect of the nature of the aromatic moiety (i.e., phenyl, naphthyl, biphenyl), the position of attachment of the glycidyl groups, and the nature of substituents on the aromatic moiety (i.e., chloro-, benzyl-, ethyl-, nitro-) upon the char yield of these systems was shown. Char enhancement attributable to the above structural variations was notable only in the case of nitro-substitution. It was shown that pyrolysis of an epoxide resin derived from 2-nitroresorcinol gave a residue at 800°C that was quantitatively increased and qualitatively different from other epoxide systems studied previously. A further investigation of the extent and nature of this unique method of char enhancement by nitro-substitution was undertaken. The thermal analysis of several of the nitro-substituted polymers studied is the subject of this paper.

EXPERIMENTAL

Materials

The following are the materials used, together with their purity (melting point) and source.

2-Nitroresorcinol (I). Twice recrystallized from water to give orange crystals (83–83.5°C) (J. T. Baker).

* Present address: Fiberite Corporation, Minona, Minnesota 55987.

2-Nitro-p-phenylenediamine (II). Recrystallized from water (122–123°C) (Aldrich Chemical).

3-Nitro-o-phenylenediamine (III). Used as received (157–158°C) (Aldrich Chemical).

4-Nitro-o-phenylenediamine (IV). Used as received (198–200°C) (Aldrich Chemical).

m-Nitrophenylboric Acid (V). Used as received (>200°C) (Aldrich Chemical).

6-Nitrobenzimidazole (VI). Used as received (210–212°C) (J. T. Baker Co.).

Resorcinol (VII). Used as received (110–111°C) (J. T. Baker Co.).

p-Phenylenediamine (VIII). Recrystallized from water (139–140°C) (Aldrich Chemical Co.).

Benzimidazole (IX). Used as received (170–172°C) (J. T. Baker).

Nadic Methyl Anhydride (NMA) (X). Used as received (straw-colored liquid) (Allied Chemical).

N,N-Dimethylbenzylamine (XI). Used as received (liquid) (J. T. Baker).

Epon 826 (XII). Diglycidyl ether of bisphenol-A, epoxide equivalent weight (EEW) of 188 (Shell Chemical Co.).

Epon 1031 (XIII). Tetraglycidyl ether of tetraphenylene ethane, EEW of 230 (Shell Chemical Co.).

Kopox 171 (XIV). Triglycidyl ether of trihydroxybiphenyl, EEW of 145 (Ciba Products Co.).

DEN 438 (XV). Polyglycidyl ether of phenol-formaldehyde novolac, EEW of 180 (Dow Chemical Co.).

Resorcinol Diglycidyl Ether (XVI). Obtained as ERE-1359 from Ciba Products. It was vacuum-distilled to give a resin with an EEW of 113 (theoretical EEW of 111).

Diglycidyl Ether of 1,5-Naphthalenediol (XVII). Synthesized by the author via the base-catalyzed epichlorohydrin-phenol condensation route. The specific procedure was similar to that of Kelly et al.² Analysis of this resin showed it to have an EEW of 147 and a chlorine content of <0.2%.

Diglycidyl Ether of 1,6-Naphthalenediol (XVIII). Synthesized in a similar manner as XVII. Analysis of this resin showed it to have an EEW of 160 and a chlorine content of <0.2%.

Diglycidyl Ether of 2,7-Naphthalenediol (XIX). Synthesized in a similar procedure as XVII. Chemical analysis showed this resin to have an EEW of 180 and a chlorine content of <0.2%.

Diglycidyl Ether of 2-Nitroresorcinol (XX). Repeated and varied synthesis attempts failed to give an EEW of less than 500 for this resin. The resin used in this work has an EEW of 510.

Polymerization

The resins and curing agents in this study were not always employed in stoichiometric quantities. The following are the concentration levels at which the curing agents were used.

X. This was used at the level of 85% of the stoichiometric amount (S.A.) with 1% by weight of resin of N,N-dimethylbenzylamine (BDMA) being used as catalyst.

I, VII. These were used at levels below stoichiometric amounts—0.3 mole/EEW—unless otherwise noted. BDMA catalyst was used in these systems in the concentration of 1% by weight of resin.

V. This was also used at the 0.3 mole/EEW stoichiometry. The cure mechanism with this material seems to be both catalytic and coreactive. No optimization of concentration was attempted.

II, III, IV, VIII. These were used at stoichiometric levels (i.e., one amino hydrogen per epoxide group).

VI, IX. These were used at the level of 0.2 mole/EEW since these curing agents are both of the coreactive and the catalytic type. Again no optimization of concentration was attempted.

The above were admixed with the various epoxy resins and gelled at 100°C for 2–5 hr, with a subsequent cure of 4 hr at 140°C and 16 hr at 165°C. The exact temperature and time for gelation and initial cure varied somewhat with the reactivity and solubility of the curing agent and resin. Castings of the epoxide polymers varied greatly in quality and appearance. Excellent castings, however, were obtained with most of the resins using the curing agents I and II.

Thermal Analysis

Thermogravimetric analysis was performed on the various resin systems employing a 20-mg powder sample (>60 < 80 mesh) in an apparatus described previously.³ The heating rate employed was 5°C/min under vacuum.

RESULTS AND DISCUSSION

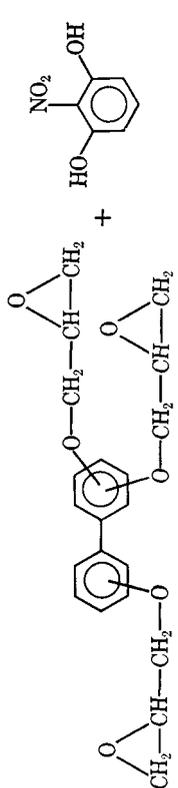
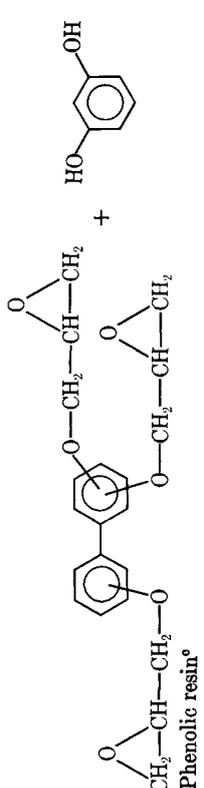
Thermal performance data of several nitro-substituted epoxide polymers is presented in Figures 1–10. In general, one observes that nitro-substitution (within the limits explored in this investigation), greatly enhances the char yield while substantially lowering the maximum rate of weight loss in these systems compared to their nonnitrated analogs. Also, weight retention is increased by the use of resins having a high degree of aromaticity and functionality. The thermal behavior of the cured polymer seems to be insensitive to the origin of the nitro group (i.e., substitution on the resin or curing agent) and to the position of substitution on the aromatic nucleus.

Mechanism and Parametric Effects

The exact mechanism of thermal degradation and char enhancement by nitro-substitution is not known but is now being investigated. That it is different from the normal epoxide degradation scheme is obvious from the thermograms and rate-of-weight-loss plots. The increased char formation

TABLE I
Effect of Polymer Structure on Chemical Composition of Char at 800°C^a

Resin and curing agent structures	%C	%H	%O ^b	%N
	82.2	1.7	11.0	5.1
+				
+				
	73.2	1.8	22.8	2.2

	87.5	1.6	8.6	2.3
	95.6	1.1	3.3	—
Phenolic resin ^c	96.0	1.7	2.3	—

^a Analysis was performed in duplicate after drying to 200°C under reduced pressure. A 30-mg sample was pyrolyzed under vacuum at a heating rate of 5°C/min; temperature was held for 1 hr.

^b By difference.

^c Data were obtained on a base-catalyzed phenol-formaldehyde resin (Madorsky⁴).

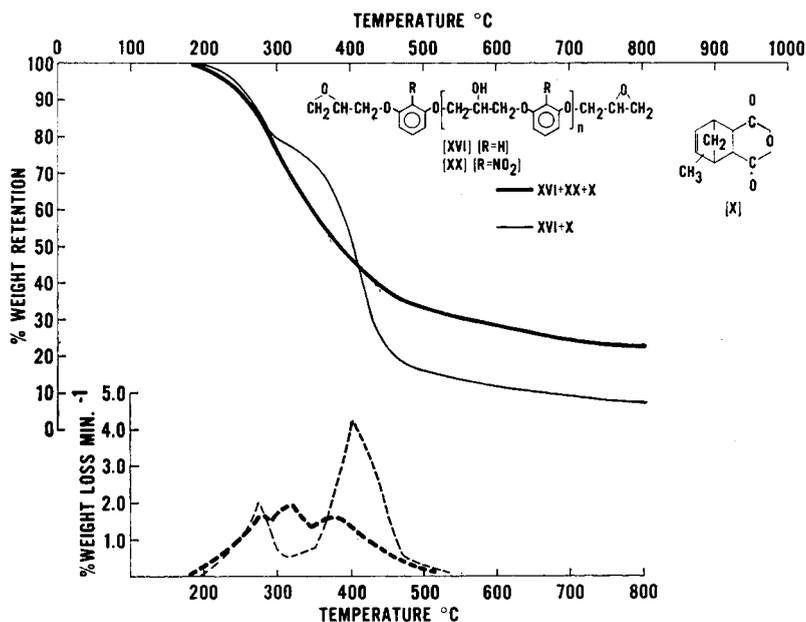


Fig. 1. Thermograms and rate of weight loss plots for resorcinol diglycidyl ether and 2-nitroresorcinol diglycidyl ether cured with nadic methyl anhydride. Roman numerals here and through Figure 10 are those listed in the experimental section for the materials used.

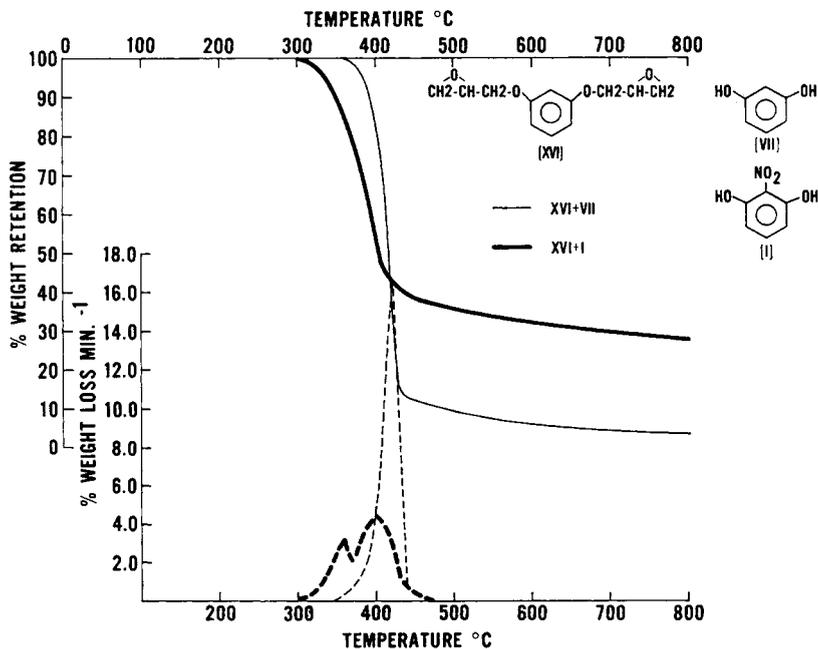


Fig. 2. Thermograms and rate of weight loss plots for resorcinol diglycidyl ether cured with resorcinol and 2-nitroresorcinol.

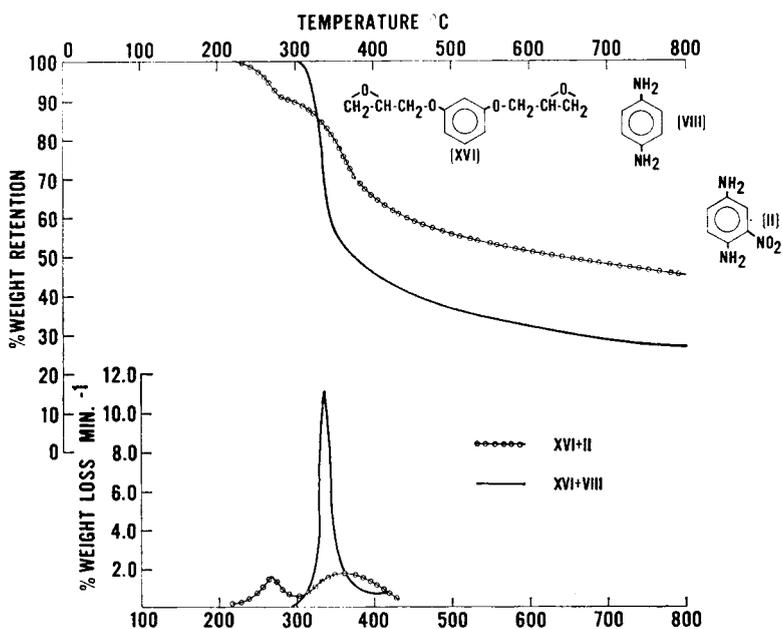


Fig. 3. Thermograms and rate of weight loss plots for resorcinol diglycidyl ether cured with *p*-phenylenediamine and 2-nitro-*p*-phenylenediamine.

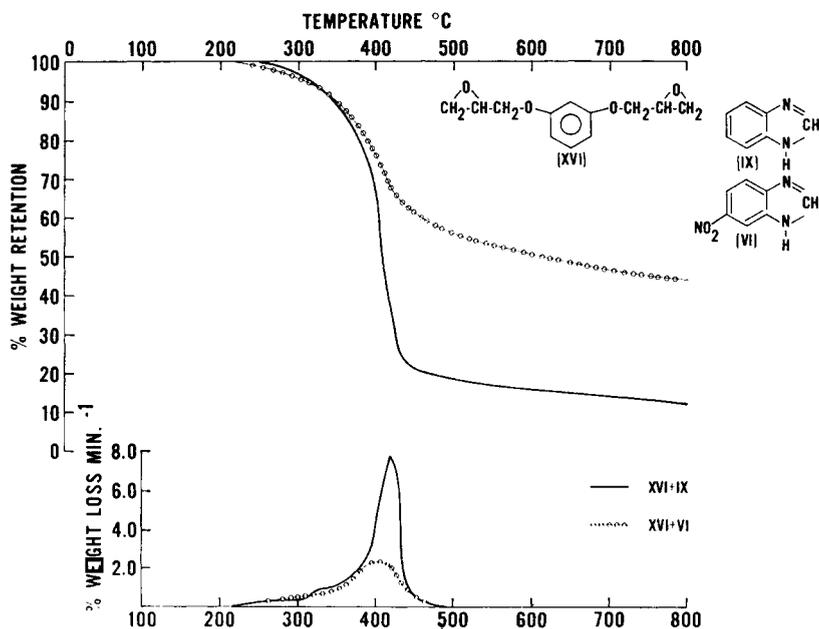


Fig. 4. Thermograms and rate of weight loss plots for resorcinol diglycidyl ether cured with benzimidazole and 6-nitrobenzimidazole.

and lower maximum rates of weight loss induced by the nitro-substitution during thermal degradation may in particular be the result of (1) activation of sites on the aromatic ring for condensation reactions, (2) participation of the nitro group itself in thermal reactions leading to additional cross-

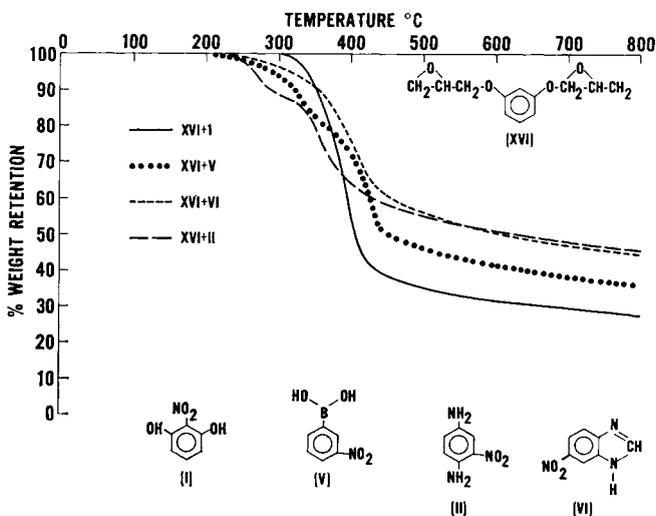


Fig. 5. Thermograms of resorcinol diglycidyl ether cured with several nitro-substituted curing agents.

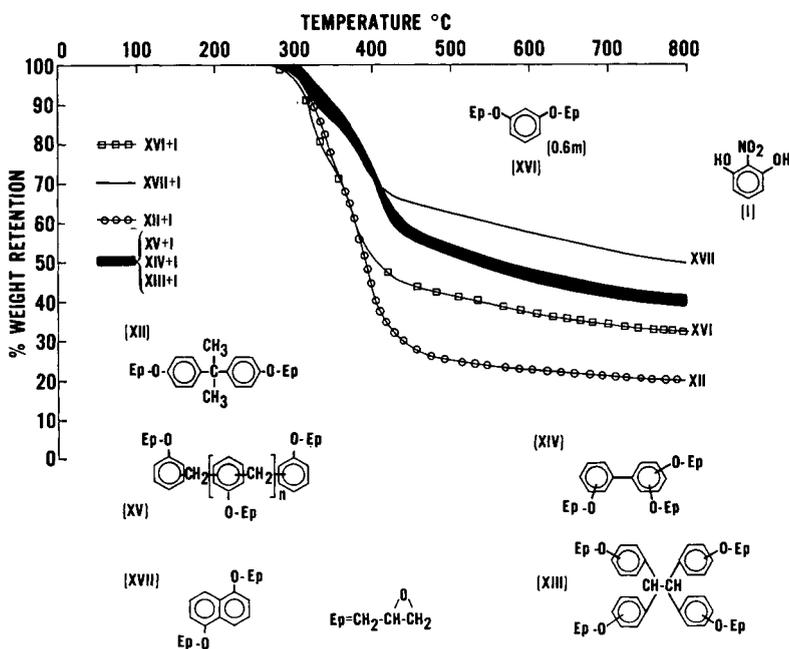


Fig. 6. Thermograms of several epoxy resins cured with 2-nitroresorcinol.

linking as well as heteroring formation, and (3) cleavage of the nitro group itself producing free radicals which can participate in crosslinking and char building reactions. Undoubtedly all of these effects are contributory to the complex degradative scheme.

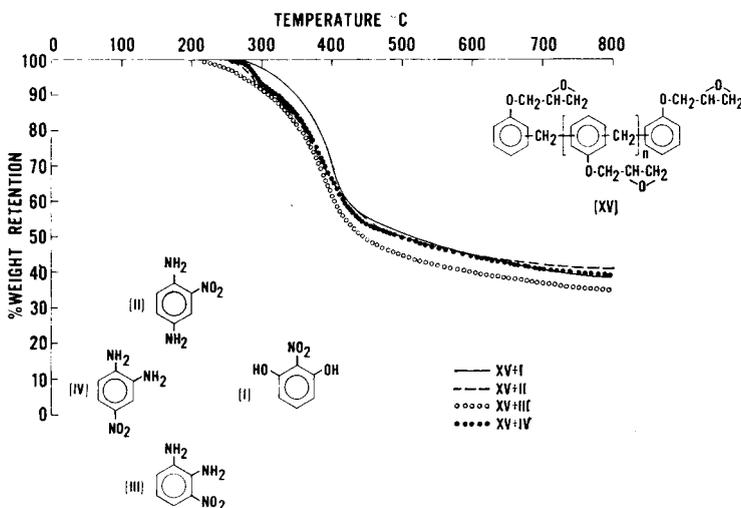


Fig. 7. Thermograms of an epoxy novolac resin cured with several nitro-substituted phenylenediamines.

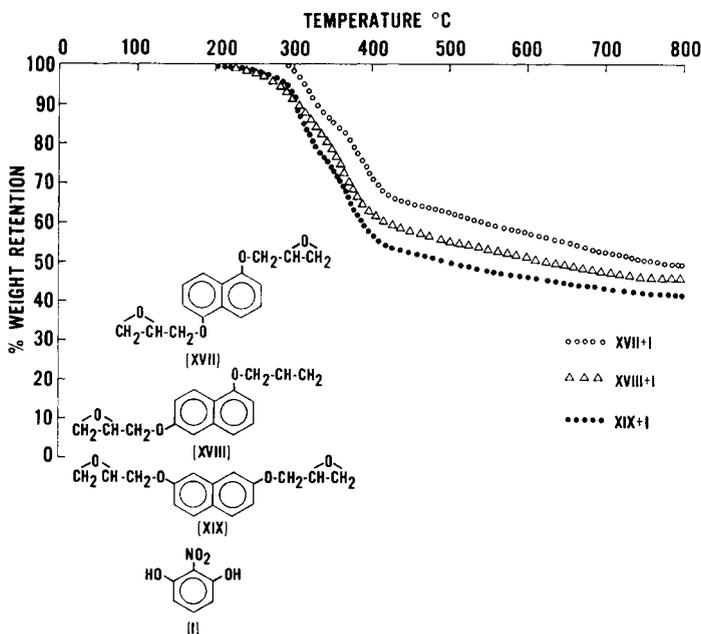


Fig. 8. Thermograms of the diglycidyl ethers of 1,5-, 1,6-, and 2,7-naphthalenediol cured with 2-nitroresorcinol.

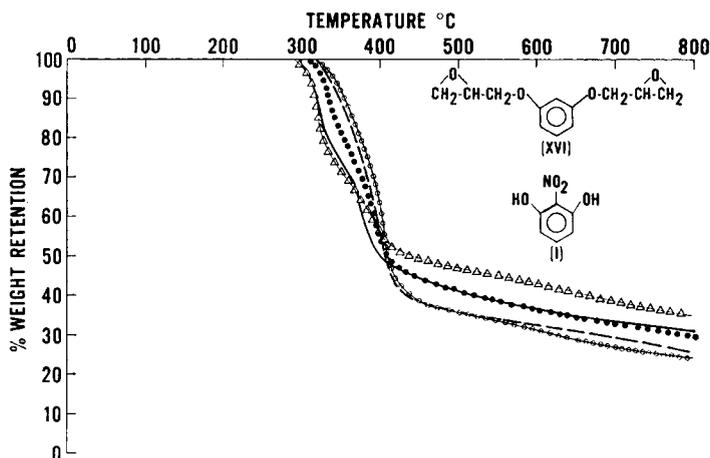


Fig. 9. Thermograms of resorcinol diglycidyl ether cured with various concentrations of 2-nitroresorcinol: (○) 0.2 mole/EEW; (---) 0.3 mole/EEW; (●) 0.4 mole/EEW; (—) 0.5 mole/EEW; (Δ) 0.6 mole/EEW.

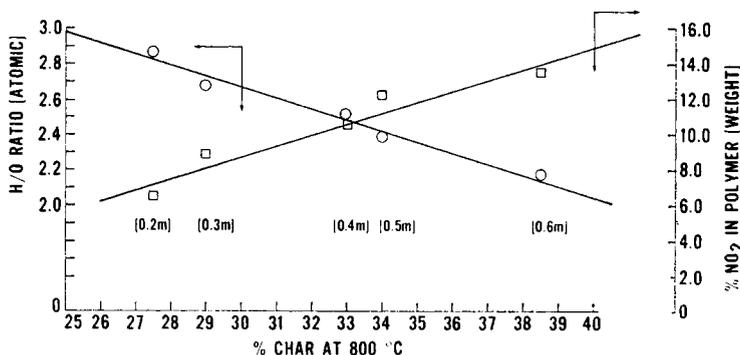
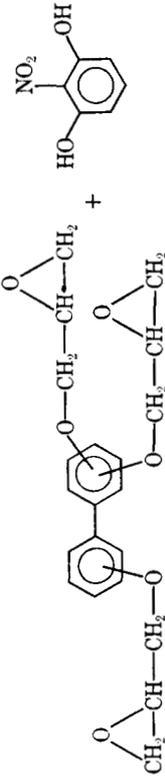
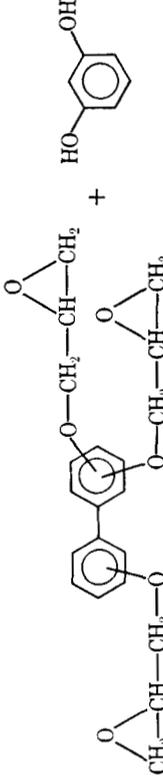
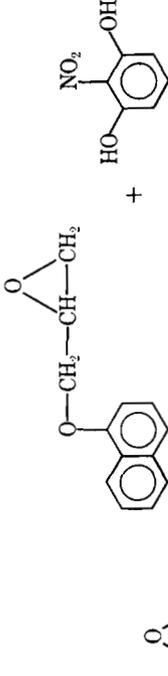


Fig. 10. Linear dependence of quantitative char enhancement upon the nitro group content of an epoxide polymer (resorcinol diglycidyl ether cured with 2-nitroresorcinol).

Chemical analysis of the chars of several systems heated to 800°C are shown in Table I. The high oxygen and nitrogen values of the nitro-substituted epoxides would seem to indicate heteroring formation as one of the modes of char enhancement since no other structure containing C, N, and O would be expected to be stable at 800°C. Data are also presented for a conventional phenolic resin and a nonnitro-substituted epoxide for comparison.

An investigation of the effect of heating rate and sample mass upon quantitative char yield for a nitro-substituted and an analogous non-nitro-substituted polymer system was undertaken. As we can see from Table II, increases in char yield for a conventional epoxide resin system (diphenyl triglycidyl ether, cured with resorcinol) are realized when the mass is increased and again when the heating rate is lowered. Obviously

TABLE II
Parametric Effects upon Quantitative Char Yield

Resin and curing agent structures	% Char at 800°C ^a		
	A	B	C
	39.5	13.0	56.0
	11.5	18.2	29.5
	50.0	—	61.0

^a (A) 20-mg sample (>40 <60 mesh), heating rate of 300°C/hr in vacuum; (B) 6-g sample (1.25" × 2.37" × 0.10"), heating rate of 300°C/hr in vacuum; (C) 6-g sample (1.25" × 2.37" × 0.10"), heating rate of 15°C/hr in vacuum.

there are maximum and minimum masses and heating rates for these effects, but these parameters were not investigated.

For the nitro-substituted system (diphenyl triglycidyl ether cured with 2-nitroresorcinol), a decrease in weight retention was observed for an increase in mass at fairly high heating rates (5°C/min). A reduction in the heating rate, however, gave an increase in the char formation in a similar manner as for the nonnitrated polymer system.

The increase in char yield by a reduction in heating rate was also observed for the diglycidyl ether of 1,5-naphthalenediol cured with 2-nitroresorcinol. Initial differential thermal analysis work has indicated that under certain conditions (B in Table II) a pronounced exotherm occurs in the range of 200–300°C. At higher heating rates and with larger masses, the nitro group may act as an oxidizing agent, thus initiating exothermic reactions the heat of which cannot be dissipated readily; and hence a rapid autocatalytic-type thermal degradation results. This leads to a rapid mass-fragmentation of the polymer system, with the overall effect being a reduced char yield. A further more detailed explanation of these results will be presented in a future publication on the exact mechanism of thermal degradation of these systems.

Comparison of Analogous Systems

The weight retention upon pyrolysis of several epoxide polymers containing the nitro group in the resin or curing agent was compared to that of their nonnitrated analogs. The results are given in Figures 1 to 4. In Figure 1, resorcinol diglycidyl ether is compared to 50–50 weight mixture of resorcinol diglycidyl ether and 2-nitroresorcinol diglycidyl ether, both cured with nadic methyl anhydride. The increase in char yield and the decrease in the maximum rate of weight loss for the nitro-substituted polymer is typical.

Figures 2, 3 and 4 show similar results for resorcinol diglycidyl ether cured with resorcinol, *p*-phenylenediamine, benzimidazole, and their nitrated analogs. In every case, a twofold or greater increase in the amount of char, and decrease in the maximum rate of weight loss, were realized for the nitro-substituted polymer system. The nitro systems also possess at least two rate maxima indicative of a complex yet semidistinct degradative scheme. These maxima may be difficult to discern from the TGA plots since these have been greatly reduced from the original experimental records. However, the rate plots clearly show them. In general, the nitro-substituted systems initiate thermal degradation before their non-nitrated analogs. This seems reasonable in view of the oxidative thermal degradative scheme promoted by the nitro group which was mentioned earlier.

Polymer Structure Versus Quantitative Char Formation

The thermograms of resorcinol diglycidyl ether cured with several different nitro-substituted curing agents are presented in Figure 5. 2-Nitro-*p*-

phenylenediamine appears to be the most effective in char enhancement, while 2-nitroresorcinol is the least effective. However, as we shall see shortly, these differences are negligible when an epoxide resin of higher functionality and aromaticity is used.

Just as the structure of the curing agent was of interest in regard to its quantitative effect upon char production, so was the structure of the epoxide resin. In Figure 6, the thermograms of several epoxide resins cured with 2-nitroresorcinol are displayed. Again, as in previous work on the thermal properties of epoxide resins, the bisphenol-A-diglycidyl ether gives the lowest amount of char, although the 20% char formed at 800°C is far greater than if it were cured with a nonnitro-substituted compound.⁵ The highly functional and aromatic resins, as exemplified by an epoxy novolac, diphenyl triglycidyl ether, and the tetraglycidyl ether of tetraphenylene-ethane, all exhibit excellent weight retention (40% at 800°C). The diglycidyl ether of 1,5-naphthalenediol gave the highest weight retention of all epoxide resins studied to date, with a 50% weight retention at 800°C.

The thermograms of an epoxy novolac resin cured with several nitro-substituted phenylenediamines and 2-nitroresorcinol are shown in Figure 7. There appears to be no dependence of quantitative char formation on the position of nitro-substitution. Also, as mentioned previously, the dependence of char formation on the type of curing agent (i.e., phenolic or amine) has become negligible with the use of this highly functional and aromatic resin. The slightly poorer performance of 3-nitro-*o*-phenylenediamine can probably be attributed to the steric crowding and hence lower reactivity of this compound.

The thermograms of a series of diglycidyl ethers of isomeric naphthalenediols cured with 2-nitroresorcinol are given in Figure 8. Again, as noted previously when these were cured with NMA, the order of quantitative char yield is 1,5 > 1,6 > 2,7-naphthalene diglycidyl ether.¹ This may be due to a higher reactivity of ring positions 4 and 8 of the naphthalene nucleus as a result of substitution in the 1- and 5-positions. In the case of the 1,6-naphthalene system, this activation occurs in only one of the rings, and in the 2,7-system, in none of the rings.

Concentration Effects

The concentration of the nitro group in the polymer system was varied by changing the molar ratio of 2-nitroresorcinol relative to the epoxide equivalent weight (EEW) of resorcinol diglycidyl ether. The stoichiometric amount of curing agent is obtained using the 0.5 molar equivalence of 2-nitroresorcinol per EEW. However, optimum thermal and mechanical properties for phenolic-type curing agents have been reported when 0.3 mole/EEW stoichiometry is used.⁶ This is evidently a result of the increased crosslink density produced by etherification reactions of the alcoholic hydroxyls generated during cure of the resin. We can see from the thermograms in Figure 9 that the char production is dependent upon

the concentration of the nitro group within the limits studied. The weight retention increases from 24% at the 0.2 mole/EEW level to 35% char at the 0.6 mole/EEW level.

A dual plot of the weight per cent of nitro group in the epoxide polymer and the atomic hydrogen oxygen ratio versus the per cent char at 800°C is given in Figure 10. There appears to be linear dependence of the char produced at 800°C upon the nitro group content of the epoxide polymer system within the concentration limits examined. This is also related in the H/O ratio. As the oxygen content of the system increases and the ratio approaches the value for water (2.0) (as a result of increasing nitro group content), the weight retention increases. This is of course suggestive of a constructive thermal-oxidative mechanism which selectively removes the hydrogen at an early stage of degradation.

CONCLUSIONS

The introduction of a nitro-substituent into a conventional epoxide polymer system greatly increases the char yield and decreases the maximum rate of weight loss compared to analogous nonnitrated epoxides during thermal degradation. These effects, however, were found to be mass and rate dependent.

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