

# The Thermo-Oxidative Degradation of Phenol-Formaldehyde Polycondensates: Thermogravimetric and Elemental Composition Studies of Char Formation

HOWARD W. LOCHTE, ERIC L. STRAUSS, and  
ROBERT T. CONLEY,\* *Research Department, Baltimore Division,  
Martin Company, Baltimore, Maryland*

## Synopsis

An investigation of the char formation process during the thermal-oxidative degradation of phenol-formaldehyde polycondensates by thermogravimetric analysis and elemental analyses of the degraded residues has been found to support the char-forming proposals previously reported. The resins investigated, once fully cured at elevated temperatures, were all found to degrade identically under the conditions studied despite differences in the phenol-formaldehyde ratios of the liquid resins. Test data indicated that the elevated temperature degradation is fundamentally associated with the chemical stability of the dihydroxydiphenylmethane unit. Small differences in the mode of degradation were observed up to 300°C. and could be attributed to the post-curing processes and volatilization of solvent and other low molecular weight species. The present study presents a useful alternate approach to the study of high temperature degradation, based on residue analyses, which when coupled with data obtained by other methods allows a more complete evaluation of resin degradation in the temperature range 150-300°C.

## INTRODUCTION

In a number of previous reports,<sup>1-5</sup> the oxidation chemistry of phenol-formaldehyde polycondensates has been described in some detail. The correlation of data on changes in resin structure collected by infrared spectroscopy, gas chromatography, and other physical methods of analysis and by model compound studies has led to a proposed mechanism for the formation of carbon char at elevated temperatures. The primary evidence for char formation rests on the fact that quinoid species are readily formed during resin oxidation from dihydroxybenzophenone moieties. The rate of quinoid species formation increases markedly as the temperature is increased.<sup>2</sup> Gas chromatographic monitoring of the volatile products formed during controlled temperature pyrolysis<sup>3</sup> indicated that the formation of carbon char during decomposition of the phenolic polymer parallels the

\* Present address and address to which inquiries should be directed; Department of Chemistry, Seton Hall University, South Orange, New Jersey.

evolution of carbon monoxide. Figure 1 summarizes the postulated char-forming reactions starting from the dihydroxydiphenylmethane unit.<sup>3</sup> The indicated reaction scheme is idealized, since experimental verification for differences in reactivity of 2,2', 2,4', and 4,4'-isomeric units has not been possible.

Since the application of phenol-formaldehyde polycondensates to ablative thermal protection systems for reentry vehicles requires an understanding of the degradation processes taking place, particularly those reactions leading to char formation, further investigation of high temperature degradation was deemed of value. The problem of elucidating changes in structure of complex resin systems at elevated temperatures, i.e., above 400°C., presents a formidable task, due to the limited applicability of physical methods such as spectrophotometric monitoring of functional group changes at the reaction temperature. The present report delineates an approach to high-temperature degradation studies which monitors changes in elemental composition as a function of temperature and time. When this information is coupled with gas-phase product distribution, spectral examination of the residual material, and other physical data, a more detailed view of the actual

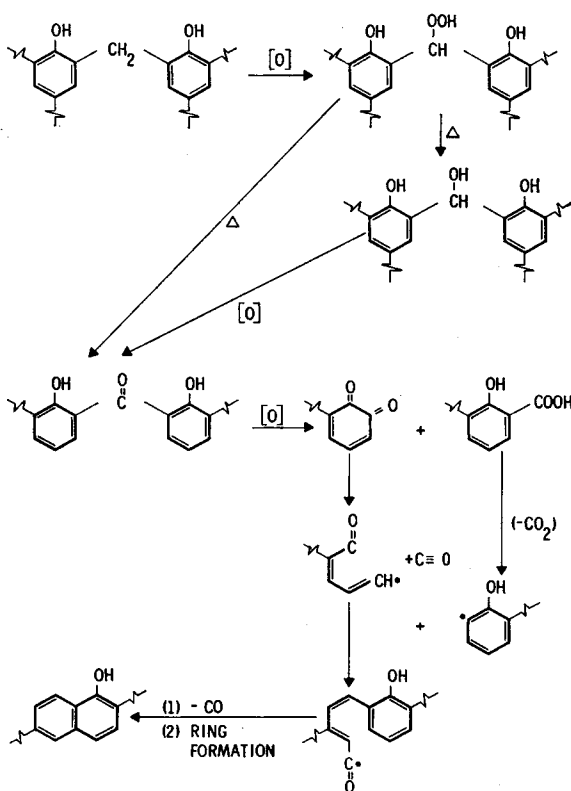


Fig. 1. Postulated reaction scheme for the formation of carbon char from the dihydroxydiphenylmethane unit.<sup>1-5</sup>

degradation processes can be rationalized. The techniques employed in this study were chosen in order to combine weight loss information with elemental changes within the residual polymeric material over a wide range of temperature. The reason for this approach was due to the fact that above the very early weight losses caused by volatilization of low molecular weight fragments such as water, phenol, etc., all phenol-formaldehyde resins appeared to exhibit very similar high temperature degradation (i.e., parallel weight losses regardless of phenol-formaldehyde ratio). It was therefore desirable to have a method which studied the residue as the focal point rather than the volatilized degradation products.<sup>3</sup> The objective, naturally, was to gain correlative solid-phase residue data for comparison with information available from other methods of analysis.

## EXPERIMENTAL

### Resins Studied

The phenol-formaldehyde resins utilized in this study were specifically prepared for comparison with previously reported investigations<sup>2,3</sup> or were commercial samples either utilized in other investigations of high-temperature degradation<sup>6</sup> or employed for correlative purposes with the laboratory-prepared materials. All samples were alkaline-catalyzed (resole type) liquid resins and are designated by letters for discussion purposes in this report.

Resins A, B, and C (prepared for this study by Dr. L. S. Miller, Adhesive and Resin Products Division, Martin Marietta Corporation, Seattle, Washington) were catalyzed with  $\text{Ca}(\text{OH})_2$  and had phenol-formaldehyde ratios of 0.50, 0.42, and 0.36, respectively. Resin D (prepared as described by Conley and Bieron<sup>2</sup>) was catalyzed with NaOH and had a phenol-formaldehyde (P/F) ratio of 0.50. Resin E, a commercial product (CTL-91-LD), has been investigated by Coffman and Friedman<sup>6</sup> and was obtained from the American Reinforced Plastics Company, Los Angeles, California. Resin F is a commercial product (SC-1008) obtained from the Monsanto Company, Plastics Division, Springfield, Massachusetts.

Resin samples A, B, C, E, and F are designated as either cured or post-cured, depending on the total curing process used in terms of time and temperature. Cured resin samples were subjected to the following sequence of elevated temperature exposure in air: 72 hr. at 74°C., 2.5 hr. increasing from 74 to 108°C., 2 hr. at 108°C., and finally 19 hr. at 127°C. In order to increase the degree of methylene bridges by thermally condensing the residual methylol species,<sup>3</sup> an additional curing process was employed (post-cured samples). The typical post-curing cycle was as follows: 6 hr. at 149°C., 8 hr. at 177°C., 8 hr. at 199°C., 30 min. increasing from 199 to 232°C., 30 min. at 232°C. Resin D was cured by a slightly different method (3 hr. at 120°C.) for specific comparison with previous studies on volatile product distribution.<sup>3</sup>

The thermogravimetric and chemical analyses samples were filings from the cured or post-cured sample blocks.

### Thermochemical Analysis Technique

All thermogravimetric analyses (TGA) were conducted by a standardized testing technique. Samples consisting of 200 mg. of filings in a porcelain crucible were heated in an argon atmosphere at a constant temperature rise rate of 3.3°C./min. to a final temperature of approximately 815°C. The change in sample weight was measured on a Cahn model RA recording electrobalance with a sensitivity of 0.1 mg. It should be pointed out that since the weight loss rate is affected by heating rate and by the atmosphere surrounding the sample, standardization of both parameters is essential for data comparison.

For elemental analysis studies, 200 mg. of filings of resins B, C, E, and F were placed in separate small Inconel containers and simultaneously exposed to the TGA heating cycle until a predetermined sample temperature was attained. Equipment was the same as was used in the TGA testing except that there was no need for the recording balance. A thermocouple was inserted into the sample inside one of the metal containers, thus allowing direct reading of sample temperature by use of a null balance potentiometer. When the sample temperature reached the desired point, samples were immediately removed from the furnace and quenched in water. The purpose of this quench was to abruptly terminate degradation reactions by means of a rapid reduction in specimen temperature. The time required for the quench was less than 5 sec. so that the amount of air diffusing through the argon enveloping the samples was negligible. Sample temperatures were selected to give residues differing by increments of approximately 0.05 in residual weight fraction as determined from the TGA data.

Visual effects accompanied the degradation of these materials. The color transition was from tan (up to 300°C.) to brown (350–500°C.) to dark brown (500–600°C.) to black (above 600°C.).

After drying for several hours near 100°C. in a circulating air oven, residues were analyzed to determine their elemental composition. Nitrogen analyses were conducted on cured but nondegraded samples of each material using a Coleman Model 29 Nitrogen Analyzer. Trace amounts of nitrogen (less than 0.5%) were detected in the commercial materials which were not post-cured (resins E and F). The consequence of this nitrogen was trivial, so that from a practical standpoint these materials were considered nitrogen free. A Coleman Model 33 carbon-hydrogen analyzer was used to determine percentages of carbon, hydrogen and (by difference) oxygen on all residues. The precision of the instrument in determining carbon or hydrogen is approximately  $\pm 0.2\%$ . In actual operation, accuracy tended to vary and it was necessary to frequently test standard reagents of verified composition in order to confirm proper functioning of the instrument.

By separate combustion of undegraded samples of each material, an ash of 0.3% or less was obtained. These experiments indicate the presence of negligible amounts of inorganic constituents.

## DISCUSSION

### Thermogravimetric Analysis

The thermogravimetric method of polymer analysis provides an accurate record of the change in sample weight as a function of linearly increasing temperature. Typical weight changes in the cured materials are summarized in Figure 2. Figure 3 indicates corresponding weight loss data for the post-cured materials. In the cured materials, weight losses below 300°C. were significantly greater than those recorded for the post-cured samples. Such a change is quite consistent with losses of entrapped solvent,

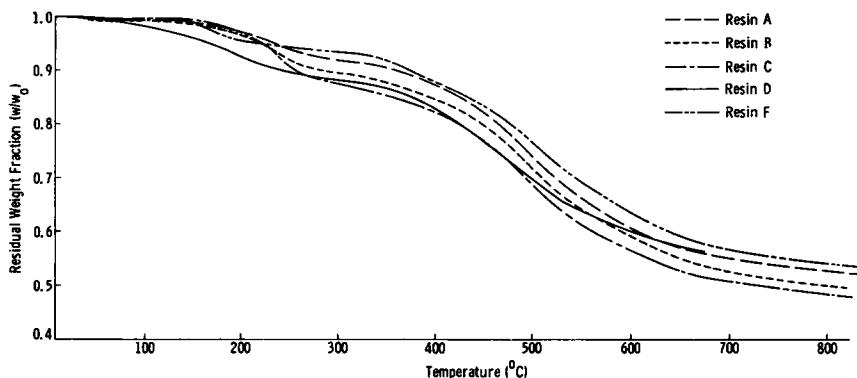


Fig. 2. Thermogravimetric analysis curves for cured phenol-formaldehyde polycondensates heated at 3.3°C./min. in argon.

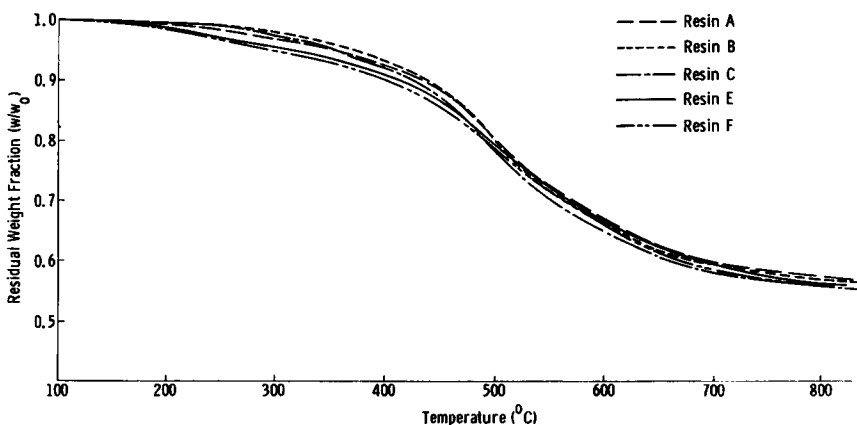


Fig. 3. Thermogravimetric analysis curves for post-cured phenol-formaldehyde polycondensates heated at 3.3°C./min. in argon.

water from methylol condensation, and low molecular weight components due to volatilization as the temperature is increased. Weight losses of the cured resins A-D (Fig. 2) in the 100-300°C. temperature region seem to depend upon the phenol-formaldehyde ratio of the liquid starting resin. The resin having a phenol-formaldehyde ratio of 0.50 (resin A) showed a smaller weight loss than resins with lower phenol-formaldehyde ratios. Resin D, with a phenol-formaldehyde ratio similar to resin A, was cured at a temperature only 100°C. lower than resins A-C but for a much shorter time (3 hr. compared to 19 hr.). The weight loss from resin D was significantly higher than that obtained from resin A. These weight losses are consistent with the ability of the resins to undergo further condensation between 100 and 300°C. In the 300-400°C. temperature region, all samples indicated similar weight loss phenomena. Since earlier work<sup>3</sup> had shown that the resin is almost fully cured by heat treatment at 300-400°C., the similarity of all resins whether cured or post-cured is not unexpected. The volatile products should be those expected from final condensation of the residual methylol groups together with products expected from the initial phases of degradation.

As noted from the TGA curves (Figs. 2 and 3), the major weight loss occurred in the 400-700°C. temperature region, and weight losses over that region are remarkably similar regardless of the starting resin or its degree of cure. This phenomenon was suspected from earlier studies, since the rates of degradation of various sample types (i.e., phenol-formaldehyde ratio) closely paralleled each other at high temperatures. For example, a resin film prepared from a resole having a phenol-formaldehyde ratio of 0.5 was spectrally the same after oxidation at 625°C. for 6 min. as the spectrum obtained from a resin having a 0.35 phenol-formaldehyde ratio.<sup>7</sup> The in-growth of bands in the infrared region showed these samples similar in both

TABLE I  
Consistency of Weight Loss Data Regardless of Sample Type  
over the Temperature Region 350-810°C.

Material	$W/W_0$ at 350°C.	Weight loss between 350 and 810°C., % of $W/W_0$ at 350°C.
A-C*	0.954	41.7
A	0.906	41.9
B-C*	0.962	41.2
B	0.880	43.5
C-C*	0.954	41.7
C	0.857	43.8
E-C*	0.936	40.1
E	0.857	40.0
F-C*	0.930	40.4
F	0.922	41.6

\* The samples were post-cured.

types and intensities of absorption bands resulting from the formation of new functional groups.

Generally speaking, weight loss differences between the various phenolic materials above 350°C. were minor, regardless of the resole sample investigated. This observation is particularly clear by examination of Table I.

From these data, it is apparent that the stability of the resin system as a molecular species is the phenomena controlling the elevated temperature degradation (350–810°C.). Therefore, the inherent stability of the dihydroxy-diphenylmethane unit would not be expected to change either from a thermal or oxidative degradation viewpoint unless fundamental modifications are made in the chemical structure of the species. With these observations in mind, a study of the residue composition as a function of temperature should be a useful tool in tracing the formation of carbon char and, as well, in evaluating other data already in the literature relating to high temperature degradation of these resin systems. For example, Coffman and Friedman<sup>6</sup> reported the mass spectrometric analysis of volatile components from phenolic degradation. No mention of oxygenated organic species such as phenol, formaldehyde, etc., was made in this report. From our previous work,<sup>3</sup> carbon dioxide, carbon monoxide, and other oxygenated products represent a major portion of the volatiles from the degrading resin and therefore the elemental analysis of the residue should reflect these changes.

#### Elemental Analysis Studies

Table II summarizes the results of carbon-hydrogen analyses on post-cured resins B, C, E, and F. As discussed in the experimental section, percentages not accounted for in Table II are assumed to be oxygen. The residual weight fractions ( $W/W_0$ ) from the thermogravimetric study are also summarized for clarity. Conversion of the elemental weight percentages into absolute weight values expressible in terms of grams or moles is possible by utilizing the residual weight fraction data. Figure 4 summarizes the relative changes in elemental composition of the residue in terms of moles as a function of temperature for the post-cured resin samples. Below 250°C., differences between resin types are evident. Resins E and F are shown to lose carbon and hydrogen (indicative of loss of an organic solvent entrapped in the resin), while resins B and C show a loss of hydrogen only (indicative of the loss of water rather than carbon-containing species). Since resin E is known to have isopropyl alcohol as the solvent for the liquid resole, the trends in the elemental composition seem to be quite significant when coupled with other known information. Above 300°C., the residue composition of all the materials studied is almost identical. These data follow consistently from the thermogravimetric data in which all major variations were noted below this temperature range. Essentially, at 300°C., the resins, regardless of initial composition, have been normalized due to curing, oxidation, and loss of volatile components. Since any individual elemental measurement is subject to an error of 0.3%,

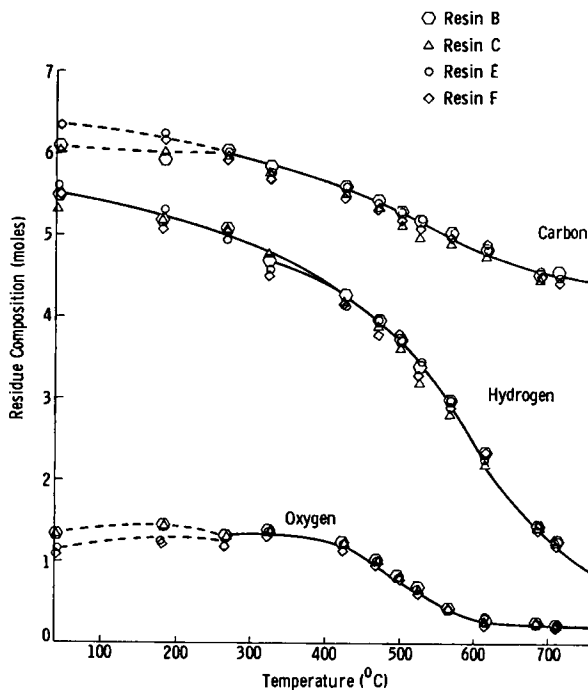


Fig. 4. Char composition vs. temperature for post-cured phenol-formaldehyde polycondensates. Initial sample weight = 100 g.; heating rate = 3.3°C./min.

these observations are quite consistent. Small changes in chemical composition due to variations in aromatic to aliphatic moieties present will not be reflected in the elemental composition measurement.

The manner in which residual weight fractions of elemental carbon, elemental hydrogen, elemental oxygen, and total weight for phenolic resin B, as a typical example, vary with temperature is shown in Figure 5. These curves are normalized with respect to initial weight of each component. The low temperature increase in oxygen may be due to residual water from the quench or to oxidative degradation of methylol and methylene groupings as reported by Conley et al.<sup>1-3</sup>

It is interesting to note the changes in mole ratios of the different elements in the residue as it degrades. Between 250 and 425°C., the empirical composition of the resin changes little and the mole ratios C/O, H/O, and C/H remain essentially constant at values of 4.5, 3.5, and 1.25, respectively. Only about 10% of the original sample weight is lost below 425°C. Above this temperature, the ratios involving oxygen rise sharply (C/O from 4.5 to 20 and H/O from 3.5 to 8), reflecting the severe loss of this element at temperatures of 450°C. and greater. These data are remarkably consistent with the data obtained from gas chromatographic analysis of the volatile components.<sup>3</sup> (In the 400°C. region, carbon dioxide and carbon monoxide were major products of the degradation.)



TABLE II  
Elemental Composition of Residues from Post-Cured Phenolics (Heating Rate 3.3°C./min. in Argon)

Temperature, °C.	B-C <sup>a</sup>			C-C <sup>a</sup>			E-C <sup>a</sup>			F-C <sup>a</sup>		
	H, %	C, %	W/W <sub>0</sub>	H, %	C, %	W/W <sub>0</sub>	H, %	C, %	W/W <sub>0</sub>	H, %	C, %	W/W <sub>0</sub>
As cured	5.49	72.81	1.000	5.31	72.37	1.000	5.60	75.78	1.000	5.57	76.63	1.000
180	5.19	71.38	0.997	5.21	72.15	0.997	5.37	75.41	0.991	5.12	74.77	0.988
260	5.15	73.22	0.989	5.13	72.99	0.985	5.15	74.49	0.965	5.24	74.49	0.959
320	4.82	72.04	0.974	4.91	72.20	0.966	4.83	72.85	0.946	4.80	72.82	0.940
420	4.68	73.33	0.914	4.63	73.56	0.902	4.67	74.99	0.892	4.74	74.67	0.882
460	4.61	75.94	0.864	4.60	75.57	0.849	4.71	76.43	0.844	4.51	76.79	0.835
490	4.61	78.60	0.811	4.56	77.37	0.792	4.64	79.04	0.800	4.82	78.93	0.793
520	4.51	82.25	0.758	4.32	80.15	0.744	4.58	81.81	0.758	4.37	81.77	0.752
560	4.23	85.65	0.704	4.12	85.29	0.688	4.22	85.44	0.709	4.10	85.43	0.701
610	3.58	89.31	0.652	3.43	88.67	0.642	3.46	88.70	0.657	3.63	90.79	0.650
675	2.35	90.75	0.601	2.43	91.12	0.592	2.44	90.45	0.604	2.34	91.32	0.595
705	2.10	92.56	0.593	2.15	—	0.581	2.17	90.75	0.591	2.06	91.25	0.583
810	1.17	93.73	0.568	1.13	94.12	0.557	1.25	93.88	0.562	1.24	93.42	0.556

<sup>a</sup> Post-cured samples (see Table I).

The rates of change of the different elements (Fig. 4) determine the empirical composition of volatile products being lost at any particular temperature. The mole ratio of oxygen to carbon in the decomposition products is larger than 1 but less than 2 between 425 and 530°C., while the mole ratio of hydrogen to oxygen in the volatile products experiences a minimum over this same region. Therefore, one would expect that carbon dioxide and carbon monoxide rather than water are the principal products. Molal ratios of hydrogen to carbon in gaseous products between 590 and 810°C. are approximately 4, indicating loss of low molecular weight aliphatics such as methane. Again, these data are consistent with the gas chromatographic data reported earlier.<sup>3</sup>

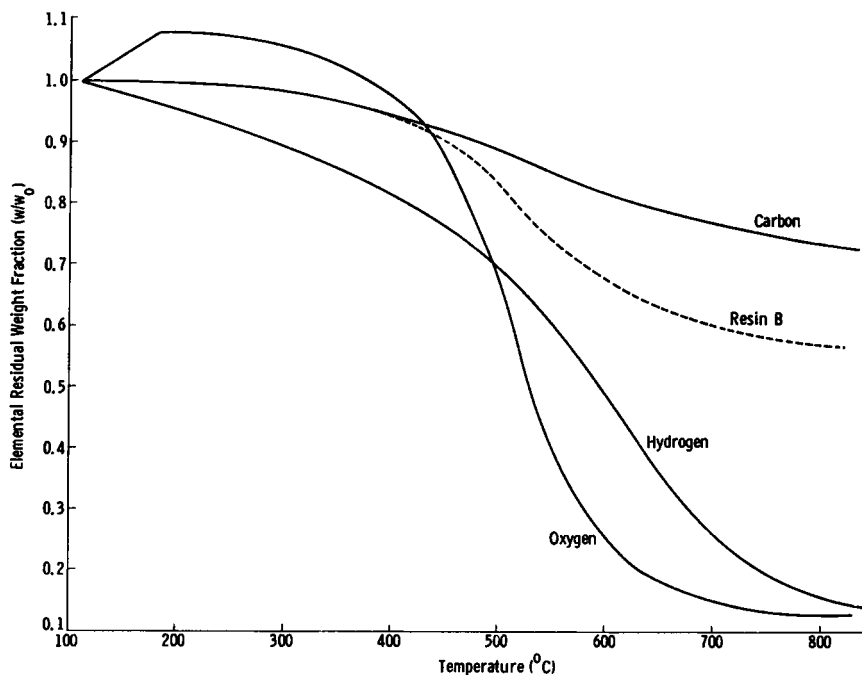


Fig. 5. Residual weight fractions of elements vs. temperature for post-cured resin B (P/F ratio = 0.42). Sample pyrolyzed at 3.3°C./min. in argon.

Residues from samples of these materials not post-cured were also subjected to elemental analysis. In general, chemical differences among these phenolics were minor above 320°C. and did not differ appreciably from results on post-cured materials. It may be recalled from the TGA results that weight loss characteristics followed this same pattern.

Earlier,<sup>3</sup> it was postulated that phenolic degradation was primarily oxidative in nature. The present study tends to confirm this observation and, in addition, lends support to the proposal that the resin itself can act as an oxygen source for the oxidative processes. Although the initial oxygen content of phenolics is only about 20% by weight, the present results show

that more than 50% of the weight loss occurring over the major decomposition region is due to oxygen loss.

Although no accurate identification of specific chemical species is possible from elemental analyses of the type performed here, the changes in composition as the char-forming process proceeds lend support for a reaction involving the loss of carbon monoxide simultaneously with the carbon char formation. The data presented here strongly suggest that regardless of the species present in the liquid resole before curing, the degradation processes occurring at elevated temperatures are dependent upon the stability of the dihydroxydiphenylmethane unit and, therefore, the polycondensates all behave similarly from a chemical viewpoint once the curing processes are complete. Early stage volatilization (up to 300°C.) is the only major difference between resole materials which are derived from phenol and formaldehyde (nonmodified resins), and, therefore, small differences observed in these materials when employed as thermal protection systems must be attributed to resin curing procedures and fabrication methods rather than to intrinsic differences in structure (i.e., molecular weight, varied substitution, etc.). Comparison of materials, prepared and cured by a variety of procedures, from a total weight loss viewpoint alone should be cautioned, since such a procedure does not adequately indicate stability differences between structural types. In fact, in many cases such comparisons may lead to erroneous conclusions regarding the suitability of a particular material for thermal protection applications.

### References

1. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 103 (1963).
2. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 171 (1963).
3. Jackson, W. M., and R. T. Conley, *J. Appl. Polymer Sci.*, **8**, 2163 (1964).
4. Conley, R. T., *J. Appl. Polymer Sci.*, **9**, 1107 (1965).
5. Conley, R. T., *J. Appl. Polymer Sci.*, **9**, 1117 (1965).
6. Coffman, J. A., and H. L. Friedman, U. S. Air Force Technical Report WADD-TR-60-646, Vol. I, Part III, 1964.
7. Conley, R. T., and J. F. Bieron, unpublished data.

### Résumé

On a trouvé qu'une étude du processus de formation de produit de carbonisation pendant la dégradation thermique oxydante des polycondensats phénol-formaldéhyde, étude effectuée par analyse thermogravimétrique et par analyses élémentaires des résidus dégradés, confirme les propositions antérieurement décrites concernant la formation de produit de carbonisation. Les résines étudiées, recuites complètement à températures élevées, se dégradent toutes d'une façon identique dans les conditions étudiées malgré les différences dans les rapports phénol-formaldéhyde des résines liquides. Les résultats des essais montrent qu'à température élevée la dégradation est fondamentalement associée à la stabilité chimique de l'unité dihydroxydiphénylméthane. Des petites différences dans le mode de dégradation ont été observées jusqu'à 300°C et pourraient être attribuées au processus de post-recuit et à la volatilisation du solvant et d'autres produits de faibles poids moléculaire. Le présent travail offre une voie utile pour l'étude de la dégradation à température élevée, étude basée sur l'analyse des résidus qui, lorsqu'on la combine avec les résultats obtenus par d'autres méthodes, permet une évaluation

tion plus complète de la dégradation des résines dans le domaine de températures allant de 150 à 800°C.

### Zusammenfassung

Eine Untersuchung des Prozesses der Kohlebildung während des thermischoxydativen Abbaus von Phenol-Formaldehydpolykondensaten durch thermogravimetrische und Elementaranalyse des Abbaurückstandes liefert eine Stütze für die früher gemachten Annahmen bezüglich der Kohlebildung. Die untersuchten, bei erhöhter Temperatur ausgehärteten Harze zeigten unter den Versuchsbedingungen identisches Abbauverhalten ungeachtet der Unterschiede im Phenol-Formaldehydverhältnis der flüssigen Harze. Versuchsdaten zeigten, dass der Abbau bei erhöhter Temperatur grundsätzlich mit der chemischen Stabilität der Dihydroxydiphenylmethaneinheit verknüpft ist. Kleine Unterschiede im Abbauverhalten traten bis zu 300°C auf und konnten auf Nachhärtungsprozesse und Verflüchtigung von Lösungsmittel und anderen niedermolekularen Komponenten zurückgeführt werden. Die vorliegende Arbeit zeigt eine brauchbare alternative Möglichkeit zur Untersuchung des Hochtemperaturabbaus auf, welche auf der Rückstandsanalyse beruht und gemeinsam mit nach anderen Methoden erhaltenen Daten eine vollständigere Beschreibung des Harzabbaus im Temperaturbereich von 150 bis 800°C gestattet.

Received August 21, 1964

Revised March 18, 1965