THE EFFECTS OF MOLECULAR STRUCTURE
ON THE THERMOCHEMICAL PROPERTIES
OF PHENOLICS AND RELATED POLYMERS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • NOVEMBER 1967
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SUMMARY

Phenolic resins and related polymers have been synthesized by established
tools to provide different types of char-forming polymers for pyrolysis
studies. Certain features of the molecular structure of these polymers which
determine the char yield have been characterized. Pyrolysis studies have been
carried out under both thermogravimetric conditions and in environments simu-
lating reentry ablation to relate the char yields of these polymers to their
molecular structure.

It has been possible to account for the char-forming reactions of these
phenolic derived resins in terms of a general pyrolysis mechanism for these
classes of polymers. An analysis based on this mechanism has been developed
which predicts from molecular structure the observed thermogravimetric char
yields accurately over a range from 11 to 65 percent yield. This analysis
makes it possible to control the primary rates of vapor to char production as
required for particular heat-shield applications.

Composites have been developed from these polymers and have been tested
under one-dimensional pyrolysis simulating reentry ablation. Up to applied
heating rates of about 25 cal cm\(^{-2}\)sec\(^{-1}\), the observed char yields agree quite
closely with those obtained in thermogravimetric tests. It is tentatively
concluded that the primary char-forming processes with these classes of mater-
ials are independent of polymer heating rate over a range of temperature rise
rates varying from \(2^\circ\) to \(5000^\circ\) C per minute. With certain composites and at
heating rates greater than 25 cal cm\(^{-2}\)sec\(^{-1}\) an additional amount of char is
formed due to secondary pyrolysis of vapor products within the char matrix
induced by high char temperatures. These secondary processes seem to depend
on surface temperature, impact pressure, and the chemical nature of the vapor
products.

INTRODUCTION

Many diverse polymers, such as phenolics, epoxy novolacs, polybenz-
imidazoles, and polyphenylenes, are char-forming resins (ref. 1). The partic-
ular combinations of thermochemical and thermophysical properties of these

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1A summary of this report was presented at the Symposium on Phenolic
Chemistry, National Meeting of American Chemical Society, Miami, Florida,
April 1967.
char-forming resins have made them of special interest as major components of reentry heat shields for manned space vehicles. Such polymers protect the vehicle substructure from aerodynamic heating during reentry by undergoing thermal degradation in place. Heat may be absorbed by chemical and physical processes within the pyrolyzing material. The pyrolysis vapors diffusing from the surface block convective heat transfer to the surface of the vehicle. The residual hot char cap formed by the pyrolysis process reradiates a part of the heat reaching the surface. At very high heating rates which result in surface temperatures exceeding 3000° K, the "sublimation" of the carbonaceous char may be another important heat blocking process. These various processes are highly coupled. For example, the more vapor produced, for a given applied heating rate, the lower will be the surface temperature and the less heat will be reradiated. The relative thermal efficiency of the processes depends both on the material and the heating environment. To secure the maximum efficiency of heat protection for a particular application, it may be necessary to vary the primary thermochemical processes by modifying the polymer constitution.

A fundamental study of the thermal degradation mechanisms of char-forming polymers is being conducted by Ames Research Center to provide information for the development of rational methods of designing ablative heat shields for entry vehicles. To relate the stoichiometric char yield to polymer composition and molecular structure, three types of phenolic-derived polymers have been studied. All were studied in homogeneous form, and some were studied in combination with either a vapor-forming polymer or quartz fibers. The study had three phases: synthesis, characterization, and pyrolysis of the polymers. The paper reports on the rationale for the choices of polymers synthesized, the synthesis routes, the methods and results of polymer characterization, the methods and results of polymer pyrolysis and on a thermal degradation mechanism that relates char yields for phenolic-derived polymers to their composition and structure.

The mechanism proposed for predicting char yield from polymer structure is also tested by examining the results obtained by Madorsky (ref. 2) from the pyrolysis of a specific phenolic resin. He reported that polybenzyl does not form a char, even though this polymer possesses intramolecular bonding similar to the phenolic resins. The application of the thermal degradation mechanism to one-dimensional pyrolysis of bulk specimens (simulating reentry ablation) is contrasted with the mechanism proposed by Conley (ref. 3) for the oxidative degradation of phenolic resins.

Finally this paper compares the yields of stable char obtained from polymers by thermogravimetric analysis in inert environments with those obtained by one-dimensional heating at high flux levels to determine the effect of high heating rate on char yield.
Three types of polymers (all derivatives of phenol) selected for this study were (1) phenolic novolacs, (2) diphenyloxide modified phenolics, and (3) anhydride-cured epoxy novolacs. The monomers, methods of synthesis, and polymerization were chosen in such a way as to permit systematic variation in the number of aromatic groups per gram of polymer, the crosslink density and the number of kinds of pendant side chains. These variations in molecular structure were expected to provide, in turn, a corresponding systematic (and wide) variation in char yield. This expectation was based on the hypothesis that, in the pyrolysis of these classes of polymers, char formation occurs through the coalescence of six-membered aromatic rings, with the elimination of pendant phenol groups, and aliphatic species. This hypothesis is tested by observing the net yield of stable char obtained, in a nonoxidative environment, by thermogravimetric analysis from polymers of known molecular structure. It will be shown in this paper that with appropriate specification of the kinds and numbers of pendant end and side groups, and the types of intramolecular bonding, this hypothesis can predict the thermochemical char yields accurately.

The test specimens were composites fabricated to prevent cracking and severe spalling of the brittle resins when pyrolyzed at high heating rates. The phenolic novolac polymer was formulated with 6-6 nylon and phenolic microspheres. The anhydride-cured epoxy novolacs were combined with chopped pure quartz fibers. To secure quantitative yields of char under simulated ablation testing for the specimens with nylon added, it was necessary to account for the effect of the presence of that vapor producer on the char-forming pyrolysis of the phenolic novolac. The epoxy novolacs were reinforced with pure quartz fibers at as low a concentration as possible to secure uniform ablation; the high melting temperature of these fibers minimized chemical interactions between the silica and pyrolysis products.

POLYMER SYNTHESIS AND CHARACTERIZATION

Phenolic Novolac Resins

A series of model polymers of varying crosslink density, number of pendant end groups, and number of aromatic rings were synthesized from a low molecular weight, isomeric oligomer prepared from the acid catalyzed reaction of phenol and aqueous formaldehyde (ref. 4). This phenolic novolac oligomer was subsequently crosslinked by reaction in the melt with hexamethylene tetramine (hexa). The crosslink density was controlled by varying the concentration of hexa. The resultant polymers were characterized by elementary analysis, molecular weight, and sol gel content as a measure of the crosslink density.

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2Prepared and characterized by L. F. Sonnabend at Dow Chemical Company, Midland, Michigan, under contract NAS 7-347.
3Prepared and characterized by B. H. Miles at Dow Chemical Company, Texas Division, Freeport, Texas, under contract NAS 7-347.
**Isomeric oligomer (I).**- One-hundred and forty-four grams (1.78 moles) of a 37-percent aqueous solution of uninhibited formaldehyde, 200 g (2.13 moles) of reagent-grade phenol and 1.0 g of oxalic acid were reacted by refluxing at 100-101° C for 2.5 hours. The pH of the reaction mixture was 0.9 at 25° C. No uncontrolled exotherm was observed. At the end of the reaction, the mixture was negative for formaldehyde when tested with 2,4 dinitrophenylhydrazine. After distillation of excess water and a small amount of unreacted phenol, 213 g of the phenolic novolac resin, (I), was obtained as a brittle glassy solid with a melting point of 89° C.

The resin was found to be completely soluble in acetone, ethyl alcohol, and methyl ethyl ketone, but insoluble in nonpolar solvents (carbon tetrachloride and toluene). The IR spectra of this resin was obtained from a KBr pellet. No absorption in the 9.5-10 μ region, characteristic of methylol groups, was observed. Under the reaction conditions used, Woodbrey (ref. 5) has shown that no ether bridges are formed in the polymer. It may be concluded, therefore, that all of the formaldehyde reacted and only methylene bridges were formed in this oligomer. From these observations, oligomer yield, molecular weight, and the initial mole ratio of 6.0/5.0 of phenol to formaldehyde, it may be concluded that the reaction giving phenolic novolac (I) proceeds to completion in accordance with the equation shown in figure 1 to give

![Figure 1](image)

**Analysis:** Calculated for C_{56}H_{48}O_{8}; C, 78.7; H, 5.8; O, 15.3
Found: C, 77.0; H, 5.6; O, 17.4

This structural representation is consistent for all possible isomers, linked ortho-ortho, ortho-para, and para-para, which could be arranged to give from two to five pendant hydroxyphenyl-methylene groups. The calculated molecular weight for this structure is 837, compared with a molecular weight of 794 found by ebulliometry for this resin.

The presence of the singly bonded pendant groups, as shown in the structure of oligomer (I), is readily apparent from the IR spectra of this isomeric oligomer given in figure 2. Strong absorption bands appear at 820 and 755 cm⁻¹.
characteristic of ortho and para disubstituted aromatic rings. The possibility of contribution to this absorption by 1,3 disubstituted or monosubstituted derivatives is ruled out by the absence of an absorption band between 710 and 680 cm\(^{-1}\). When oligomer (I) is cured with varying amounts of hexa to give multiple bonded aromatic rings, the intensity of the diagnostic pair is reduced accordingly, as shown in figure 2.

Polymers from oligomer (I) with hexamethylene tetramine.- The phenolic novolac (I) was polymerized in the melt, with various amounts of hexa from 1.5 to 8.3 percent by weight. Intimate mixtures were prepared by grinding together the dried oligomer (I) with hexa. Ten-gram samples of these mixtures were fused and polymerized under dry, oxygen-free argon at a flow rate of 1 liter per minute. The samples were heated to 157° C at a rate of 1.3° C per minute. The cured polymers were cooled under argon and dried to constant weight in vacuo. All reasonable precautions were taken to prevent oxidation of the specimens. No oxidized structures were evident in the IR spectra (not shown herein).

These polymers were characterized by determining the sol fraction as a measure of the degree of crosslinking. Finely ground 1.0-g samples were extracted with acetone in a Soxhelet extract and the sol content determined. The results obtained are given in table I for the polymers studied:

### TABLE I.- SOL FRACTION, EQUIVALENCE RATIO, AND AVERAGE MOLE WEIGHT OF PHENOLIC NOVOLAC (I) WITH ADDITIONS OF HEXAMETHYLENETETRAMINE

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Weight % hexa</th>
<th>Mole ratio, phenolic (I) hexa</th>
<th>Sol fraction</th>
<th>r, equivalence hexa equivalence phenolic (I)</th>
<th>Mole weight, average mer unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I-a)</td>
<td>1.52</td>
<td>11.0</td>
<td>1</td>
<td>0.111</td>
<td>844</td>
</tr>
<tr>
<td>(I-b)</td>
<td>1.96</td>
<td>8.33</td>
<td>.76</td>
<td>.152</td>
<td>847</td>
</tr>
<tr>
<td>(I-c)</td>
<td>3.12</td>
<td>6.95</td>
<td>.51</td>
<td>.230</td>
<td>851</td>
</tr>
<tr>
<td>(I-d)</td>
<td>3.85</td>
<td>4.19</td>
<td>.41</td>
<td>.285</td>
<td>857</td>
</tr>
<tr>
<td>(I-e)</td>
<td>5.66</td>
<td>2.79</td>
<td>.21</td>
<td>.433</td>
<td>867</td>
</tr>
<tr>
<td>(I-f)</td>
<td>8.26</td>
<td>1.86</td>
<td>.09</td>
<td>.645</td>
<td>882</td>
</tr>
</tbody>
</table>

The weight percent hexa, the mole, and equivalence ratios are also given in table I. If all the hexa reacts at an initial mole ratio of 1.86:1.00 oligomer (I), to hexa, this would amount to the addition of three methylene bridges for each molecule of (I), to give the crosslinked polymer (I-f), the isomeric representation of this structure is given in figure 1.
The structure of the oligomer (I), as well as its crosslinked derivatives, may be established indirectly by correlating the observed sol fractions with the initial equivalence ratios by means of Flory's branching mechanism (ref. 6). If oligomer (I) has the isomeric structure, there can be 10 reactive sites per molecule of (I). The point branching functionality, \( f \), as defined by Flory is the number of these sites per mole of the polyfunctional reactant. The branch index, \( \alpha_{\text{crit}} \), at the gel point has been given by Flory as

\[
\alpha_{\text{crit}} = \frac{1}{f - 1} \tag{1}
\]

For the phenolic novolac (I), this expression gives a value of 0.110 for the structure and reactivity proposed. The probability of forming an infinite or crosslinked network with a sol fraction just less than unity is given by

\[
\alpha = \rho P_H P_p [1 - P_H P_p (1 - \rho)] \tag{2}
\]

where

- \( P_H \) extent of reaction with respect to hexa
- \( P_p \) extent of reaction with respect to phenolic novolac (I)
- \( \rho \) functional group distribution

Since all branch sites are on (I), \( \rho = 1 \) and the equation reduces to

\[
\alpha = P_H P_p \tag{3}
\]

The extent of the reaction of the hexa, \( P_H \), in the presence of excess phenolic novolac (I) at the completion of the reaction must be unity. It follows then that the extent of the reaction of the phenolic novolac (I), \( P_p \), must be equal to the equivalence ratio, \( r \), defined as the ratio of equivalents of hexa, \( n_H \), to the number of equivalents of phenolic novolac (I), \( n_p \) present in polymerization mixture

\[
r = \frac{n_H}{n_p} \tag{4}
\]

The hexa with a molecular weight \( M_H \) has \( f_H \) phenolic reactive equivalents per mole. The phenolic (I) with a molecular weight \( M_p \), under these conditions and consistent with structure (I), has \( f_p \) hexa reactive equivalents per mole. If \( X_H \) is the fraction of hexa used per unit weight of phenolic, the equivalence ratio is given by

\[
r = \frac{f_H M_p X_H}{f_p M_H (1 - X_H)} \tag{5}
\]
Under these conditions

$$a_{crit} \neq r_{crit}$$  \hspace{1cm} (6)

where \( r_{crit} \) is just the amount of hexa required to gel the system and produce a sol fraction just less than unity (ref. 7). When \( r \) is unity, the system is completely crosslinked and the sol fraction becomes zero. The sol fractions obtained from this series with different weight fractions of hexa, and the calculated values of the equivalence ratio, \( r \), are given in table I.

If the structures and reactions are indeed as indicated in figure 1, a plot of the measured sol fraction against \( r \) as calculated from the amount of hexa used, should intercept the \( x \) axis at unity for a sol fraction of zero and intercept a value of \( r \) equal to 0.111 for a sol fraction of unity. In figure 3, the experimental results are so plotted and agree with these theoretical requirements. It can be concluded that the structures given in figure 1 are good isomeric representations of phenolic novolacs.

Diphenyloxide Modified Phenolic Resins

Diphenol oligomer (II).- In order to obtain a single isomeric phenolic oligomer with a finite number of pendant end groups, uniquely defined by an unambiguous synthetic route, \( 4,4' \)-oxybis-(p-phenylene) diphenol (II), was prepared by reacting 5349 g (2 moles) of \( 4,4' \)-dichloromethyl diphenyl ether with 2620 g (30 moles) of phenol in 800 g of chlorobenzene at 505\(^\circ\) C. After reaction was complete, the excess phenol was removed in vacuo at 145\(^\circ\) C. The diphenol (II) was fractionally crystallized from benzene and recrystallized from ethanol water to give 100 g (20-percent yield) of white crystals, melting point 150\(^\circ\)-152\(^\circ\) C.

A molecular weight of 389 was found by ebulliometry for this compound with a value of 382 calculated for the expected diphenol. The structure of this diphenol has been reported by Murao (ref. 8) and a melting point of 152\(^\circ\)-153\(^\circ\) C. The structure of this pure isomer is given as follows:

Analysis: Calculated for \( C_{26}H_{22}O_3 \) L C, 81.7; H, 5.8; O, 12.6
Found: C, 80.9; H, 6.0; O, 13.1
From the structure of diphenol (II) as given, it can be seen that the molecule comprises two phenolic groups singly bonded by methylene bridges and two rings multiply bonded.

Methylol diphenol oligomer (III).—To provide a comonomer for polymerization with diphenol (II) in order to secure model polymers having networks characterized by \( r \) values both greater and less than unity, a tetramethylol derivative of diphenol (II) was prepared. Condensation of this monomer with diphenol (II) was expected to provide a range of crosslink density and variation in the number of aromatic rings not possible in the case of the hexa-cured phenolic novolac. In a 1-liter flask equipped with a condenser, a stirrer, and an additional funnel, 100 g (0.262 mole) of diphenol (II), and a solution of 24.0 g (0.60 mole) of sodium hydroxide in 300 mole of water was heated to 50\(^\circ\) C with stirring. When the solution became homogeneous, 220 g of 37-percent formalin solution (2.66 moles) was added by drops. The mixture was then stirred and heated at 50\(^\circ\)-55\(^\circ\) C for 2 hours. The solution was cooled and 300 ml of ethyl acetate was added. The mixture was acidified with 60 ml of concentrated hydrochloric acid. The organic phase was separated, washed successively with 10-percent sodium bisulfite, and finally with 10-percent sodium chloride. The ethyl acetate solution was dried over anhydrous sodium sulfate and evaporated to dryness in vacuo at room temperature. The solid obtained was dissolved in 540 ml of acetonitrile and 150 ml of hot water and allowed to cool. The 5,5'-[oxybis-(phenylene-methylene)]-bis-(2-hydroxy-m-xylene-\(\gamma\')-diol) separated as a white crystalline solid from the mixture. The yield was 60 g (46 percent).

A molecular weight of 501 was found by ebulliometry for this compound, as compared with a value of 502 for the tetramethylol (III), with a proposed structure as follows:

\[
\begin{align*}
\text{HOH}_2\text{C} & \quad \text{CH}_2 \quad \text{O} \quad \text{CH}_2 \quad \text{H}_2\text{CH}_2
\end{align*}
\]

Analysis: Calculated for \( \text{C}_{30}\text{H}_{43}\text{O}_7 \): C, 71.7; H, 6.0; O, 22.3
Found: C, 71.4; H, 6.0; O, 23.0

These analyses and the molecular weight are in good agreement with those required for this structure.

Diphenol oligomer (IV).—In order to evaluate the effect of ortho-para isomerism, in the thermochemical char yields of these phenolic derivatives, the mixed isomers, contained in the benzene filtrate after separation of the diphenol (II) as given above, were recovered by evaporation of the solvent to give 730 g of mixed isomers. This mixture can be represented by the general structure (IV) as follows:
It was found, as expected, to give the same elementary analysis and molecular weight as found for the diphenol (II) isomer. This mixture was further characterized by gas-liquid chromatograph and found to have the following isomeric distribution given as area percent:

<table>
<thead>
<tr>
<th>Diphenol isomers</th>
<th>Area percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2'-isomer</td>
<td>11</td>
</tr>
<tr>
<td>2-4'-isomer</td>
<td>48</td>
</tr>
<tr>
<td>4-4'-isomer</td>
<td>41</td>
</tr>
</tbody>
</table>

Polymethylol-diphenol monomers (V, VI, VII, and VIII). To evaluate the effect of the molecular weight of the oligomer on char yield, the mixed diphenol isomers were condensed with a limited amount of formaldehyde to give a series of monomers.

In a 2-liter, 3-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and a condenser 248 g (0.65 mole) of diphenol (IV) and 520 g (1.3 mole) of 10-percent sodium hydroxide solution were heated under nitrogen atmosphere to 50°-60° C until the solution became homogeneous. Then the solution was cooled to 40° C and 960 ml of 37-percent formaldehyde (11.7 moles) was added. The mixture was stirred at 40° C for 4 hours. After the mixture was neutralized to pH of 5.5 with 18.4 ml of 10-percent sodium bisulfate, it was extracted with two 250-ml portions of ethyl acetate. The ethyl acetate solution was washed successively once with water, four times with 20-percent sodium bisulfite, and finally, once with water. After drying over anhydrous sodium sulfate, the solvent was evaporated in vacuo at room temperature to yield 263 g of a tan solid.

Based on this method of synthesis, an empirical formula representing the general structure of the reaction product may be given as follows:
Repetition of the synthetic method gave monomers with molecular weights from 883 to 1380. Four such monomers were prepared and characterized by elementary analysis and molecular weight as given in Table II.

**TABLE II. - ANALYSIS OF POLYMETHYLOL MONOMERS**

<table>
<thead>
<tr>
<th>Analysis</th>
<th>(V)</th>
<th>(VI)</th>
<th>(VII)</th>
<th>(VIII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>---</td>
<td>72.8</td>
<td>72.0</td>
<td>71.4</td>
</tr>
<tr>
<td>H</td>
<td>---</td>
<td>5.9</td>
<td>6.0</td>
<td>6.2</td>
</tr>
<tr>
<td>O</td>
<td>---</td>
<td>21.3</td>
<td>21.9</td>
<td>23.6</td>
</tr>
<tr>
<td>OH</td>
<td>16.4</td>
<td>16.8</td>
<td>16.8</td>
<td>16.6</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>1380</td>
<td>940</td>
<td>778</td>
<td>885</td>
</tr>
<tr>
<td>n</td>
<td>3</td>
<td>2</td>
<td>1.63</td>
<td>1.87</td>
</tr>
<tr>
<td>f</td>
<td>8</td>
<td>6</td>
<td>5.26</td>
<td>5.29</td>
</tr>
</tbody>
</table>

The average methylol functionality, f, and the value of repeat unit n were calculated from the formula for elementary analysis and measured weights.

**Dialkyldiphenol oligomer (IX).** - An attempt was made to evaluate the effect of aliphatic side chain substitution on the char yield of diphenol oxide modified phenolics by preparing the dialkyl disubstituted phenol, 2,2' [oxybis-(p-phenylene-methylene)] bis 4-tert-butyl phenol (IX) for polymerization with the tetramethylol derivative (III). In a 5-liter, 3-necked flask equipped with a stirrer, a thermometer, an addition funnel, and a condenser was placed in a solution of 1500 g (10 moles) of 4-tert-butyl-phenol in 2000 g of chlorobenzene. The system was heated to 60°-65° C and a solution of 178 g (0.67 mole) of dichloromethyl diphenyl ether in 280 g of chlorobenzene was added over a period of 1 hour. The solvent and excess 4-tert-butylphenol were then removed in vacuo at 155°-160° C. The residue was dissolved in three times its weight of cyclohexane with heating and the solution allowed to cool. There was obtained 219 g (66 percent) of white crystals, melting point 140°-4° C.

A molecular weight of 505 was measured by ebulliometry for this solid. It compares well with a molecular weight of 495 calculated for the expected dialkyldiphenol (IX). Elementary analysis gave: Analysis: calculated for C₃₄H₆₈O₉; C, 82.6; 4, 7.8; O, 9.6. Found: C, 82.7; 4, 7.9; O, 9.4.

![](image-url)

The method of synthesis and the characterization agree well with the structure for diphenol (IX). It can be seen that this molecule has two alkyl substituted phenolic groups, which are singly...
bonded through methylene groups, and two multiple bonded aromatic rings in the diphenyl oxide structure. It should be expected that para substitution with the tertiary butyl group would reduce the reactivity of the remaining ortho sites in diphenol (IX) by both steric and electronic effects. For this reason, it is not possible to assign a definite functionality to this monomer for polymerization with the tetramethylol derivative. It is, therefore, not possible to calculate an effective equivalence ratio for polymers derived from this monomer. An alternative method of correlating this structure with char yield will be discussed.

Diphenol Modified Phenolic Resins

The diphenols and methylol diphenols were polymerized at different mole ratios by dissolving the monomers in methanol and evaporating the resulting solution to dryness at room temperature in vacuo using a rotary dryer. The solid mixture, about 80 g, was heated to a temperature below 90°C. To minimize air bubbles, pressure was reduced. The tube was placed in a 2-liter Parr Bomb which was then purged with nitrogen. The pressure was then maintained with nitrogen bleeding continuously. The temperature was raised to 200°C over 5 to 6 hours and held there for about 22 hours. The cooling of the system, under nitrogen, took about 20 hours.

This polymer was characterized only by elementary analyses. A comparison of the observed carbon hydrogen analyses of the resulting polymer, assuming that only water was lost during polymerization, with those of the reaction mixture, indicated that for every four reactive diphenol sites about 3.2 have reacted to form crosslinks evolving 3.2 moles of water. Incidental ether formation has not been considered. As assumed in the case of the reaction of hexa with the phenolic novolac (I), the extent of reaction of the methylol diphenol in presence of excess diphenol can be considered unity. To calculate an effective equivalence ratio, r, for these systems, r is defined as

$$ r = \frac{n_1}{n_2} $$

where

- $n_1$ number of methylol equivalents reacted at completion
- $n_2$ number of reactive diphenol sites reacted at completion

It has been assumed that all methylol groups react at r values less than 1, and terminate at r values greater than 1. Therefore, $n_1$ is equal to the product of the number of methylol groups per mole and the number of moles. But it has been shown that only 3.2 diphenol groups react out of four possible sites. Thus $n_2$ is given by

$$ n_2 = fPm $$

(8)
where $m$ is the number of moles of diphenol with an apparent functionality $f$ equal to $4$ and $P$ the extent of reaction which amounts to 80 percent. The composition and characterizing $r$ values for the diphenol oxide modified polymers is given in Table III.

**TABLE III.- CHARACTERIZATION OF DIPHENOLOXIDE MODIFIED PHENOLICS**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition in moles</th>
<th>Reactive equivalents</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(II)</td>
<td>(III)</td>
<td>$n_1$</td>
</tr>
<tr>
<td>A</td>
<td>1.00</td>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>B</td>
<td>1.50</td>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>C</td>
<td>2.00</td>
<td>1.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition in moles</th>
<th>Reactive equivalent</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(IV)</td>
<td>(V)</td>
<td>(VI)</td>
</tr>
<tr>
<td>D</td>
<td>1.50</td>
<td>1.00</td>
<td>---</td>
</tr>
<tr>
<td>E</td>
<td>1.50</td>
<td>---</td>
<td>1.00</td>
</tr>
<tr>
<td>F</td>
<td>1.30</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>G</td>
<td>1.00</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$Char yield not reported

Polymers from (IX) with (II) and (III)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition in moles</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(IX)</td>
<td>(II)</td>
</tr>
<tr>
<td>H</td>
<td>1.00</td>
<td>0.50</td>
</tr>
<tr>
<td>I</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

**Anhydride Cured Epoxy Novolac Resins**

A third class of polymers derived from phenol was synthesized by polymerizing epoxy novolacs of different molecular weight and corresponding glycidyl ether functionality with Nadic methyl anhydride. This synthetic scheme permits a systematic variation in the number of phenolic rings both singly and multiply bonded through methylene bridges. Unlike the phenolic resins, already discussed, it is not possible to effect this desired change in structure by altering the reactivity ratio.
The three basic glycidyl ethers used in this study were obtained from commercial sources. In general, they were prepared by reacting epichlorohydrin with the sodium salt of the phenolic derivatives.

Nadic methyl anhydride, the 1:1 Diels Alder reaction product of maleic anhydride and methyl cyclopentadiene, was also obtained commercially and used without further purification, as was the amine catalyst DMP-30.

The glycidyl ethers were characterized by IR, elementary analysis, molecular weight and epoxide equivalent weight. The results of these characterizations are given in table IV.

<table>
<thead>
<tr>
<th>Glycidyl ether</th>
<th>Percent C</th>
<th>Percent H</th>
<th>Percent O</th>
<th>Molecular weight</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X)</td>
<td>73.14</td>
<td>7.37</td>
<td>19.49</td>
<td>164</td>
<td>2</td>
</tr>
<tr>
<td>(XI)</td>
<td>73.34</td>
<td>6.30</td>
<td>20.34</td>
<td>604</td>
<td>7.6</td>
</tr>
<tr>
<td>(XII)</td>
<td>73.98</td>
<td>6.40</td>
<td>19.48</td>
<td>1226</td>
<td>15.3</td>
</tr>
</tbody>
</table>

These data are consistent with the following structures proposed for these three glycidyl ethers:

![Structures](https://via.placeholder.com/150)

Anhydride cured epoxy novolac samples were prepared as follows: The glycidyl ether was preheated to approximately 80°C to facilitate pouring and the desired amounts of resin and anhydride were accurately weighed into a 3-necked round-bottomed flask. The flask was then placed in a heating mantle and the temperature was maintained at 60°C-70°C. A dry nitrogen purge was kept on the resin mixture to exclude moist air. The resin and hardener are mixed for a minimum of 20 minutes using a glass stirrer attached to a variable speed laboratory stirrer motor. During the final 5 minutes of mixing, a pressure of 1-3 mm Hg was held on the system to remove entrapped gases and volatiles that might be present in the system. The stirrer was turned off, the vacuum released, and the correct weight of DMP-30 was then added by hypodermic syringe. The stirrer was turned on and the mixing continued for 20 minutes. The vacuum was applied again for the final 5 minutes of stirring. After the stirrer was turned off and the vacuum released, the mixture was carefully poured into the molds so as not to entrap air bubbles. The molds which had been sprayed with Fluoro-Glide, a Teflon-like dry film lubricant, were preheated to 100°C before being filled. For the 1.5-inch-diameter billets, the
molds were made from 1.5-inch (schedule 80) pipe that was reamed to about 1.56 inch I.D. The 5.5-inch-diameter billets and the 3.0-inch-diameter billets were cased in triple-tight cans of 1 gallon and 1 pint, respectively. After the molds were filled, the billets were cured for 4 hours at 100°C and then for 16 hours at 200°C. They were then removed from the oven and placed in a well-insulated box where they were allowed to cool slowly for about 24 hours.

Two approaches were investigated to vary the structures of polymers prepared by this method. First, the equivalence ratio of the anhydride to epoxide was varied to alter the crosslink density through termination, and secondly the average functionality of the epoxy novolac was varied by polymerizing (X), (XI), (XII), and mixtures thereof with Nadic methyl anhydride at a fixed equivalence ratio of 0.85.

It was found that variation in the equivalence ratio from \( r = 0.25 \) to 1.05 with (XI) had no effect on the crosslink density. This surprising result is shown in figure 4. Here the measured swelling volume, a direct measure of crosslink density, is plotted as a function of the equivalence ratio. It can be seen that measured swelling volume is constant over the entire equivalence range investigated. It can be concluded that unlike the phenolic polymers, the degree of crosslinking in the epoxy novolac system is independent of the equivalence ratio. This result may be explained by the fact that if there are not available anhydride groups to react with the epoxy groups present, the latter will react with themselves to form polyethers to produce an equivalent network. Because of the complexity of the structures produced when the \( r \) values are varied, no further characterization was carried out on these polymers. It was concluded the only way that the crosslink density could be varied in an anhydride epoxy system was to vary the functionality of the reacting monomers.

The functionality of the glycidyl ether moiety with structures as given above can be varied if they are made to react individually or as mixtures at a fixed equivalence ratio with respect to the anhydride. This simplifies the structure by producing primarily ester crosslinks. The increase in the number of multiple bonded phenolic rings is, of course, proportional to the increase in functionality. This approach was carried out by decreasing the functionality of the mixture containing (XI) by adding (X) and increasing it by adding (XII).

All polymers were prepared by polymerizing the glycidyl ether at an equivalence ratio of 0.85 with respect to Nadic methyl anhydride.
Since no materials are lost during polymerization, the mole ratios of the monomers of known structure and the measured swelling volume suffices to specify these polymers. These results are given in table V.

### Table V. Comparison of Resin Composition with Swelling Volume at $r = 0.85$ for (X), (XI), and (XII) with Nadic Methyl Anhydride

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Resin composition in epoxide equivalents (X)</th>
<th>(XI)</th>
<th>(XII)</th>
<th>Swelling volume volume solvent per volume unswollen polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.933</td>
<td>0.167</td>
<td>0</td>
<td>Burst</td>
</tr>
<tr>
<td>2</td>
<td>0.667</td>
<td>0.333</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>0.500</td>
<td>0.500</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.333</td>
<td>0.667</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>0.167</td>
<td>0.833</td>
<td>0</td>
<td>0.510</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1.000</td>
<td>0</td>
<td>0.476</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0.680</td>
<td>0.32</td>
<td>0.444</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0.350</td>
<td>0.65</td>
<td>0.424</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0.407</td>
</tr>
</tbody>
</table>

The experimentally determined swelling volumes are compared with the composition of the epoxide composition in this table. It can be seen that at swelling volumes greater than about 0.510, the networks are too weak to withstand the internal pressure created by the included solvent. Below 0.510 there is a decrease in swelling volume (an increase in crosslink density) as the average functionality of the epoxide moiety increases. It can be shown that the measured swelling volume is directly proportional to the number of phenolic groups that are singly bonded through methylene groups in these polymers. For this reason, as will be discussed, it is a useful characterizing parameter to assess the effect of these structures on the char yield of epoxy novolac systems.

### Formulation of Composites

In order to investigate the effect of interactions between vapor producing polymers and char-forming resins, polyblends were prepared from mixtures of 6-6 nylon and phenolic novolac (I) cured with hexa. The phenolic (I) was polymerized in the melt with 8.26-percent hexa to give polymer (I-f) as given in table I. This resin was ground and screened. The screen fraction with a particle size greater than 80 mesh was intimately mixed with powdered 6-6 nylon of similar particle size. This state of aggregation, namely, a heterogeneous blend of unfused nylon particles in a cured phenolic resin matrix, is that found in structural composites derived from these resinous blends (ref. 3). Four such blends were prepared covering a range of mass fraction of nylon from 0.10 to 0.40. The polyblends were dried and stored in vacuo.

To investigate the behavior of these resin systems under one-dimensional heating, phenolic novolac (I-c) was compounded with 6-6 nylon and phenolic
microspheres and fabricated into a low-density phenolic-nylon composite (LDPN) with a bulk density of 35 lb/ft$^3$. The components, their functions, and the composition of the LDPN composite are given in table VI.

TABLE VI.- COMPOSITION AND FUNCTION OF COMPONENTS OF A LOW-DENSITY PHENOLIC-NYLON COMPOSITE (LDPN)

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Percent weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon (6-6)</td>
<td>Vapor producer</td>
<td>70</td>
</tr>
<tr>
<td>Hexa-cured phenolic novolac resin</td>
<td>Char former and binder</td>
<td>37</td>
</tr>
<tr>
<td>Phenolic microspheres</td>
<td>Char former and density reducer</td>
<td>23</td>
</tr>
</tbody>
</table>

Complete details for the formulation and processing of this composite are described in references 4 and 9.

The anhydride-cured epoxy novolac resins, 1 and 6, as given in table V, were reinforced with 5 percent by weight of chopped quartz fiber. The highest purity and best characterized quartz fibers, commercially available, were used in these composites. The fiber was pretreated with polyethylene in the melt to reduce brittleness, and then chopped in a modified hammer mill to give an average fiber length of 1/16 inch. This pretreatment was found to reduce the amount of "fines" encountered with the untreated fibers. The polyethylene surface was removed by sintering the fibers in air at 800$^\circ$ C. The fibers were mixed with the anhydride epoxy resin before the catalyst was added. These composites were cured under the same conditions as given for bulk resin specimens. The composition of the two epoxy novolac composites (ENC) is given in table VII as follows:

TABLE VII.- EPOXY NOVOLAC COMPOSITES REINFORCED WITH 5-PERCENT QUARTZ FIBER

<table>
<thead>
<tr>
<th>Composite</th>
<th>Epoxy novolac system</th>
<th>Epoxy equivalents</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN C-1</td>
<td>(X)</td>
<td>0.833</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td>(XI)</td>
<td>.167</td>
<td></td>
</tr>
<tr>
<td>EN C-2</td>
<td>(XI)</td>
<td>1.00</td>
<td>.85</td>
</tr>
</tbody>
</table>

An important thermochemical property of these polymers with respect to their use in ablative heat shields is the stoichiometric char yield $Y_a$. It is defined here as the mass of stable carbonaceous residue formed by the thermal decomposition of unit mass of the polymer. The importance of the char to heat protection has already been touched upon in the Introduction. The question to be considered here is how to obtain, in the laboratory, values of char yield that are meaningful for an ablating heat shield. For this consideration, it is helpful to refer to the schematic representation of the pyrolysis of an ablative heat shield, which is given in figure 5. A char cap forms with a surface temperature $T_s$. The thickness of this char cap, in the absence of surface removal reactions, increases with the time of exposure to
Primary char formation is essentially complete at the zone boundary temperature given as $T_c$. However, in addition to this primary yield of char, there is the possibility of producing a secondary yield through thermal cracking of the carbon-containing vapor products of primary pyrolysis which could deposit as pyrolytic graphite on the matrix of the primary char. The extent of this process would be expected to depend on the nature of the vapor species, the rate of production, internal char temperatures and residence time of the gases in the hot matrix. The internal char temperatures are roughly proportional to the surface temperature $T_s$. If secondary char formation is a possibility, it should be expected to occur at relatively high surface temperatures, and to increase somewhat with increasing surface temperature. This process would produce an increase in ablation char yield as compared with that observed from primary processes.

It can also be seen in figure 5 that the pyrolysis zone is clearly bounded by the two characteristic thermogravimetric temperatures, $T_s$ and $T_c$, as defined. The velocity of the motion of the isotherms at $T_c$ and $T_s$ can be observed by means of thermocouples placed in the ablation model of the kind shown in figure 5. At heating rates simulating reentry, it has been found that the volume of material in the pyrolysis zone is heated at the temperature rate of $5000^\circ-8000^\circ$ C per minute. The effect of heating rates on the primary char yield must be considered when yields obtained at different heating rates are compared. This effect could be important for those polymers which form char by a series of multiple competitive reactions.
Thermogravimetric analysis provides a means of carrying out the polymer pyrolysis reactions in an inert environment which closely simulates that of the pyrolysis zone. In addition, this method provides a programmed heating-rate environment which forms the char and permits the gases to escape at low temperatures with no secondary cracking and, hence, provides a direct measure of the primary char yield. The only major difference between the thermogravimetric test in an inert gaseous environment and the ablation case, as far as the pyrolysis zone is concerned, is the polymer heating rate. In the usual thermogravimetric analyses, heating rates of the order of 20-100°C per minute are used. A comparison of the char yields obtained at thermogravimetric heating rates with those obtained from models heated one-dimensionally at rates simulating reentry ablation provides a means of evaluating this effect. Agreement between primary char yields obtained by thermogravimetric techniques and ablation simulation will result only if the reaction mechanism within the pyrolysis zone is independent of heating rate. Later, comparisons will be made between thermogravimetric and ablation char yields.

Samples of cured polymers and composites were pyrolyzed by two different thermogravimetric techniques, a Stone thermogravimetric balance with argon as the transpiration gas, at one atmosphere, and an Aminco thermogravimetric balance with an atmosphere of dry, oxygen-free nitrogen at a pressure of 1 mm Hg. Heating rates were varied from 0.5° to 120° per minute. Sample size and sample configuration were varied from 40 to 200 mg with both an 80 mesh powder and small cylindrical billets. The char yields observed were found to be independent of sample size and heating rate over the ranges stated, and independent of the particular apparatus used.

Phenolic Novolacs

The phenolic novolacs given in table I were pyrolyzed in a Stone thermogravimetric balance, at 0.5° to 3.0° C per minute, with argon as the transpiration gas. In most cases, the heating rate of the furnace was 3° C per minute. The effect of heating rate on the thermograms was negligible. All of the thermograms for the hexa-cured phenolic novolac resins were obtained on 80 mesh powdered samples dried in vacuo. The sample size was maintained between 40 and 100 mg. In this range, no effect of sample size on the thermograms was observed. The argon used as the transpiration gas was purified to remove all traces of water and oxygen. A constant flow rate of 0.05 liter/min of argon was used in these experiments. At this gas flow rate, the observed weight losses are at a maximum, and cannot be increased by any further increase in the flow rate. The thermograms obtained for the phenolic novolac were started at room temperature and finally terminated at temperatures above 800° C when the weight loss rates of the char residues became less than 1 percent per minute. The final char yields were determined by permitting samples to cool to room temperature, and then weighing residues on an analytical balance. This procedure eliminated gravimetric errors caused by high temperature conditions in the thermobalance. The numerical values for thermogravimetric char yields given in the following tables were obtained in this manner.

Three basic thermograms for hexa-cured phenolic novolac polymers (I-f), and (I-c), and oligomer (I) with measured sol fractions of 0.09, 0.51, and
1.00, respectively, are given in figure 6. The remaining weight fraction, \( Y \), is plotted as a function of the programmed temperature at a constant heating rate of 3°C/min. It can be seen that the remaining stable char residue, \( Y_c \), obtained at 800°C varies with the degree of crosslinking, expressed as the measured sol fraction. A char yield of 64.0 percent is obtained from the most highly crosslinked polymer (sol fraction 0.09) prepared. The isomeric oligomer (sol fraction of 1.00) gives a char yield of 43.2 percent. The observed char yields for each phenolic novolac polymer is summarized in table VIII.

![Figure 6: Effect of degree of conversion on thermograms of phenolic novolac resins.](image)

**TABLE VIII.** A COMPARISON OF THE THERMOGRAVIMETRIC CHAR YIELDS WITH EQUIVALENCE RATIO AND SOL FRACTION FOR PHENOLIC NOVOLAC RESINS

<table>
<thead>
<tr>
<th>Phenolic novolac</th>
<th>Equivalence ratio</th>
<th>Sol fraction</th>
<th>Char yield ( Y_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I-a)(^a)</td>
<td>0.111</td>
<td>1.00</td>
<td>---</td>
</tr>
<tr>
<td>(I-b)</td>
<td>0.152</td>
<td>.76</td>
<td>50.2</td>
</tr>
<tr>
<td>(I-c)</td>
<td>0.230</td>
<td>.51</td>
<td>51.2</td>
</tr>
<tr>
<td>(I-d)</td>
<td>0.285</td>
<td>.41</td>
<td>58.9</td>
</tr>
<tr>
<td>(I-e)</td>
<td>0.433</td>
<td>.21</td>
<td>62.9</td>
</tr>
<tr>
<td>(I-f)</td>
<td>0.645</td>
<td>.09</td>
<td>64.7</td>
</tr>
</tbody>
</table>

\(^a\)Char yield not determined.

It can be seen that the observed char yield increases monotonically with the equivalence ratio and decreases with increasing sol fraction. It may be noted that the primary char yield for (I-c) as used in the preparation of the LDPN composite is 51.2 percent.

**Diphenyloxide Modified Phenolics**

A somewhat different thermogravimetric procedure was used to determine the primary char yields of the diphenyloxide modified phenolic resins given in table III. These polymers were pyrolyzed in an Aminco thermogravimetric balance under dry, oxygen-free, nitrogen at a pressure of 1 mm Hg at a constant heating rate of 120°C/min. For these studies, 200 mg cylindrical samples were cut from billets of the cured polymer. (A comparison with selected polymers showed that the same char yield was obtained with the other thermogravimetric technique.) Examples of typical thermograms obtained for two diphenyloxide...
modified phenolics, polymers A and C, are shown in figure 7. These polymers like the simple phenolic novolacs gave a finite yield of stable primary char by the time a temperature of \(800^\circ\) C was obtained. Continued heating to \(900^\circ\) C produced no measurable change in these yields. The char residue was obtained as an extremely hard carbonaceous cylinder. The char yields for this series of polymers is given together with the effective equivalence ratio \(r\) in table IX.

### Table IX.- A Comparison of Thermogravimetric Char Yields with Equivalence Ratio for Diphenyloxide Modified Phenolics

<table>
<thead>
<tr>
<th>Diphenyloxide modified phenolics</th>
<th>Equivalence ratio</th>
<th>Char yield, (Y_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.25</td>
<td>65.0</td>
</tr>
<tr>
<td>B</td>
<td>0.85</td>
<td>63.6</td>
</tr>
<tr>
<td>C</td>
<td>0.64</td>
<td>60.3</td>
</tr>
<tr>
<td>D</td>
<td>1.64</td>
<td>61.6</td>
</tr>
<tr>
<td>E</td>
<td>1.42</td>
<td>63.0</td>
</tr>
<tr>
<td>F</td>
<td>1.67</td>
<td>62.0</td>
</tr>
</tbody>
</table>

It can be seen that the primary char yield for the particular diphenyloxide modified phenolic resins examined in this study vary, albeit slightly, with the effective equivalence ratio, \(r\). The char yield appears to go through a maximum between \(r = 0.85\) and 1.25.

### Anhydride Cured Epoxy Novolacs

Thermograms were obtained for the anhydride cured epoxy novolacs by the same techniques and apparatus used for the diphenyloxide phenolics. Typical thermograms for these polymers are shown in figure 8. It can be seen that polymer 1 which gave the lowest char yield for this series, namely 11 percent, also began to lose weight at the lowest initiation temperature. The initiation temperature appears to increase with increasing char yield. All of
these polymers gave definite yields of stable char by the time they reached a temperature of 800° C. The anhydride cured epoxy novolacs obtained from the glycidyl ether (XI) and Nadic methyl anhydride with equivalence ratios from 0.25 to 1.05, characterized by a constant swelling volume of 0.45, gave approximately the same char yield of 23 percent. However, those polymers obtained from curing mixtures of the two glycidyl ethers (X) and (XII) with (XI) at a fixed equivalence ratio of 0.85 gave char yields which varied from 11 to 29.3 percent. The variation in char yield with the measured swelling volume for these polymers is given in table X.

TABLE X.- VARIATION IN THERMOGRAVIMETRIC CHAR YIELD, $Y_C^*$, WITH MEASURED SWELLING VOLUME OF ANHYDRIDE CURED EPOXY NOVOLACS

<table>
<thead>
<tr>
<th>Swelling volume, Anhydride-cured epoxy novolac</th>
<th>Char yield (900°), $Y_C^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydride-cured epoxy novolac</td>
<td>Char yield (900°), $Y_C^*$</td>
</tr>
<tr>
<td>volume solvent per volume unswollen polymer</td>
<td>Char yield (900°), $Y_C^*$</td>
</tr>
<tr>
<td>1</td>
<td>Burst</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>17.0</td>
</tr>
<tr>
<td>4</td>
<td>18.5</td>
</tr>
<tr>
<td>5</td>
<td>0.510</td>
</tr>
<tr>
<td>6</td>
<td>4.76</td>
</tr>
<tr>
<td>7</td>
<td>4.44</td>
</tr>
<tr>
<td>8</td>
<td>4.24</td>
</tr>
<tr>
<td>9</td>
<td>4.07</td>
</tr>
</tbody>
</table>

It can readily be seen that the polymer containing the highest concentration of the bifunctional epoxide (X) gave the lowest char. It perhaps would have given the largest swelling volume if the gel had not burst. The polymer containing the highest concentration of the glycidyl ether (XII) with a functionality of 15.3, polymer 9, gave the highest char yield and lowest swelling volume. Clearly, the char yield increases with the glycidyl functionality and decreases as expected with increasing swelling volume.

Composites

Polyblends of 6-6 nylon, the hexa-cured phenolic novolac, and phenolic microspheres.- The thermogravimetric analysis of the composites and their components was determined with the Stone thermogravimetric balance under the same conditions used for the phenolic novolac resins alone. The thermograms of low-density phenolic-nylon composite and each of the included components is given in figure 9. Here it can be seen that
the nylon gives no char yield and the phenolic resin and phenolic microspheres contribute 51.2 and 55 percent char, respectively. These results are summarized in table XI as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight fraction</th>
<th>Char yield, $Y_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon</td>
<td>0.40</td>
<td>0</td>
</tr>
<tr>
<td>Phenolic novolac</td>
<td>0.37</td>
<td>51.2</td>
</tr>
<tr>
<td>hexa cured (I-c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenolic microspheres</td>
<td>0.23</td>
<td>55.0</td>
</tr>
<tr>
<td>Composite</td>
<td>1.00</td>
<td>29.5</td>
</tr>
</tbody>
</table>

The measured value of the thermochemical char yield for this composite agrees quite well with a value of 31.4 percent calculated from the individual components.

The effect of the presence of nylon on the thermogravimetric char yields of composites containing phenolic novolac resins was assessed by determining the char yields of the two component polyblends of 6-6 nylon and the phenolic novolac (I-f). The measured char yields are shown in figure 10 as a function of the weight fraction of nylon initially present in the polyblend. The straight line given in the figure was obtained by calculating the char yield from the following equation:

$$Y_C = Y_T (1 - X_N)$$

where

$Y_T$ thermogravimetric char yield of the phenolic novolac (I-f)

$X_N$ weight fraction of 6-6 nylon in the polyblend

It can be seen that the data points fall well on this line. From this result, it can be concluded that under thermogravimetric conditions, the primary char yield of the phenolic novolac component is unaffected by the presence of the nylon constituent; that is, there are no thermochemical interactions between these components. This result confirms the assumption made in calculating the char yield for the low-density phenolic-nylon composites (LDPN).

Epoxy novolacs with quartz fibers.- Thermogravimetric analyses were performed on the two quartz fiber modified epoxy novolacs described in table VII. After the observed char yields were corrected for the residual weight fraction of quartz fiber, these composites (C-1 and C-2) gave 11.0 and 23.1 percent char in agreement with results obtained on the polymers alone.
Thermochemical Reaction Mechanism

The results obtained from the thermogravimetric analysis in inert environments of these phenolic resins and their derivatives can be explained by assuming that the stable chars observed result from the coalescence of certain benzenoid structures present in the principal chains of these polymers. The overall reaction mechanism for this process is postulated for phenolic novolac resins as given in figure 11. It is suggested that, in the absence of environmental oxygen or preoxidized structures in the virgin polymer, the initiation step for the pyrolysis of the phenolic novolac resin, given as (I) in figure 11, is the homolytic scission of the carbon-carbon bond connecting the aromatic pendant group to the main chain. This bond is thermodynamically the weakest carbon-carbon bond in the system. Because of resonance stabilization, the aromatic carbon ring systems may be expected to remain intact. Pendant group elimination can occur on either side of the single bonded phenol ring to give both a phenol radical and a cresol radical ((III) and (III-a) in fig. 11). Elimination of these radicals from the main chain is followed rapidly by abstraction of hydrogen atoms from the methylene groups in the main chain to give phenol and cresol as primary vapor products.

The free radical main chain intermediates (II) and (V) formed by initiation and abstraction, respectively, are expected to rearrange, as shown in figure 11, to give the more stable radical intermediates (VI) and (VII). It can be seen that there is formed one terminal radical for each pendant group eliminated, and one diarylketone for each abstraction.

Figure 11.- Principal steps in nonoxidative thermal degradation of phenolic novolac resins.
It is postulated that char formation proceeds through a stable thermally
crosslinked intermediate, shown in figure 11 as (VIII), formed by termination
of the main chain radical pairs (VI) and (VII). A new crosslink, namely a
diaryloxy group, is formed in this process. The formation of this stable bond
prevents elimination of those aromatic rings which were initially bonded by
two or more methylene groups in the principal chain. This argument can be
restated to specify that only those phenolic ring structures which are multi-
ple bonded in the virgin polymer are retained in the thermally crosslinked
intermediate. The stage is now set for the elimination of the terminal methyl
groups as methane and the keto groups as carbon monoxide at temperatures above
500° C.

The thermally crosslinked intermediate (VIII) is postulated to lose
methane and carbon monoxide above 500° C by chain scission and recombination
to give the unstable char (IX) observed at 500° C as shown in figure 11(c).
This unstable char is in effect a highly crosslinked diphenyl ether polymer.

Thermally stable char networks are depicted as forming by continued
crosslinking of the aromatic rings present in char (IX) with the elimination
of both hydrogen and water. It can be seen that the overall reaction mecha-
nism leading to a stable char proceeds through a thermally crosslinked inter-
mediate with elimination of pendant aromatic rings and retention of all those
aromatic carbons which existed as multiple bonded aromatic rings in the virgin
polymer.

This mechanism was evaluated in part by applying it to the experimental
results obtained by Madorsky (ref. 2) for the stepwise isothermal analysis of
a simple phenol formaldehyde resin. Madorsky suggests no mechanism. He
reports only the elementary analysis of the cured polymers with a 1:1 ratio of
phenol to formaldehyde in the test polymer. He considers an empirical formula
of C7H60, and a general structure as follows:

This structure gives an apparent average molecular weight of the repeat unit
of 106. The overall yield of stable char which would be predicted by the
application of the reaction mechanism given in this paper, provided all the
phenol groups are multiple bonded, can be estimated from the following
expression:

$$Y_c = \frac{6(N)12.01}{M}$$

(10)

where

N    number of aromatic rings per average mer unit
M    molecular weight of average mer unit
in which there are six aromatic carbons per ring and 12.01 is gram atomic weight of carbon. No pendant end groups are assumed in this equation which predicts a char yield of 67.8 percent for Madorsky's phenolic resin. But Madorsky reported a char yield of 56 percent at 800°C. At the ratio of 1:1 phenol to formaldehyde (an equivalence ratio of 0.67) there is insufficient formaldehyde to provide multiple bonds for all of the phenolic groups. This polymer would be expected to give a sizable sol fraction and a finite number of pendant phenolic end groups. Although Madorsky did not determine the number of pendant groups, the number can be calculated by application of the postulated mechanism to the elementary analysis and char yield.

The general structure for the 1:1 phenol formaldehyde resin can be rewritten to include both multiple and singly bonded aromatic rings as follows:

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{CH}_2 & \\
\end{align*}
\]

It follows from the elementary analyses that

\[
\frac{x + y}{z} = 1.00 \quad (11)
\]

The molecular weight of average mer unit is given by

\[
Ax + By + Cz = M \quad (12)
\]

If only the carbons of multiple bonded rings are retained in the char, then

\[
x = N \quad (13)
\]

and

\[
Y_c = \frac{72.01 \times x}{M} \quad (14)
\]

Letting \( A \) equal \( B \), and substituting \( M \) in terms of \( A, B, C, \) and \( z \) in \( 4 \) and rearranging, one obtains:

\[
\frac{x}{y} = \frac{106.5}{\left(\frac{72.01}{Y_c} - 106.5\right)} \quad (15)
\]

Applying the char yield obtained by Madorsky of 56 percent at 800°C one obtains a ratio of 5:1 for \( x \) multiple bonded rings to \( y \) singly bonded rings. An average mer unit in which \( x = 5, y = 1, \) and \( z = 6 \) is postulated for Madorsky's resin. The possibility of using the thermochemical char yield as a structural parameter is illustrated by this application.
Winkler (ref. 10) has observed that both the parent ions of phenol and cresol are formed in about equal amounts when a phenolic novolac resin is decomposed at 300° C directly in a time-of-flight mass spectrometer at 10^-7 torr. It is suggested, and the mechanism requires, that the 3 and 4 carbon oxygenated species, reported as acetone, propanols and butanols have their origin in the fragmentation of phenolic pendant groups after they are eliminated from the main chain. Madorsky observed about a 12-percent yield of these species up to 500° C. From the structural analysis for this polymer given above, and the proposed mechanism, a yield of about 15 percent can be estimated for these volatiles from the pendant end groups (eliminated as phenol and cresol) which subsequently fragment under Madorsky's conditions. Madorsky also found both carbon monoxide and hydrogen in about equal amounts as the principal vapor products formed from the phenolic resin above 500° C. These vapor products are consistent with those expected from the decomposition of the thermally crosslinked intermediate given as (VIII) in figure 11(c). The greatest yield of hydrogen observed by Madorsky was found to occur at temperatures above 800° C. This observation is also consistent with the reaction proposed for conversion of (IX) to stable char.

From the foregoing, it can be concluded that the experimental results obtained by Madorsky from the 1:1 phenol formaldehyde polymer are consistent with the proposed mechanism. Obviously, the thermal degradation of crosslinked phenolic resins is not a random chain scission process, but rather is initiated at singly bonded phenolic end groups by homolytic scission to give aromatic species as the volatile products.

The formation of the keto intermediate ((VII) in fig. 11) is compatible with the infrared analyses of thermally oxidized phenolic resin intermediates reported by Conley (ref. 3), but as indicated, does not require oxidation initiation for its formation. Conley found considerable difficulty in observing significant amounts of keto structures early in this pyrolysis required to initiate the oxidation mechanism. It is most probable that in the thermal oxidation both oxidation initiation and thermal chain scission as indicated occur in a concerted way. Random chain scission, initiated by oxygen and heat as suggested by Conley may be valid. It remains to be determined, however, in the oxidation case how important each mechanism is in contributing to the thermal degradation of polymer. As discussed, the oxidation initiation is of little interest to the ablation case, except where the polymer has been partly oxidized during fabrication.

It is also worth noting, in connection with the proposed mechanism, that polybenzyl also reported by Madorsky gives no char yield by pyrolysis in vacuo. This polymer, to be sure, possesses multiple bonded aromatic rings through methylene bridges. However, this polymer contains no hydroxyl functionalities through which it can rearrange to give the necessary aryloxy crosslinked intermediate leading to char formation in a methylene bonded system. It should be expected that the polybenzyl would decompose by repetition of the proposed initiation step to give high yields of benzene and toluene. This was found to be the case.
Phenolic novolacs (I) and its hexa-cured derivatives. This reaction mechanism can be applied to explain the char-forming reactions of the phenolic novolacs described in this paper. To do so, it is convenient to analyze the kinds of thermograms given in figure 6, by plotting the rate of vapor production \( \frac{d(l - Y)}{dt} \) as a function of the programmed thermogravimetric temperature. The results of this analysis are given in figure 12 for three hexa-cured phenolic novolac resins, namely, (I), (I-c), and (I-f). The sol fractions, \( X_S \), determined experimentally for these three polymers are indicated. Three distinct maxima are observed representing the maximum rates for three consecutive vapor producing processes at 250\( ^\circ \), 375\( ^\circ \), and 525\( ^\circ \) C, respectively. It can be seen that there is considerable overlap between these reactions. There is some indication of additional reactions between 600\( ^\circ \) and 800\( ^\circ \) C, but the overlap is so extensive as to mask these reactions almost completely.

It is possible to relate these observations to the mechanism proposed above. The first weight loss observed up to 250\( ^\circ \) is believed to be due to the loss of trace amounts of nonpolymeric impurities such as ammonia, unreacted hexa, and adsorbed moisture. The maxima for the second weight loss at about 375\( ^\circ \) C appear to vary proportionally with the observed sol fraction. In the case of these phenolic resins, the weight fraction of soluble polymer, \( X_S \), is equal to the fraction containing singly bonded phenolic end groups. It is also proportional to the total weight fraction of polymer containing these pendant groups. The reaction at 375\( ^\circ \) C is the dominant one for the uncross-linked oligomer (I) (sol fraction of 1.00). The third observed weight loss (the second thermochemical reaction) occurring at 525\( ^\circ \) C is dominant, having the most highly crosslinked derivative, (I-f) (sol fraction of 0.09). The mechanism requires that there must be a proportionate decrease in the yield of the thermally crosslinked intermediate and a consequent reduction in char yield as the sol fraction increases to 1, and the number of pendant groups increases. The areas under each of these consecutive maxima, at 375\( ^\circ \) and 525\( ^\circ \) C, are proportional to the amount of material lost by each process. The area under the 525\( ^\circ \) C maxima is proportional to the amount of the thermally crosslinked intermediate ((VII) in fig. 11) formed by the first reaction. This yield is greatest for the most highly crosslinked system. The final reaction in which the thermally crosslinked intermediates are converted to stable char cannot be resolved by these thermogravimetric techniques. It is possible to improve the resolution of the intermediate reactions by varying the extent of cure of these phenolic novolacs. Winkler (ref. 10) has taken advantage of this means to resolve the overlapping kinetics of these processes.

It can be concluded that the consecutive series of reactions observed in the course of thermogravimetric pyrolysis correspond to the principal reactions outlined in the proposed mechanism. The observed variation in the
extent of these reactions as the number of pendant phenolic groups is varied is consistent with the requirements of the proposed mechanism. Isothermal pyrolysis techniques may be required to resolve the details of the final conversion of the thermally crosslinked intermediates to stable char.

It is clear that any analytical expression developed to predict the char yield from polymer structure must take into account the number of singly bonded phenolic groups present in the polymer. This can be done most conveniently by expressing this structural parameter in terms of the sol fraction $X_s$ and the number of pendant groups initially present in the polymerizable oligomer. The total number of aromatic rings lost during the initiation process per gram of polymer decomposed, $\varphi$, is given simply as

$$\varphi = \left(\frac{N}{M} - \frac{N - P}{M'}\right)X_s$$  \hspace{1cm} (16)

where

- $N$ total number of aromatic rings per average mer unit
- $M$ average molecular weight of repeating mer unit
- $P$ average number of pendant singly bonded aromatic rings in oligomer
- $M'$ average molecular weight of oligomer

The number of aromatic rings coalescing to form char is simply the total number present minus $\varphi$. For six carbon-atom aromatic rings, and for any number of pendant groups initially present in the parent oligomer, the char yield is given by

$$Y_c = 72.06\left[\frac{N}{M} - \left(\frac{N - P}{M'}\right)X_s\right]$$  \hspace{1cm} (17)

The observed char yield for the various phenolic novolacs has been plotted in figure 13 as a function of the measured sol fraction. It can be seen, as expected, that the char yield decreases linearly with the increasing fraction of soluble polymer. A char yield of 43.2 percent was observed for the completely soluble phenolic novolac oligomer (I). The proposed mechanism can be applied to this oligomer through equation (17) to calculate the number of pendant phenolic end groups, $P$, present with a sol fraction equal to 1.00 and a char yield equal to 43.2. These observations require that the parent phenolic novolac must have three pendant groups. This necessary condition is completely admissible with the structure determined. The line in figure 13 was obtained by
use of equation (17) and the structural parameters and sol fraction as given previously. The observed char yields agree well with those predicted by the equation. If this equation is applied to a completely crosslinked system in which \( X_S = 0.00 \) and \( r = 1.00 \), the char yield is 65.0 percent. It has not been possible to prepare this model. The best extrapolation through the available data points gives the calculated value of 65.0 for this completely crosslinked structure.

Diphenyloxide modified phenolic resins.— No characterization of the extent of crosslinking was performed on these polymers. However, it is possible to correlate the observed char yields for the polymers given in table III, from the information given for the monomer structure and the effective equivalence ratios, \( r \). It is possible to use three reference points which can be calculated from the monomer or prepolymer structures by means of equation (17). These are at \( r = 0 \), \( r = 1.00 \), and \( r = 5.00 \) where \( X_S \) must be 1, 0, and 1, respectively. In figure 14 the predicted char yield is given as a function of the equivalence ratio, \( r \). It has been assumed in this case that the sol fraction varies linearly with the \( r \) value. Two straight lines have been drawn with the two anchor points to the maximum char yield predicted for \( X_S = 0.00 \) for this system. The yields of char obtained experimentally from these diphenyl oxide systems have been plotted as a function of the characterizing \( r \) values. These points appear to lie close to the lines predicted by equation (17) and to go through a maximum at \( r = 1.00 \) as expected. Polymers from diphenyloxide modified phenolics with \( r \) values much different from 1 are of little interest because of the absence of useful physical properties. For this reason it is believed that the effective equivalence ratio and a knowledge of monomer structure are sufficient for characterizing the char forming properties of these systems. One may also infer that isomeric (ortho-para) differences in phenolic structure are not important in determining these char yields, since the char yields of polymers derived from isomeric mixtures of both diphenol (IV) and its polymethylol derivatives correlate with that calculated with equation (17) for these polymers.

As discussed previously, the reaction of dialkyldiphenol (IX) with polymethylol phenol (III) is not known. If one assumes that dialkyldiphenol (IX) has reacted with the methylol phenol in the available ortho positions, the proposed mechanism predicts greater char yields than those observed. This fact suggested that the dialkyldiphenol did not react to form the multiple bonded groups needed for incorporating these rings into the char structure. If it is assumed that only the unsubstituted diphenol reacts to form multiple bonded phenolic rings, and that the dialkyldiphenol exists in the polymer as
an unreacted diluent, the mechanism will predict a char yield of 52 percent; the value observed for this polymer is 54 percent. This agreement is sufficiently good to support the fact that dialkyldiphenol (IX) has not reacted in the formation of this polymer. It thus can be seen that the char yield may also be applied to determine the reactivity of a particular monomeric component.

Epoxy novolacs cured with Nadic methyl anhydride.- The pyrolysis of these complex polyester phenolic derivatives yields stable chars in inert environments by the same general mechanism outlined for the phenolics. It should be noted, however, that the sol fraction of the anhydride cured epoxy novolacs bears no direct relationship to the number of phenolic derived rings present in the final polymer. The epoxy novolac polymers given in table X are as fully crosslinked as possible through the available functions. Accordingly, equation (17) may be rewritten without the sol fraction parameter as

\[
Y_c = \frac{12.01[6(N - P)]}{M}
\]

where \(N\) and \(M\) have the same definition as given above, but \(P\) must be further specified as the total number of aromatic rings possessing only one methylene bridge per mer unit. This specification is necessary since these groups are not pendant end groups in the anhydride-cured epoxy novolac, but still are singly bonded through one methylene group to the main chain.

If this modification of equation (17) is used for calculating the char yield expected for each of the nine polymers given in table V, the difference between the calculated and experimental char yields is relatively consistent.

\[
Y_c(\text{exp}) - Y_c(\text{calc}) \approx 12 \text{ percent}
\]

The differences observed in each case are exactly and uniquely equal to the contribution that would be made by the three carbons of each epoxy group in each polymer. The contribution of these epoxy carbons to the total char yield may be accounted for by the modification of equation (18) to give

\[
Y_c = \frac{12.01[6(N - P) + S]}{M}
\]

where \(S\) is the total number of epoxy group carbons per average mer unit \(M\).

Equation (19) was used to calculate the expected thermochemical char yields for the nine epoxy novolac polymers given in table V from their composition. These results are compared in table XII. The calculated values agree quite well with those found by thermogravimetric analyses of these polymers.
**TABLE XII.**—COMPARISON OF CHAR YIELDS OBTAINED FROM TGA WITH THOSE CALCULATED BY EQUATION (19), $r = 0.85$

<table>
<thead>
<tr>
<th>Epoxide equivalents</th>
<th>Calculated char yield</th>
<th>Thermogravimetric char yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>of monomers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X)</td>
<td>(XI)</td>
<td>(XII)</td>
</tr>
<tr>
<td>0.833</td>
<td>0.167</td>
<td>0</td>
</tr>
<tr>
<td>0.667</td>
<td>0.333</td>
<td>0</td>
</tr>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>0</td>
</tr>
<tr>
<td>0.333</td>
<td>0.677</td>
<td>0</td>
</tr>
<tr>
<td>0.167</td>
<td>0.833</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0.680</td>
<td>0.320</td>
</tr>
<tr>
<td>0</td>
<td>0.350</td>
<td>0.650</td>
</tr>
<tr>
<td>0</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The thermogravimetric char yields of these epoxy novolacs are plotted in figure 15 as a function of the values obtained by applying equation (19) to the known structure of these resins. This agreement is sufficiently close to lend considerable support to the proposed mechanism. Furthermore, the results are consistent for the entire series of epoxy novolacs with widely varying structures.

McAllister (ref. 11) pointed out that certain epoxy resins derived from bisphenol A, although crosslinked, give no char when pyrolyzed. The aromatic ring system for such epoxides may be represented as

It can be seen that the bisphenol A monomer contributes only aromatic groups which are singly bonded through one aliphatic bridge and do not possess the basic conformation required by the mechanism to retain these aromatic rings. Consequently, no char is produced. One may conclude that if the bisphenol A moiety is the only source of aromatic rings, its polymeric derivatives will produce no char. For this reason polycarbonates based on bisphenol A do not form chars.

To understand the extension of the proposed mechanism for simple phenolic novolacs to these complex anhydride-cured epoxy novolacs, it is necessary to compare both structural differences in these polymers and similarities.
observed in the course of the pyrolysis reactions. The following general structure for these anhydride cured epoxy systems has been established by IR and elementary analyses:

Like the simple phenolic, the epoxy novolac comprises a main chain of both single and multiple-bonded phenolic rings. In the structure as given, there are \( n \) multiple-bonded phenolic rings. For example, monomer (X) contributes no multiple-bonded rings to its derivatives, whereas monomers (XI) and (XII) contribute 1.80 and 5.64 aromatic rings, respectively, which are multiple bonded through phenyl methylene phenyl bridges. Accordingly, these are the only aromatic rings in these polymers, the carbons of which can be expected to contribute to char yield. Monomer characterization is sufficient to define these structures. It can be seen that after reaction with the anhydride, an ester and secondary hydroxyl group is obtained from the ring opening of the epoxide group. No such ester crosslink exists in the phenolic novolacs.

Thermal decomposition of these polymers is not initiated by aromatic group elimination. Rather pyrolysis begins at 260\(^\circ\)C (350\(^\circ\) required for aromatic group elimination) with the loss of Nadic methyl anhydride and cyclopentadiene. The anhydride forms from the decomposition of the half ester present in the polymer and the cyclopentadiene from a reverse Diels Alder reaction occurring at the cluster linkage. (These processes agree with those reported by Fleming (ref. 12).) The remaining malic ester then ruptures and the secondary hydroxyl group is eliminated as water. In this process, the resulting unsaturated three-carbon derivative condenses to give a new six-membered aromatic ring. Finally at 350\(^\circ\)C, the phenyl groups which are only singly bonded are eliminated by the same process as for the simple phenolic novolac.

It can be concluded that the same basic char-forming mechanism prevails for the anhydride-cured epoxy novolac as for the simple phenolics so far as retention of multiple bonded phenolic rings is concerned. But, in addition, the degradation of the epoxide side chain followed by condensation produces additional phenoxy-bonded aromatic rings which are also retained as char.

Additional experimental evidence to support the application of the basic pyrolysis mechanism developed for simple phenolic novolac to account for the char yields of these anhydride-cured epoxy novolacs can be provided by examination of the thermograms obtained for these resins. The thermogram for the anhydride-cured epoxy novolac (polymer 6) was analyzed by plotting the
differential vapor production rates $d(1 - Y)/dt$ as a function of the thermogravimetric temperature. The result is shown in figure 16. Initial loss of trapped impurities begins at $175^\circ C$ with thermal decomposition. The maxima for the first reaction appear at $250^\circ C$. No phenolic derivatives were found as vapor products during this reaction. It is particularly interesting to note that the maxima for the second reaction in the case of the anhydride-cured epoxy novolac occur at $375^\circ C$. This is precisely the temperature for elimination of the pendant phenolic end groups observed for the simple phenolic novolac. It is clear that this is the temperature for aromatic group elimination for both kinds of polymers. In figure 16 there is evidence of reactions between $450^\circ C$ and $600^\circ C$ by which the thermally crosslinked intermediates formed by the second reaction are decomposed to give char. Again these reactions are not well resolved by thermogravimetric techniques. It is also an essential part of this argument that the initial decomposition of the anhydride-cured epoxy novolac, below $260^\circ C$, is not competitive with the second reaction. That is, the amount of phenolic derivative formed by this initial reaction is independent of the way in which the ester groups have been eliminated and this reaction gives a definite product which then proceeds to decompose as the simple phenolic. If the programmed pyrolysis is carried out up to a temperature of $260^\circ C$, the first reaction is completed. When thermogravimetric analysis is carried out on this residue, the first reaction is wiped out. Only the second reaction with its maxima at $375^\circ C$ is observed. The second reaction in absence of the first begins as indicated by the dotted portion of the curve. It can be concluded that the Nadic methyl anhydride ester side chain is eliminated at the low temperature of $250^\circ C$, after which pyrolysis of the phenolic residue proceeds as with the simple phenolic at $375^\circ C$.

As mentioned above, the crosslink density of the epoxy novolacs can only be modified by changing the number of multiple bonded phenolic rings through methylene bridges. As the number of these groups increases, one should expect a corresponding increase in crosslink density. For the epoxy novolacs this parameter was characterized by swelling volume. The number of these char-forming groups increases with decreasing swelling volume. The char yield should then be expected to increase with decreasing swelling volume. In figure 17 the char yield for those anhydride-cured epoxy novolacs that gave measurable swelling volumes is plotted as a function of the crosslink parameter. It
can be seen that the char yield varies linearly with swelling volume. From this figure it can be concluded that the only aromatic rings that contribute to char formation are those which are multiply bonded by methylene groups, as required by the general mechanism.

A COMPARISON OF THE THERMOGRAVIMETRIC CHAR YIELDS WITH THOSE OBTAINED BY SIMULATED REENTRY HEATING

In this investigation it has been shown that a general reaction mechanism can predict accurately the primary char yield of phenolic resins and related polymers if their molecular structure is known. Furthermore, it has been demonstrated that these predicted primary char yields can be used to predict the yields of composites derived from these polymers. It is now of interest to compare these results with those obtained under environments that simulate reentry heating.

Two methods of simulating reentry heating environments were employed. The radiation component of aerodynamic heating was simulated by means of an arc-imaging furnace, and the convective heating was simulated by an arc jet as described by Lundell (ref. 13). By these techniques it was possible to apply heating rates ranging from 20 to 150 cal cm$^{-2}$sec$^{-1}$. These heating rates produced surface temperatures between 1700° to 3500° K. As mentioned above, the applied heating rates gave polymer temperature rise rates of 5000° to 8000° C per minute as compared with 20° to 120° C per minute in the thermogravimetric tests.

To prevent surface combustion reactions, the one-dimensional pyrolyses were carried out either in vacuum or in helium in an arc imaging furnace, and in a nitrogen arc jet. To determine the ablation char yields, the char cap was removed at approximately the pyrolysis zone and the conversion of polymer to char was measured gravimetrically. The results are shown in table XIII.

**TABLE XIII. - A COMPARISON OF THERMOGRAVIMETRIC CHAR YIELDS WITH ARC FURNACE CHAR YIELDS AT 200 MICRONS PRESSURE**

<table>
<thead>
<tr>
<th>Composite</th>
<th>Calculated char yield, $Y_c$</th>
<th>TGA, $Y_c$</th>
<th>Arc furnace $Y_c$ at low and high heating rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPN</td>
<td>31.4</td>
<td>29.1</td>
<td>25$^a$ 150$^a$</td>
</tr>
<tr>
<td>EN C-1</td>
<td>22.5</td>
<td>23.1</td>
<td>24.0 38.1</td>
</tr>
<tr>
<td>EN C-2</td>
<td>11.0</td>
<td>11.0</td>
<td>9.0 28.0</td>
</tr>
</tbody>
</table>

$^a$cal cm$^{-2}$sec$^{-1}$ = applied heating rate

For the phenolic-nylon composite there is good agreement between the thermogravimetric char yields and arc furnace char yields produced at heating rates of approximately 25 cal cm$^{-2}$sec$^{-1}$ which causes char surface temperatures of 1600° K. It can be concluded that the effect of heating rate on primary char formation is negligible. The char yield increases about 9 percent at
the high heating-rate condition which produces a surface temperature of about 3000° K. The increase in char yield is believed to be due to the cracking of carbon-bearing vapor species on the hot char matrix formed as primary char. This increase in char yield can be accounted for if the nylon vapors are assumed to contribute exactly four atoms of carbon for every mer unit decomposed by secondary cracking. Achhammer (ref. 14) identified the primary vapor products of 6-6 nylon vaporization as cyclopentanone, cyclohexylamine and ammonia. One might expect the cyclopentanone to decompose by cracking at the high heating rate (high char temperature) to give carbon, hydrogen, and carbon monoxide.

The composite derived from the anhydride cured epoxy novolac (polymer 6) also gave ablation char yields in good agreement with the calculated primary char yield at the low heating rate. Again, with this polymer system char yield increases about 4 percent at the high heating rate. This increase is also attributed to cracking and secondary char deposition. In this case, the principal source of secondary char yield is probably the cyclopentadiene decomposing by cracking. It appears that the aromatic species also evolved as vapor products are not cracked at the high heating rate.

This conclusion is supported by the result obtained with the low char yield composite EN C-2. Here the principal vapor products are aromatic species. In table XIII, it can be seen that the ablative char yield of this composite agrees fairly well with the primary char yield from thermogravimetric analyses at both the low and high heating rate. It can be concluded that the formation of secondary char depends on both the char surface temperature and the chemical constitution of the vapor products produced by the primary char-forming processes.

Under certain test conditions, the char yields obtained from the low-density phenolic-nylon composite in the arc image furnace and arc jet may be compared. Both kinds of tests should be carried out in inert atmospheres to preclude surface combustion and at heating rates which do not produce char sublimation. These conditions were met in the arc furnace by carrying out the pyrolyses at a constant static pressure of 3x10^-4 atmosphere of helium and in an arc jet at impact pressures of nitrogen which varied from 1x10^-2 to 2.7 atmospheres. The char yields, obtained under these conditions, with the LDPM composite are given as a function of surface temperature in figure 18. It can be seen that the measured char yields obtained in both the arc furnace and arc jet up to surface temperatures of 2000° K agree with the thermogravimetric char yield observed at 800° C. This agreement suggests that the primary char-forming reactions of this composite are independent of polymer heating rates, from 2° to 5000° C per minute. This result is consistent with the fact that the char-forming reactions are consecutive noncompetitive processes. It has been found, by differential
thermal analysis of the phenolic novolac (I-c), used in this composite, that
the reactions producing the crosslinked intermediates required to form char
are exothermic. The reactions converting these intermediates to char are
endothermic. It is interesting that the net enthalpy change (heat of pyroly-
sis) from these two processes is negligible. Only the heat absorbed by the
endothermic heat of pyrolysis of the nylon need be considered in estimating
the heat absorbed by pyrolysis of this composite. For the nylon this heat
has been estimated to be about 500-600 cal/g.

It can also be seen in figure 18 that, under arc-furnace conditions,
there is a gradual increase in char yield with increasing surface temperature
from 2000° to 3000° K. The yield seems to attain a constant value again at
the higher temperature. This incremental increase has been explained by the
partial cracking of the nylon vapors to give secondary char. At impact pres-
sures greater than 0.10 atmosphere (produced in the arc jet) a further
increase in char yield is observed. This increase in char yield may be due to
an increased residence time of the primary pyrolysis vapors in the hot char
matrix since the increase in impact pressure decreases the velocity of gases
passing through the char.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, California 94035, July 18, 1967
124-07-01-10-00-21
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