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Prediction of Heat Shield Performance in Terms of Epoxy Resin Structure

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SUMMARY

High-strength, readily processable, char-forming, insulative materials are being sought for application in ablative heat shields for re-entry vehicles. Toward this end, the family of epoxy resins has been evaluated. The structure of epoxy resins and curing agents in terms of their functionality, aromaticity, and chemical nature is discussed in relation to its effect on ablative properties. The concept of controlled, constructive thermal degradation is extremely important in ablative epoxide compositions. Bridged Diels-Alder adducts based upon cyclic dienes and maleic anhydride perform well as epoxy resin curing agents in this respect. The mechanism of thermal ablative degradation of these systems is discussed in terms of in situ thermal control and char-forming reactions. The position of attachment of glycidyl groups, as well as the nature and position of other substituents around the aromatic nucleus, has little effect in general upon the ablative properties of epoxy resins. Thermal and ablative data of both benzene and naphthalene derivatives are given. A new epoxy resin based upon 2-nitro resorcinol has been synthesized. This resin gives significant char increases, both quantitatively and qualitatively, over conventional epoxides. The unusual mechanism of polymerization and thermal degradation of this resin is discussed.

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INTRODUCTION

It is the purpose of this paper to relate the key chemical building blocks essential to good ablative performance of re-entry vehicles in terms of epoxy resin structure. The concept of controlled, constructive, pyrolytic degradation is also discussed with respect to in situ thermochemical reactions leading to endothermic control processes and char formation.

The theoretical and practical aspects of material requirements and environmental parameters for ablative materials have been discussed by numerous authors previously. Well-referenced summaries of these considerations are given in Refs. [1] and [2]. Briefly, however, by way of background, what kind of material do we need for high-performance ablative heat shields? Essentially we need one which consumes great amounts of heat per unit mass and does so while transmitting very little of this heat backward to some unprotected surface. This thermal control process can be viewed as a function of the overall heat capacity of a material which is composed of (a) the heat capacity of the virgin material and its degradative products, (b) endothermic chemical reactions, (c) thermodynamic phase changes, and (d) heat blockage and reradiation at the boundary layer by degradative gases and char. A typical temperature and density profile of a charring ablative body is shown in Fig. 1.

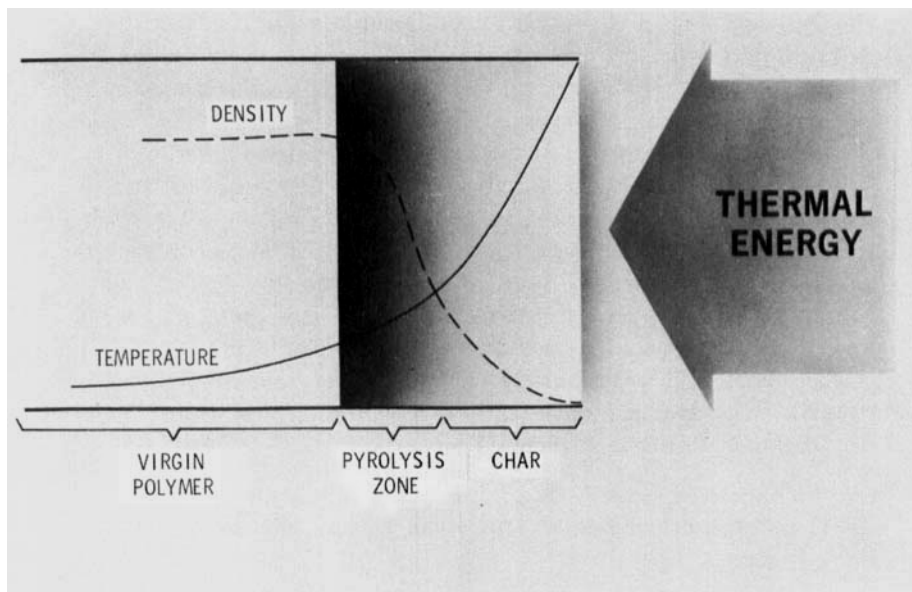


Fig. 1. Typical temperature and density profile in a charring ablative body.

It should also be noted that the formation of a strong char is essential for a number of reasons: (a) Aerodynamic considerations often require that dimensional configuration of the heat shield be maintained; (b) char surfaces provide catalytic sites for further endothermic cracking of pyrolysis gases in the interior as they percolate outward; and (c) the char itself is a good insulator by virtue of its porosity and heat capacity. The aerodynamic shear effects are important to the performance of a heat shield, since they may remove weak chars and hence destroy one of the main thermal control mechanisms of ablative materials. Therefore, the two most important characteristics of a heat shield material are its overall heat capacity and its ability to form substantial amounts of strong carbonaceous char. Epoxy resins, as can be seen, fulfill the requirements for ablative materials and have, in addition, the advantages of easy processability as well as high mechanical strengths.

STRUCTURAL CORRELATIONS

General Considerations

The family of epoxy resin systems encompasses a wide spectrum of chemical structure in terms of both resin and curing agent. The resin may be highly aromatic, aliphatic, or a blend of both. It may be cured by a variety of amines, anhydrides, and ionic initiators of the Lewis acid type to give essentially polyamines, polyesters, or polyethers, respectively. The functionality may also be varied to give a broad spectrum of materials ranging from rubbers to highly cross-linked, brittle materials. With this in mind, we have systematically evaluated the family of epoxide resins for ablative heat shield materials. The level of ablative performance was found to be as varied as the types of structure. Some epoxy polymers perform similarly to Teflon and polyethylene while others perform as phenolics or other high charring ablators, depending on the choice of structure. The structure-property relationships derived and reported herein are the result of test data generated from formulations of resins and curing agents listed in Tables 1 and 2.

Every curing agent reported was not necessarily used to cure every resin due to problems of mixing or curing. Detailed analyses of these systems in regard to both chemical structure and ablative performance have been reported previously [3, 4].

Table 1. Effect of Epoxy Resin Structure on Ablative Performance^a

Ablator	Trade name	Chemical type	Supplier
Low-char ablators Increasing ablative performance Char- forming ablators	ERL-4201	Cycloaliphatic	Union Carbide
	Epon 871	Aliphatic	Shell Chemical
	ERLA-0400	Cycloaliphatic	Union Carbide
	Epon 828	Bisphenol-A-epichlorohydrin condensate	Shell Chemical
	KER 997A	Polyglycidyl ether of orthocresolformaldehyde novolac	CIBA
	Kopox 170	Polyglycidyl ether of polyhydroxy terphenyl	CIBA
	DEN 438	Polyglycidyl ether of phenolformaldehyde novolac	Dow Chemical
	ERE-1359	Resorcinol diglycidyl ether	CIBA
	Kopox 171	Triglycidyl ether of trihydroxy biphenyl	CIBA
	Epon 1031	Tetraglycidyl ether of tetraphenylene ethane	Shell Chemical

^aCured with NMA.

Table 2. Effect of Epoxy Resin Curing Agent Structure on Ablative Performance^a

Ablator	Abbreviation	Chemical name	Supplier
Low-char ablators	TETA	Triethylene tetramine	Eastman Organic
	MPDA	m-Phenylene diamine	Eastman Organic
Increasing ablative performance	DADPS	p,p'-Diamino diphenyl sulfone	Shell Chemical
	MD	p,p'-Methylene dianiline	Allied Chemical
	THPA	Tetrahydrophthalic anhydride	Baker
	TMA	Trimellitic anhydride	Amoco
	BF ₃ MEA	Boron trifluoride monoethyl amine	Shell Chemical
Char- forming ablators	BTCD	3, 3', 4, 4'-Benzophenone Tetracarboxylic dianhydride	Gulf Oil Corp.
	NMA	Methyl norbornene-2, 3-dicarboxylic anhydride	Allied Chemical

^a Resin used was resorcinol diglycidyl ether (RDGE).

Testing

Two principal analytical tools were used in this work. One was a conventional thermal gravimetric analysis (TGA) apparatus, operated in vacuum with a heating rate of $5^{\circ}\text{C}/\text{min}$ and employing a powdered 10- to 20-mg sample. The other was the "alpha rod" test facility shown in Fig. 2. The

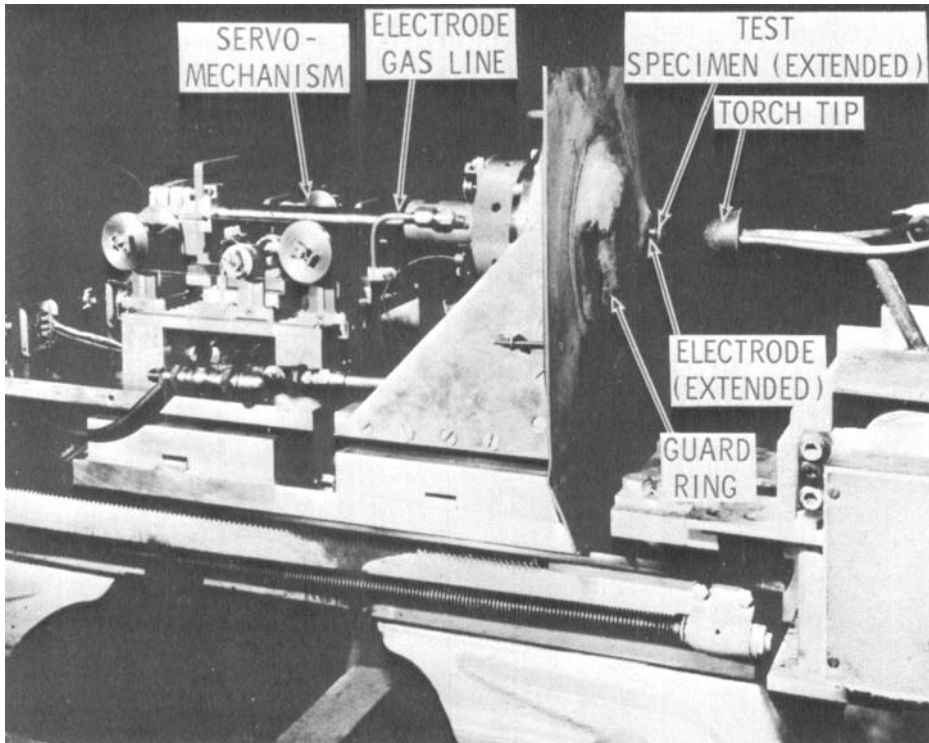


Fig. 2. General view of automatic feed device and oxyacetylene burner.

alpha rod technique is discussed experimentally and theoretically in previous reports [5, 6] and by Koubek of this laboratory [6a]. The unidirectional heat flux encountered by the $3/4$ -in.-diam specimen is $60 \text{ cal}/\text{cm}^2/\text{sec}$. The ablative data presented in the tables and figures are generated from this device. All specimens tested contained 20% by weight of silica powder homogeneously dispersed for relative comparison. Several tests were run with other fillers or reinforcement, in an attempt to optimize performance, and are so noted.

Although the conditions of thermogravimetric analysis and ablative testing may seem quite different, and hence correlation between the two meaningless, it has been possible to derive empirical relationships from thermograms in terms of ablative performance. In general, a slope angle < 1 of the weight loss vs temperature curve with a high yield of char formed above 700°C is desired. A polymer which degrades catastrophically over a small temperature range and leaves little or no char residue in the TGA would not be expected to give good ablative performance.

Resins

Several resins cured with nadic methyl anhydride (NMA) are listed in Table 1 in the order of increasing char yield and overall ablative performance. The indicated break shows where two- and threefold improvements or greater are observed over the resins listed previously. The differences between those below the break are not nearly as great as for those above. In general, increased char yields leading to greater thermal protection per unit mass are obtained with increasing aromaticity and functionality of the resin. One can progress from a subliming or clean melt-type ablator to a high-char-forming ablator by simply going from top to bottom, respectively, in Table 1. The bisphenol-A-epichlorohydrin condensates give compromise ablative performance in the middle.

Curing Agents

The ablative performances of various curing agents with resorcinol diglycidyl ether (RDGE) are listed in Table 2 in similar manner as for the resins in Table 1. Despite the thermal stability imparted to epoxy resins by aromatic diamines, as viewed in thermograms, the ablative performance of these systems is extremely poor as compared with that of anhydride-cured systems. The Lewis acid-type cure of epoxides resulting in polyethers gives good performance in subsonic ablative testing. They produce relatively weak chars, however, which would lead to possible catastrophic failure in a high-shear environment. The best overall performance was given by NMA. This appeared to be unusual, since this curing agent possesses no aromaticity and does not have the functionality that BTCD has, for example. The explanation lies in the unusual bicyclo structure of NMA and is discussed shortly.

The differences between the amine types of curing agents and NMA are shown in Fig. 3; the ideal ablative material is in the lower right corner and the most undesirable is in the upper left corner. If one could extrapolate

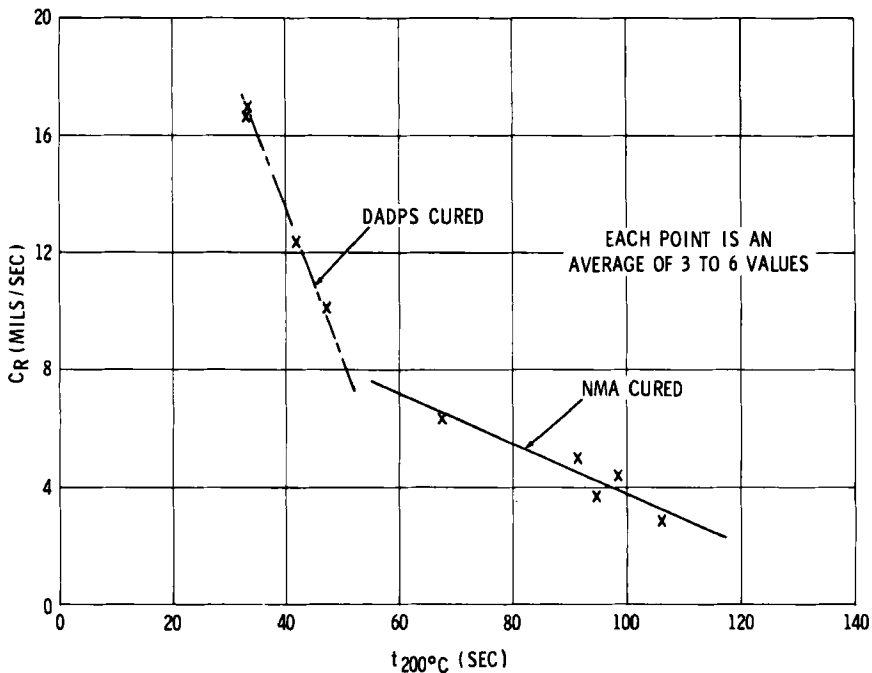


Fig. 3. Char rate vs. $t_{200^\circ\text{C}}$ for polyglycidyl ethers of phenyls, polyphenyls, and novolacs cured with NMA and DADPS (20% SO_2 filler).

to zero char rate, the maximum obtainable thermal protection in terms of keeping the back-face temperature below 200°C would obviously be much lower for the amine-cured systems than for the NMA-cured systems.

Figure 4 depicts typical time vs back-face temperature plots for materials in an ablative environment. The melt or sublime-type ablaters, such as Teflon and exemplified by the aliphatic epoxides, are noted for high erosion rates but extremely low thermal conductivity and, hence, low back-face temperature rise until burn-through. These types, however, might be of value in some specific areas of ablation where a "clean," smooth surface is desired after ablation or where essentially a zero feedback of thermal energy through the virgin polymer is desired.

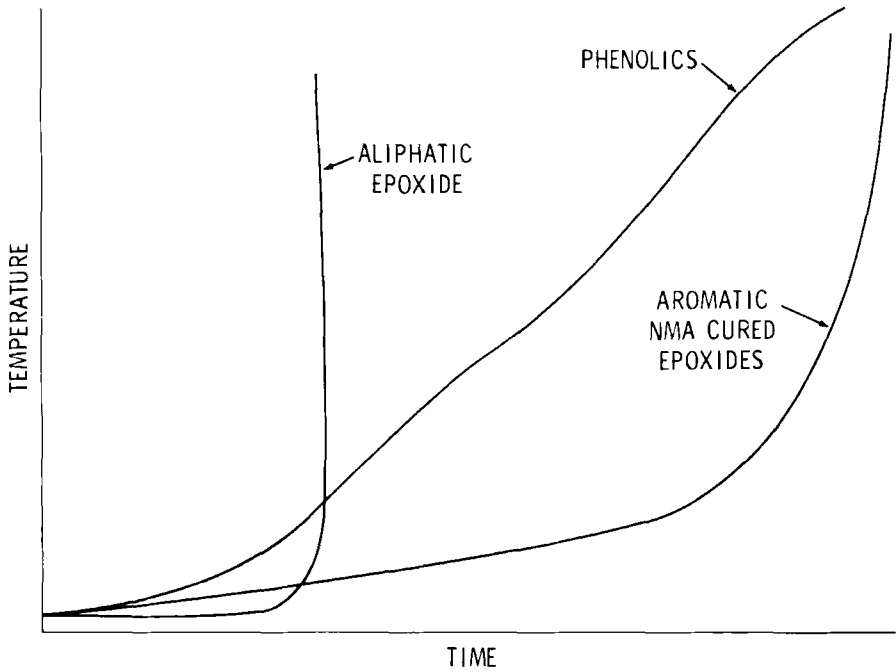


Fig. 4. Typical time-temperature curves for ablating materials.

CONTROLLED CONSTRUCTIVE THERMAL DEGRADATION

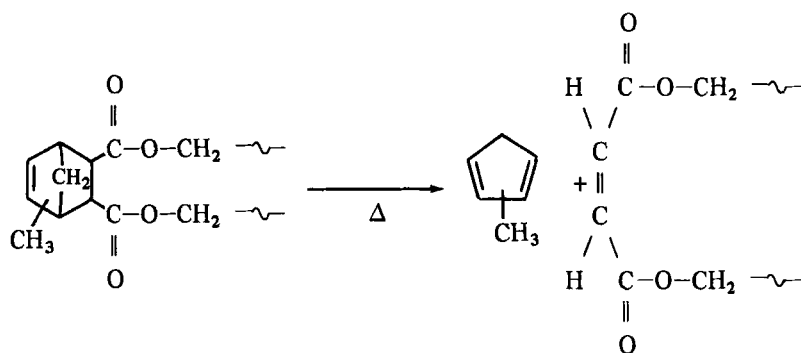
General Considerations

The operative thermal environment of an ablative material is such that any known organic polymer is going to degrade. The question then is not how thermally stable is the polymer but how does it degrade. We can employ our knowledge of thermal degradation to synthesize a polymer that utilizes the ablative heat source to construct a pseudoideal ablative material in situ, and in so doing consume copious amounts of heat. In essence, we construct a polymer which is mechanically strong, thermally shock-resistant, and processable in its virgin state, but which, upon encountering a hyperthermal environment, degrades in a controlled, predetermined manner to consume heat and develop a strong, self-protective char. The NMA-cured aromatic epoxide resin in Fig. 4 shows the advantage of this type of

material over a conventional phenolic. For a given type of reinforcement, the phenolic and epoxy resin will have essentially the same char rate. However, the real advantage of this material is in its decreased thermal conductivity, resulting from in situ endothermic, thermal control reactions. This usually results in a twofold increase in thermal protection with respect to keeping a back-face temperature below 200°C.

Curing Agents

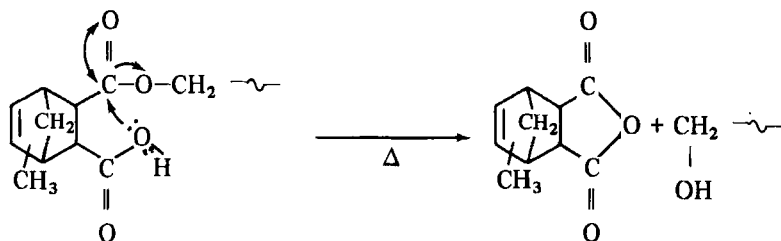
Bridged Diels-Alder anhydride adducts from alicyclic dienes and maleic anhydride are highly effective curing agents for constructive thermal degradation. These compounds undergo a two-step thermal degradation. One step is a thermal control reaction; the other increases char yield. The initial mechanism of degradation is a reverse Diels-Alder reaction which usually occurs below 350°C (main resin decomposition temperature). These adducts from alicyclic dienes undergo reverse Diels-Alder addition more readily than



those from acyclic dienes due to a combination of electronic, steric, and strain factors. This is important because the reverse reaction liberates a diene which percolates through the char, where it degrades endothermically. This leads to low molecular weight gaseous products in the boundary layer, which block heat input. Since "side group elimination" occurs prior to main chain scission, uncontrolled catastrophic degradation is avoided. This process also results in a front-face temperature which is lower than that for phenolics by 300-500°C. This is important because a high front-face temperature is a powerful driving force for pumping thermal energy into an ablative material. In addition, and equally important, the reverse Diels-Alder reaction leaves an olefinic bond, activated by ester carbonyls, in the

polymer backbone. This reactive site is capable of further cross-linking via free radicals generated during the subsequent resin degradation. This enhanced cross-link density is more conducive to carbonaceous and graphitic char formation.

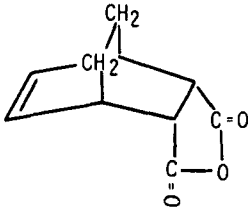
Another reaction which has also been observed is the regeneration of anhydride from residual monoester-monoacid moieties in the polymer. This also could favorably affect the overall thermochemical control and char



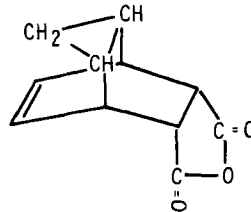
formation process. A complete discussion of this mechanism of initiating and controlling thermal degradation has been presented earlier, and it is not dealt with further in this paper [7].

The structures of a number of bridged Diels-Alder adducts synthesized at NOL or purchased commercially are shown in Fig. 5. The synthesis and thermal properties of these adducts has been presented in detail previously [8]. The unusual thermograms of these materials, as well as that of an unbridged Diels-Alder adduct, tetrahydrophthalic anhydride, are given in Figs. 6 and 7. Note how the thermal degradation is controlled over a wide temperature range from the initiation of degradation to the point where the rate of weight loss is approaching zero. Further extensions of this temperature range can be realized by using a combination of Diels-Alder adducts, each of which undergoes the reverse reaction over different temperature ranges. This is shown in Fig. 8, where a three-component mixture gives an initial 35% weight loss over a 300°C temperature range.

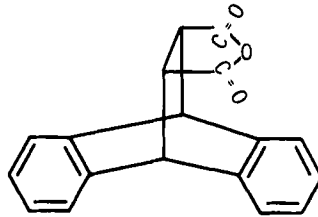
The ablative performance data for these systems were obtained in the NOL alpha rod test facility and are presented in Figs. 9, 10, and 11. The char rate (C_R) given is the rate of recession of the pyrolysis zone into the virgin polymer. The $t_{200^\circ\text{C}}$ and $t_{1000^\circ\text{C}}$ are the times required for a thermocouple embedded 3/8 in. behind the original front face to sense



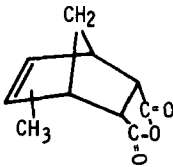
BICYCLO (2.2.2) OCTA-5-ENE-
2, 3-DICARBOXYLIC ANHYDRIDE
(BOCA)



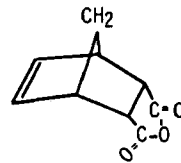
3, 6-ENDO CYCLOPROPYLENE
- Δ^4 -TETRAHYDROPHthalic
ANHYDRIDE (CPTA)



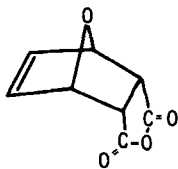
9,10-DIHYDRO-9, 10-ETHANOANTHRACENE
-11, 12-DICARBOXYLIC ANHYDRIDE (AMAA)



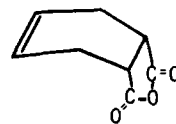
METHYL BICYCLO (2.2.1) HEPTA-5-ENE
-2, 3-DICARBOXYLIC ANHYDRIDE
(NMA)



BICYCLO (2.2.1) HEPTA-5-ENE
-2, 3-DICARBOXYLIC ANHYDRIDE
(NA)



7-OXO-BICYCLO (2.2.1) HEPTA-5-ENE
-2, 3-DICARBOXYLIC ANHYDRIDE
(FMAA)



TETRAHYDROPHthalic
ANHYDRIDE (THPA)

Fig. 5. Bridged Diels-Alder anhydride adducts useful as curing agents for epoxy resins.

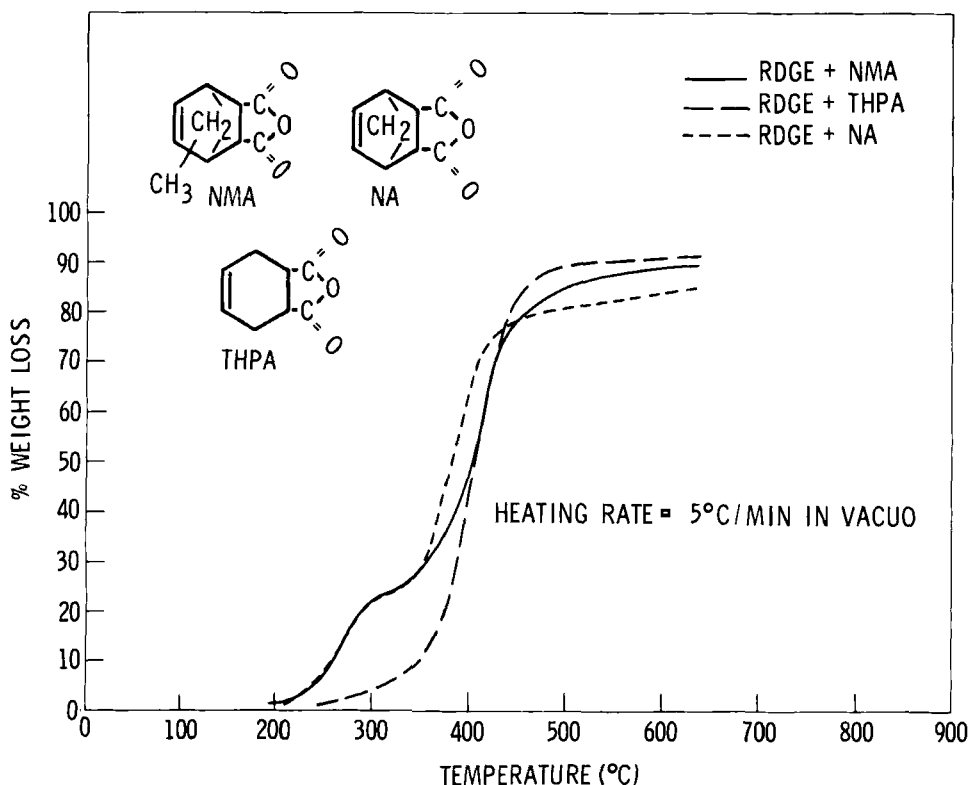


Fig. 6. Thermograms of resorcinol diglycidyl ether cured with several Diels-Alder adducts.

these temperatures. The $t_{1000^{\circ}\text{C}}$ value is the termination of the test and is usually concomitant with the burn-through of virgin polymer at that point.

Figure 9 shows the increase in ablative performance achieved by the bridged Diels-Alder anhydride adducts over the unbridged system exemplified by THPA. Further increases in performance are observed when several of these adducts are used in combination, as shown. Figures 10 and 11 compare the better epoxy systems with standard phenolic with both Pluton B-1 and graphite cloth reinforcement. Note that while the char rate and $t_{1000^{\circ}\text{C}}$ are similar for both epoxy and phenolic systems, an important difference is in the $t_{200^{\circ}\text{C}}$ or insulative effectiveness, which is 111.6 sec for the epoxy system with "Pluton" B-1 fabric as compared with 44.0 sec with the phenolic system. Similar twofold increases in insulative

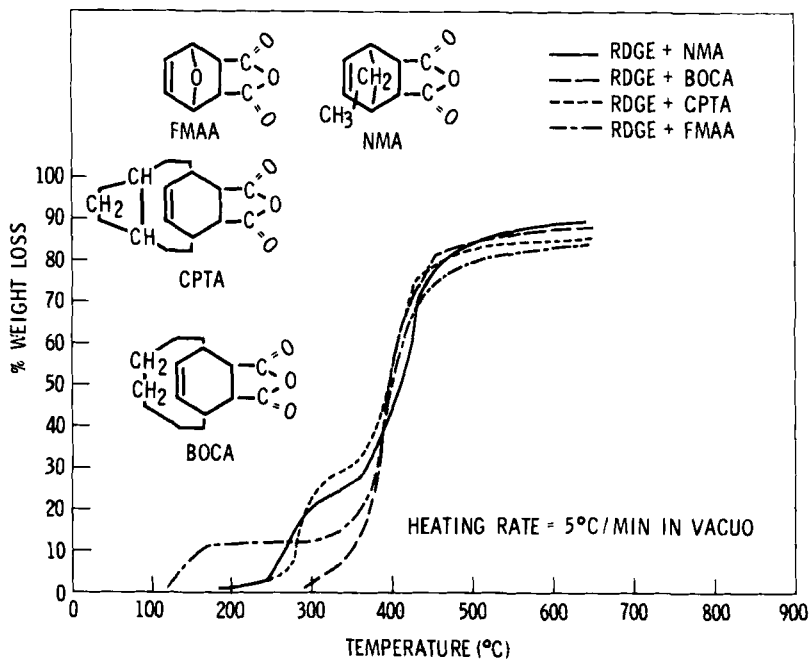


Fig. 7. Thermograms of resorcinol diglycidyl ether cured with several Diels-Alder adducts.

effectiveness are found for the graphite-reinforced specimens at both indicated heat fluxes (Fig. 11).

One added feature of a specific Diels-Alder adduct, the adduct of anthracene and maleic anhydride, which is not evident from the graphs is that it forms a very hard, coke-like char. The anthracene, which is liberated just prior to main resin decomposition, evidently acts as a nucleating agent for char formation. The adduct, however, exhibits low solubility in the epoxide system (10% solubility). This can be increased to over 50% by the use of the adduct of methyl maleic anhydride (citraconic anhydride) and anthracene.

Resins

It has been shown how one class of curing agent can increase ablative performance by employing the concept of controlled, constructive thermal degradation. What about resins? Toward this end, three variables are now being investigated in regard to ablative performance. They are the

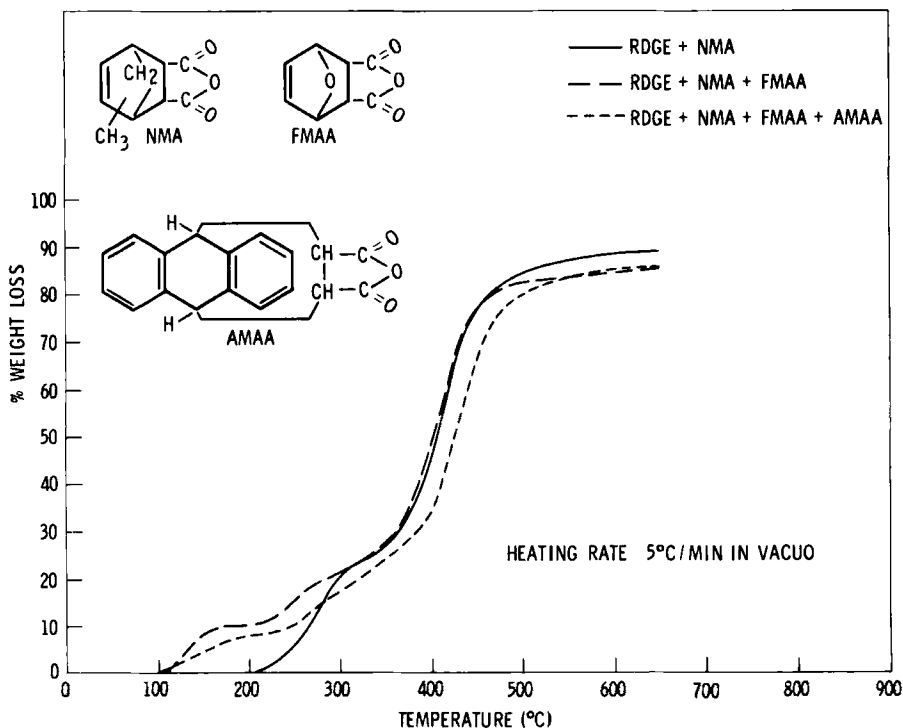


Fig. 8. Thermograms of resorcinol diglycidyl ether cured with several Diels-Alder adducts.

nature of the aromatic nucleus, the position of attachment of glycidyl groups on the aromatic nucleus, and the nature of "unreactive" substituents on the aromatic nucleus. The structure, grouping, per cent char at 700°C (TGA), and ablative performance of these resins synthesized at NOL are given in Table 3. The ablative data are given in terms of $t_{200^\circ\text{C}}$ for the usual 20% silica-filled specimens. Since all resin systems had the same thermal conductivity, this value ($t_{200^\circ\text{C}}$) is indicative also of the char rate (C_R) and length of run ($t_{1000^\circ\text{C}}$). Thermograms of these resins cured with NMA are presented in Figs. 12-14.

The value of n for the repeat unit varied from 0.1 to 0.8 for the resins. Therefore, the cross-link densities of the resins were not expected to vary greatly, and this in turn would have little effect on the char formation.

Table 3 compares the resin variables mentioned previously in a self-explanatory manner. In general, no significant differences were found in char yield among the resins as evaluated by TGA. In ablative testing, all of

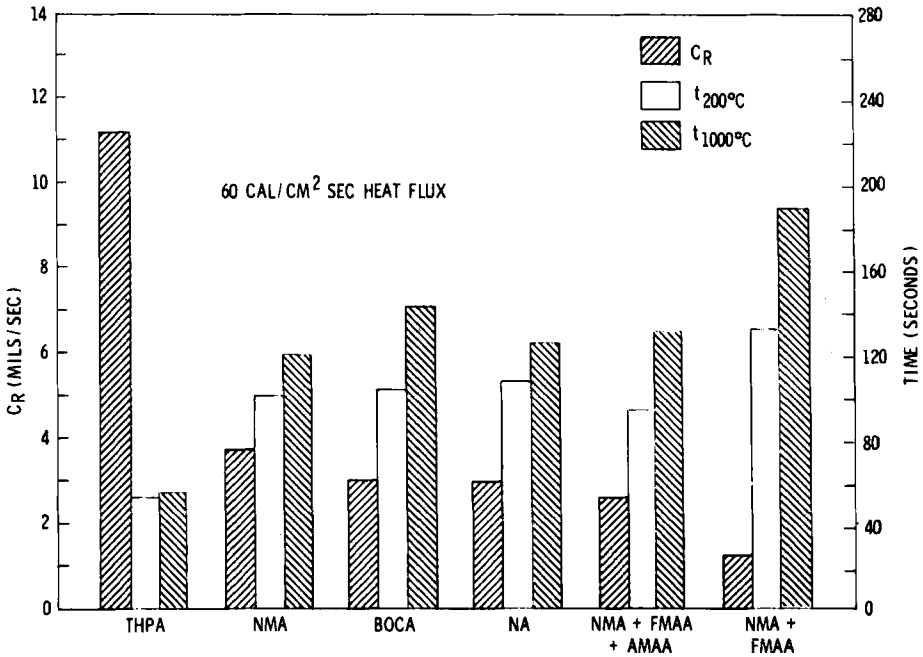


Fig. 9. Ablative performance data for resorcinol diglycidyl ether cured with several bridged Diels-Alder adducts (20% SiO₂).

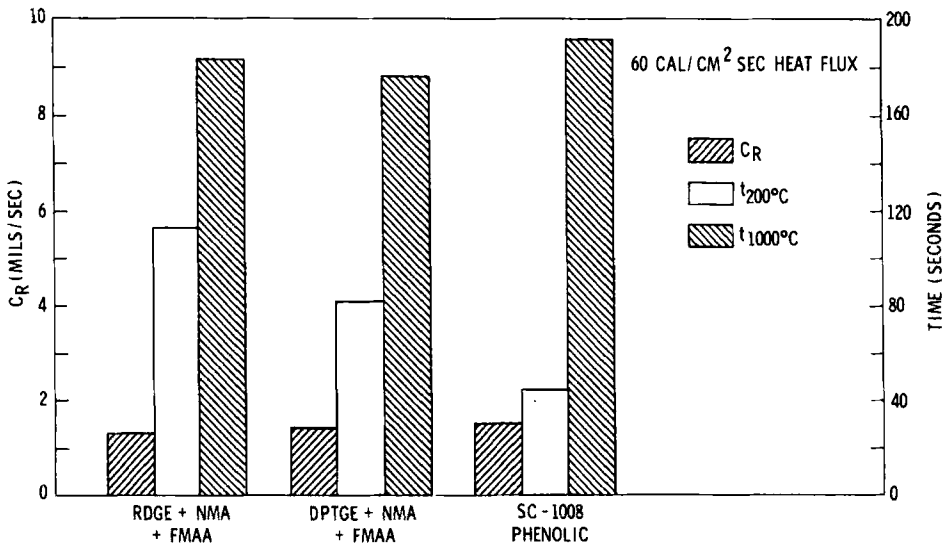


Fig. 10. Ablative performance data for several epoxide resin systems employing Pluton B-1 fabric reinforcement.

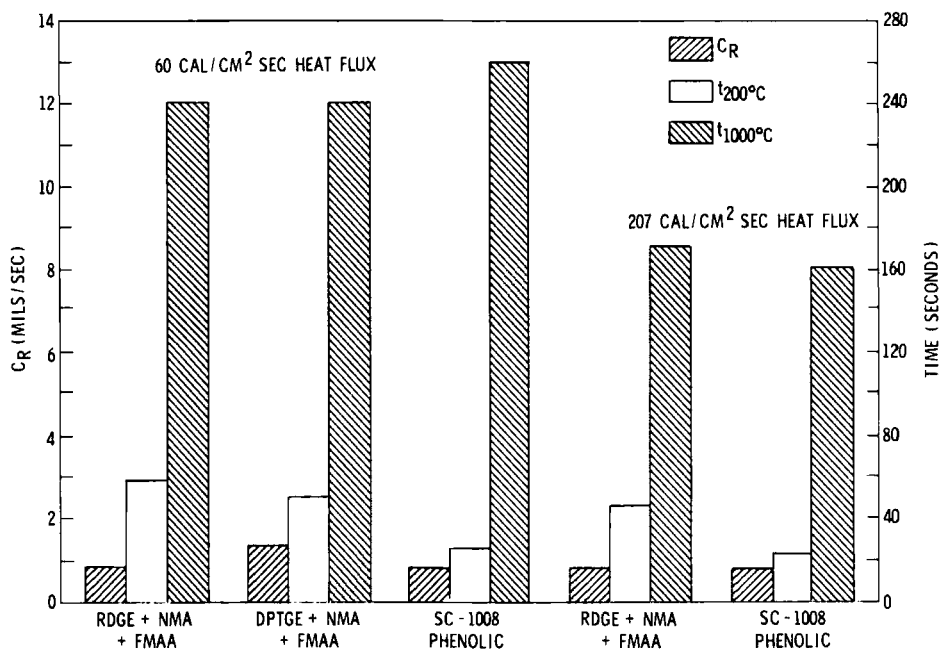




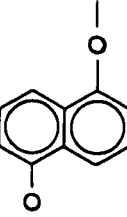
Fig. 11. Ablative performance data for several epoxide resin systems employing graphite fabric reinforcement.

the resin systems generally performed the same as, or markedly poorer than, resorcinol diglycidyl ether. Evidently, the mechanism of degradation of the glycidyl moiety and, hence, the main polymer chain is the controlling one within this grouping.

The polymer from the diglycidyl ether of 2-nitro resorcinol, however, gives completely different and unusual thermograms from those of conventional epoxy resins. A char yield of 28%, compared with 10% for resorcinol diglycidyl ether, is realized. The nitro epoxide can also be thermally polymerized without catalyst or curing agent with resultant TGA char yields of 55% at 700°C. The char formed is very similar to that of hetero-aromatic polymers in that, to a large degree, it retains its original dimensional characteristics and integrity. Films of this material have been heated to 500°C in air over a period of 1.5 hr with retention of structural integrity, although they have become embrittled.

Also, epoxide resin systems recently have been formulated from resorcinol diglycidyl ether, using 2-nitro resorcinol as a curing agent, that are thermally

Table 3. Effect of Epoxy Resin Structure on Char Formation

$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \\ \text{OH} \end{array} \left[\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \\ \text{O} \end{array} \right]_n \text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2$		% Char at 700°C (NMA-cured)	t _{200°C} (sec)
R	Chemical name		
(1) Nature of the aromatic nucleus			
(a) 	Diglycidyl ether of hydroquinone	14	86.0
(b) 	Diglycidyl ether of p, p'-biphenol	15	86.0
(c) 	Diglycidyl ether of 1,5-naphthalene diol	18	85.0

(2) Position of attachment of the glycidyl group


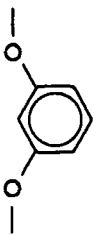
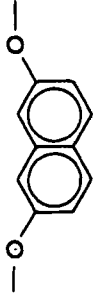
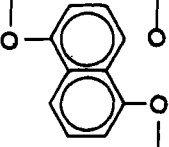
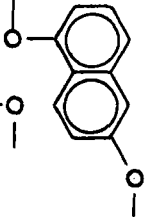
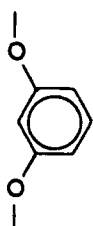
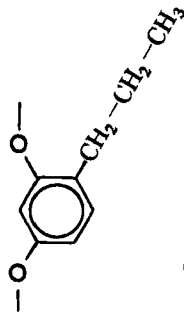
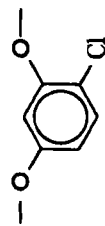
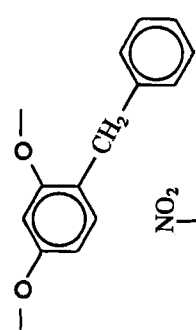
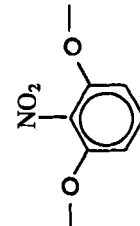
(a)		Diglycidyl ether of hydroquinone	14	86.0
(b)		Resorcinol diglycidyl ether	10	100.6
(a')		Diglycidyl ether of 2,7-naphthalene diol	11	44.0
(b')		Diglycidyl ether of 1,5-naphthalene diol	18	85.0
(c')		Diglycidyl ether of 1,6-naphthalene diol	17	63.0

Table 3. (continued)

$\left[\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \\ \text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \\ \text{OH} \end{array} \right]_n$		$\left[\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2 \end{array} \right]_n$		% Char at 700°C (NMA-cured)	t _{200°C} (sec)
R		Chemical name			
(3) Nature of "unreactive" substituents		Resorcinol diglycidyl ether			
		10	100.6		
(b)		Diglycidyl ether of 4-n-propyl resorcinol			
		8	61.0		
(c)		Diglycidyl ether of 4-chloro resorcinol			
		13	74.0		
(d)		Diglycidyl ether of 4-benzyl resorcinol			
		8	46.0		
(e)		Diglycidyl ether of 2-nitro resorcinol			
		28	—	—	—
		55 ^a	—	—	—

^a Thermally polymerized.

stable to 300°C. These systems then undergo a constructive thermal degradation yielding a strong, refractory-like char at 700°C. The char yield, depending upon pyrolysis conditions, is as high as 45% with maximum rates of weight loss in TGA (5°C min⁻¹ program rate) as low as 1% min⁻¹ compared with 16% min⁻¹ for some conventional epoxides.

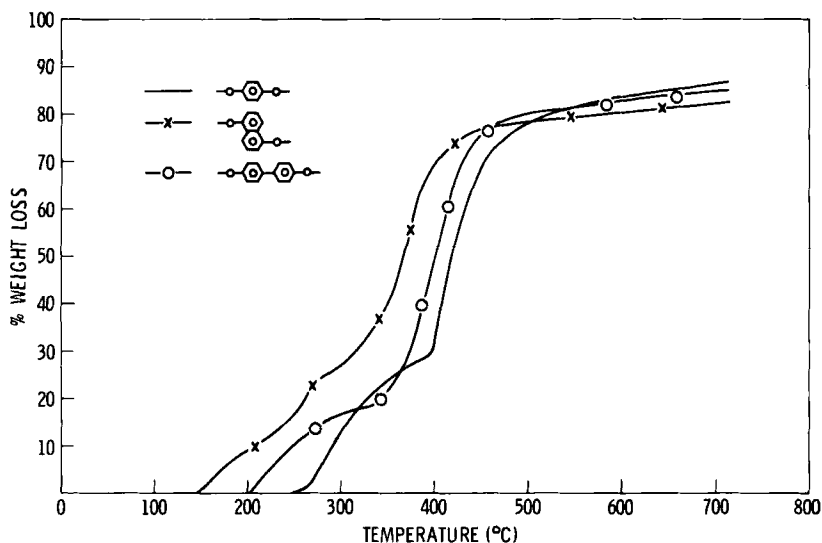


Fig. 12. Thermograms of epoxide resins cured with NMA showing the effect of the nature of the aromatic nucleus on char formation.

The degradation mechanism of these nitro epoxides is complex but seems to be an internal oxidation-reduction reaction with the nitro group participating. The formation of azoxy and azobenzene intermediate-type compounds during degradation, with resultant formation of aromatic free radicals and hence polyphenyls, seems to be indicated by the analytical data at present. Also, the formation of fused heterocyclic aromatic rings containing carbon, nitrogen, and oxygen is indicated by analysis of chars. Further work on the synthesis of various nitro polymers, as well as additional mechanistic studies on their degradation, is currently being undertaken at the Naval Ordnance Laboratory.

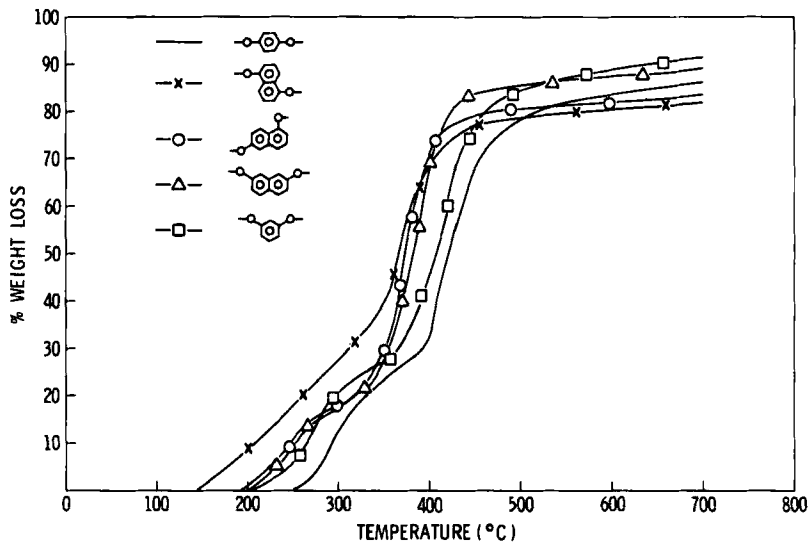


Fig. 13. Thermograms of epoxide resins cured with NMA, showing the effect of the position of attachment of the glycidyl group on char formation.

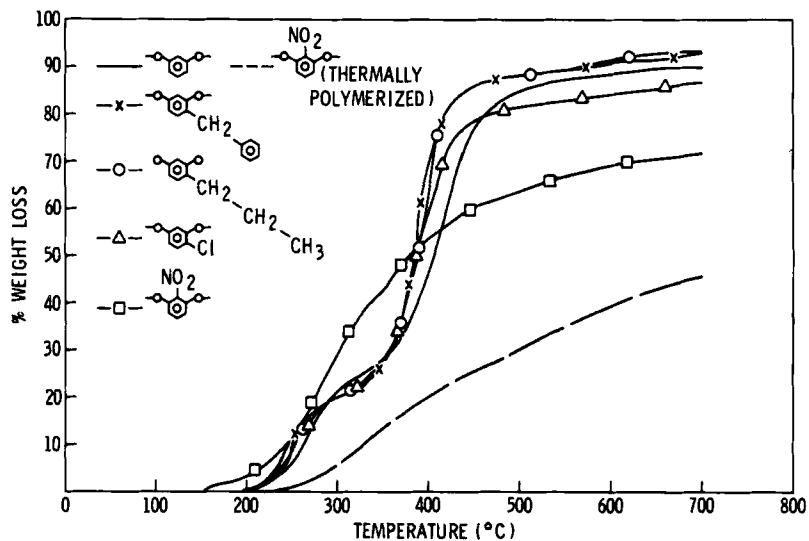


Fig. 14. Thermograms of epoxide resins cured with NMA, showing the effect of the nature of "unreactive" substituents on char formation.

CONCLUSIONS

Two principal conclusions can be derived from this paper: (a) A judicious choice of epoxy resin based on the foregoing structure vs property relationships results in predictable ablative performance ranging from that of clean melt-type to high-char, erosion-resistant ablation. (b) The concept of controlled, constructive, thermal degradation with respect to in situ thermochemical control reactions and char formation is extremely important in obtaining high-performance ablative materials.

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