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Thermal Degradation and Curing of Polyphenylene

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Thermal Degradation and Curing of Polyphenylene

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SUMMARY

The effect of chlorine and polynuclear structures on the thermal degradation of polyphenylene has been examined. The thermal dehalogenation reaction has been utilized to cross-link the polymer. Composites stabilized in this manner were evaluated by exposure to an oxyacetylene torch.

INTRODUCTION

Kovacic and co-workers have reported the synthesis of relatively pure p-polyphenylene [1, 2]. Polymers having a chlorine content of 0.8%, a C/H + Cl ratio of 1.50, and showing no evidence of containing ortho, meta, or nonaromatic linkages are readily prepared by this method. By modifying the reaction conditions, products having higher C/H + Cl ratios (assumed to be due to polynuclear ring structures) and chlorine contents can be produced [3-5].

DISCUSSION

The linear, completely aromatic polymer would be expected to thermally degrade at a relatively high temperature, forming a high percentage of char. Ideally, the major degradation mode should be simply dehydrogenation.

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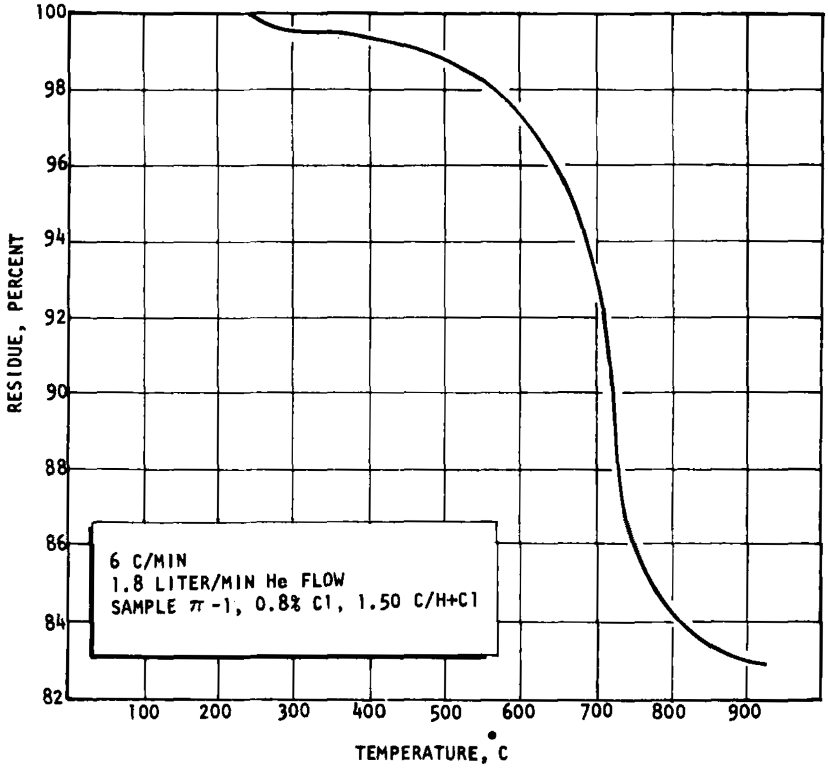

Fig. 1. TGA of p-polyphenylene.

The thermogram presented in Fig. 1 shows that this is essentially the case. Polymer degradation in an inert atmosphere occurs at about 700°C, resulting in a total weight loss of 18% (82% yield of char) at 900°C. However, it is apparent that something more than the 5% hydrogen originally contained in the polymer is lost during degradation.

Pyrolysis of this polymer on a hot nichrome coil in the gas chromatograph showed the presence of five major peaks (Fig. 2). Mass spectrographic analysis of the first peak showed that it was composed of hydrogen and methane in a 20:1 mole ratio. The other peaks, identified by retention time and infrared spectra, were found to be benzene (4.1% of the original polymer weight), biphenyl (2.5%), p-terphenyl (1.4%), and p-quaterphenyl (0.8%). The minor peaks, due to isomeric ter- and quaterphenyls, decrease with decreasing pyrolysis temperature. It would appear that they

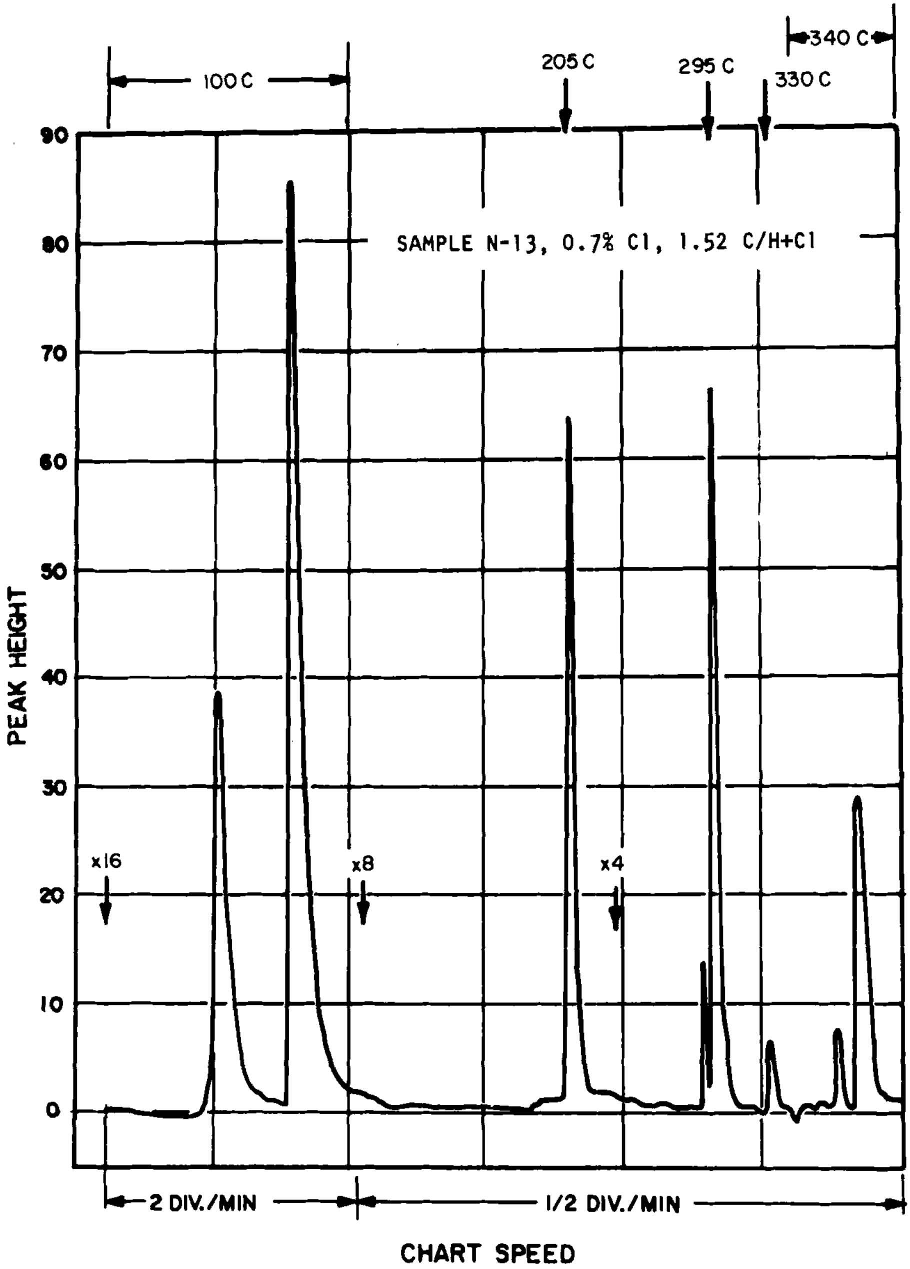

Fig. 2. Gas chromatographic pyrolysis of p-polyphenylene.

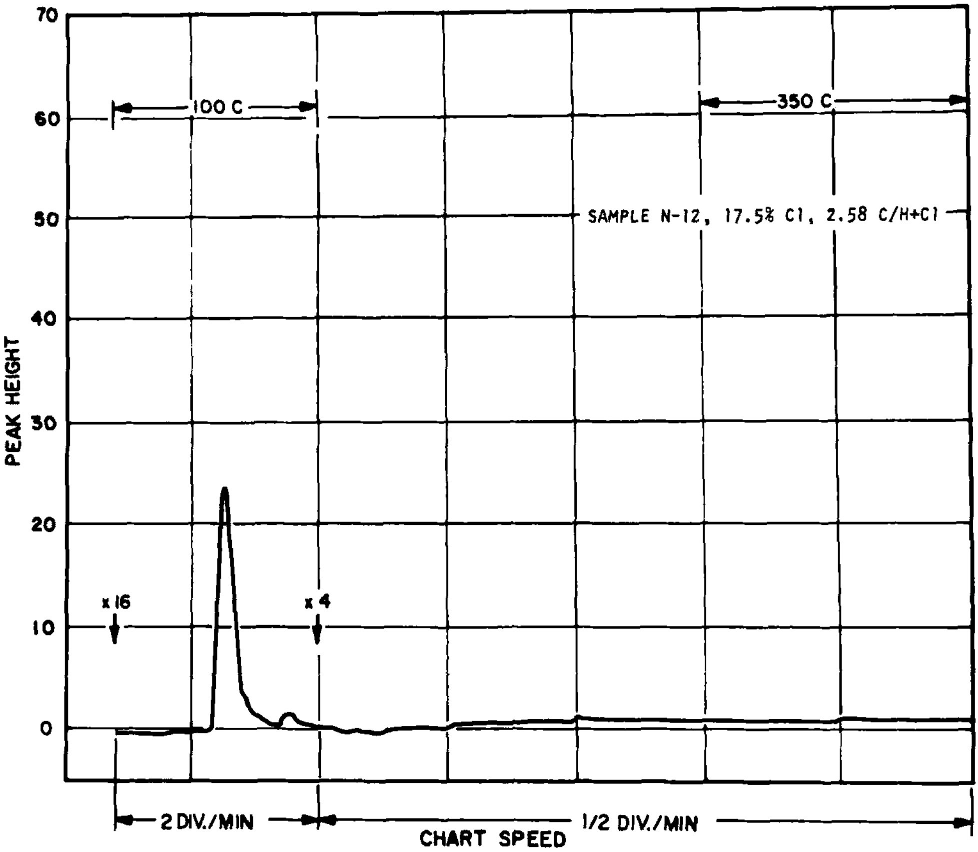

Fig. 3. Gas chromatographic pyrolysis of chlorinated polynuclear polyphenylene.

are formed by molecular rearrangements of the degradation products in the pyrolysate. The hydrogen:methane ratio was also found to be dependent on pyrolysis temperature. It is, therefore, assumed that ring cleavage is not one of the primary degradation steps at the more moderate pyrolysis temperatures.

The introduction of chlorine and polynuclear structures into the polymer results in a marked decrease in the aromatic pyrolysis products (Fig. 3). The single major peak in this chromatogram is apparently composed of very volatile or gaseous materials. The retention time of the minor peak corresponds to that of benzene. Thus, degradation by chain scission appears to be essentially eliminated for this polymer.

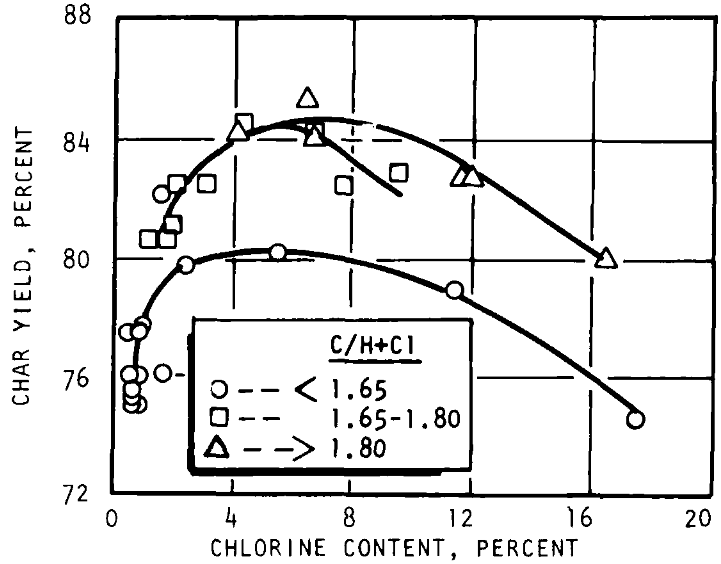

Fig. 4. Char yield as a function of chlorine content.

Char yields of a number of these polyphenylenes were measured by isothermal pyrolysis at 900°C in the TGA. These data, presented in Fig. 4, show that the char yield increases with increasing chlorine content, showing a maximum at 6-8% chlorine. At any given chlorine content, the presence of polynuclear structures (as measured by the C/H + Cl ratio) also leads to increased char yields. The effect of these structural features can be better assessed by examining their influence on the chain scission mode of degradation. This can be done by estimating the quantity of carbonaceous products lost during pyrolysis. This value, calculated by taking the difference between the total weight lost during pyrolysis and the combined initial hydrogen and chlorine content of the polymer, is presented in Fig. 5 and illustrates the effectiveness of chlorine and polynuclear structures in reducing this mode of degradation.

Thermograms of several chlorinated polyphenylenes are presented in Fig. 6. For these materials, degradation occurs in two stages. The end of the first degradation stage roughly corresponds to the initial chlorine content of the polymer. The second degradation stage appears to be the same as that seen in the unchlorinated p-polyphenylene. A silimar effect is noted in the rather complex DTA curves (Fig. 7). The initial broad

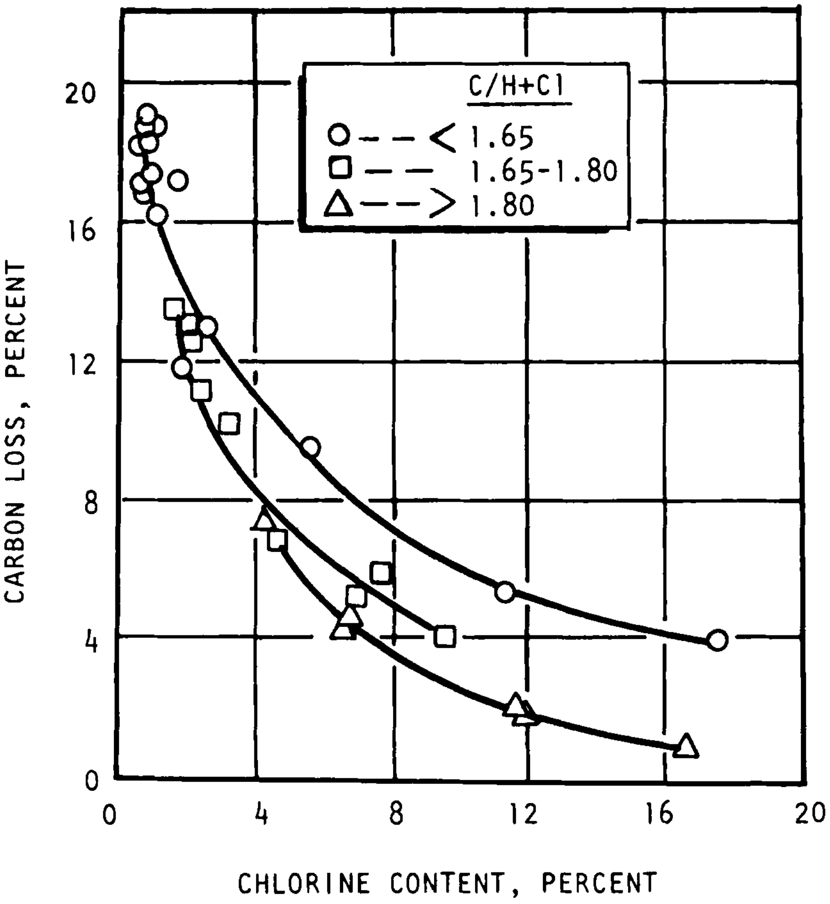

Fig. 5. Carbon loss on pyrolysis as a function of chlorine content.

exothermic peak is increased while the endothermic peak is decreased with increasing chlorine content.

Thus, it would appear that the thermal degradation of p-polyphenylene occurs initially by a random chain scission process. Either concurrent with this reaction but at a slower rate, or at a somewhat later period on the time-temperature scale, the dehydrogenation reaction begins. As this reaction progresses, interchain linkages are formed which stabilize the polymer. Thus, the frequency of successful chain scissions, those resulting in material losses, is reduced. The chain scission mechanism then decreases

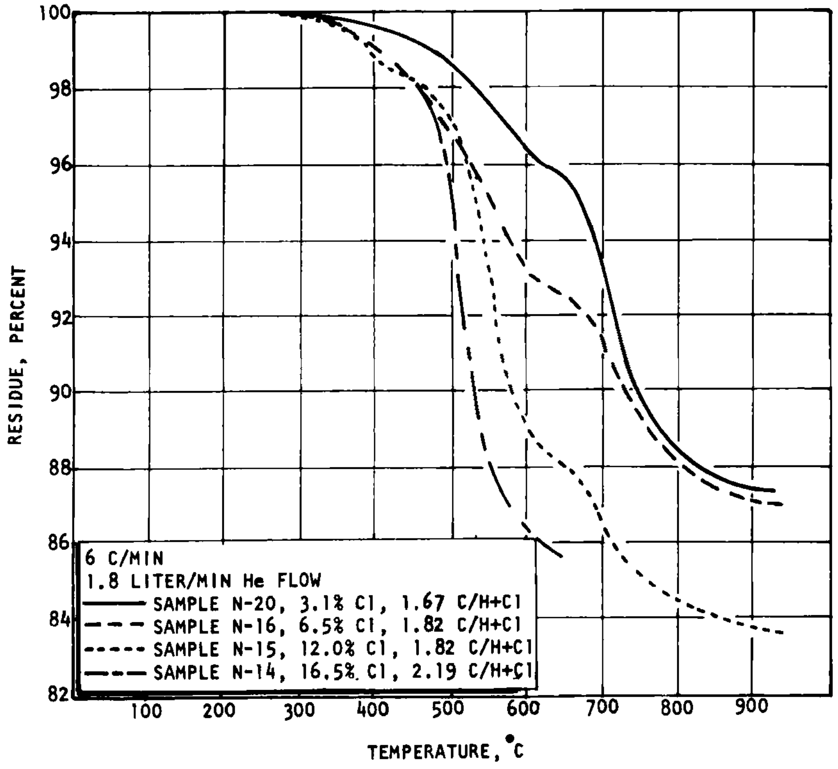

Fig. 6. TGA of chlorinated polyphenylene.

in importance and the char-forming dehydrogenation reaction prevails. The substitution of weaker C—Cl bonds for some of the C—H bonds facilitates the early formation of the interchain linkages, thereby suppressing the material losses through chain scissions.

The effect of polynuclear structures is more difficult to assess. It can be assumed, a priori, that this is due to the presence of several different C—Cl bonds, some of which dissociate to form stabilizing linkages at an earlier period.

If the first degradation stage does, indeed, consist of the elimination of chlorine followed by the formation of interchain linkages, it is, in essence, a curing reaction producing a cross-linked product. Figures 8-10 present the thermograms of several polymers cured for 30 min at 550°C. For comparison, the cumulative weight loss curve, based on the initial

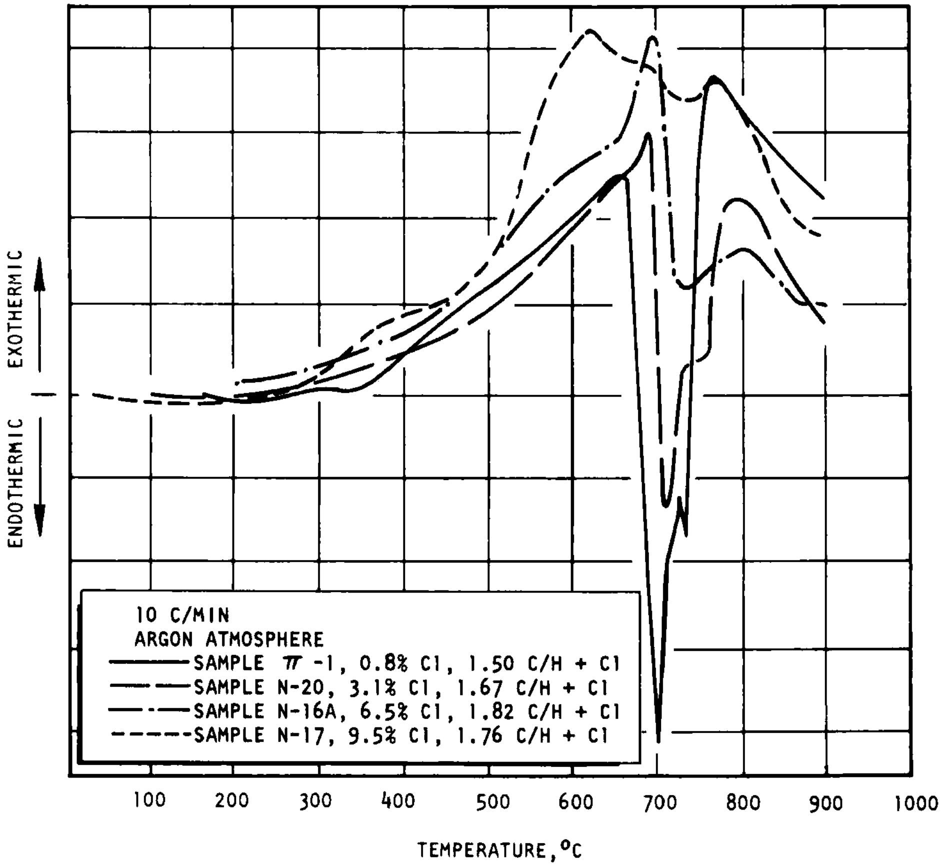

Fig. 7. DTA of polyphenylene effect of Cl content.

weight of uncured polymer, as well as the thermogram of the uncured polymer, are also presented. It can be seen that the weight lost during the curing step approximates the initial chlorine content of the polymer. The thermogram of the cured polymer is the same as that for the second-stage degradation.

Table 1 summarizes the elemental analysis data obtained on a series of samples that were cured at various temperatures. These samples were held at the indicated temperature until an essentially equilibrium weight loss value was obtained. Therefore, it would appear that only a portion of the chlorine is lost at any given temperature. The extent of cross-linking can

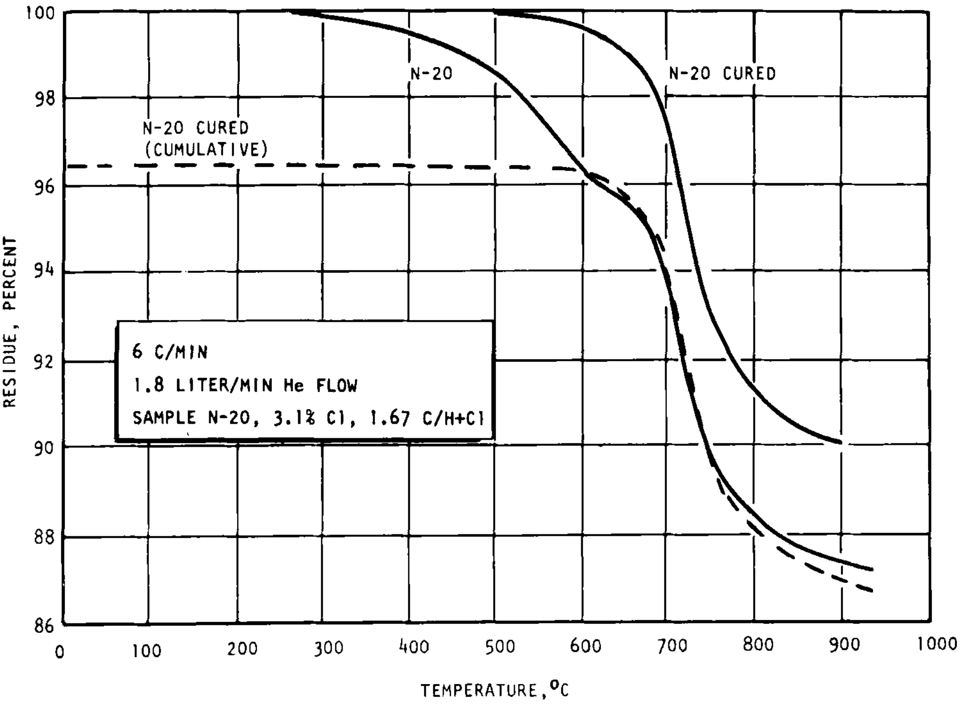

Fig. 8. TGA of polyphenylene N-20 prior to and after 30-min cure at 550°C.

be calculated from the increase in the C/H + Cl values; however, estimation of a true cross-link density would require specific knowledge of the nature of the cross-links.

Larger test samples (1-in. diam) were found to crack severely during the curing step. It was found that the incorporation of a small quantity (4-12 pph) of either chopped quartz or carbon fiber eliminated this problem. It is believed that the poor adhesion between the polymer and the fibrous filler provides some degree of porosity to the molded specimen, allowing the escape of the gaseous products generated during the curing process. Composite samples of this type were used in subsequent tests of the cured polymer.

The ablative performance of the polyphenylene composites was screened by exposing test samples to an oxyacetylene torch. The test rig consisted of a flowmeter-controlled, water-cooled torch. The oxidizing flame

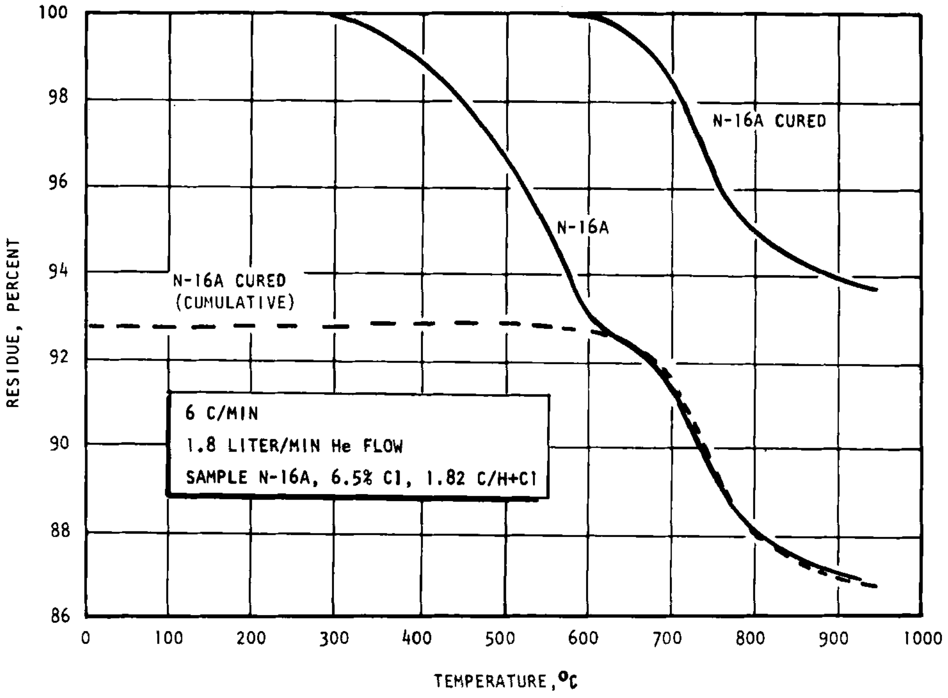

Fig. 9. TGA of polyphenylene N-16A prior to and after 30-min cure at 550°C.

impinged on a 1-in.diam molded sample cemented into a transite sheet and located 1.75 in. from the torch. The heat flux, measured by using a guarded copper block calorimeter, was found to be approximately 350 Btu/ft^2/sec. The surface temperature of the test specimen was monitored with an optical pyrometer and found to be about 2000°C. Less than a 50°C temperature difference was noted across the sample face. After a 20-sec exposure, the torch was pivoted to the up position and the next specimen rotated into position.

The unchlorinated p-polyphenylene produced a fragile, fluffy char growth above the polymer surface, illustrated in Fig. 11. The chlorinated but uncured polymer showed improved performance, but spallation and cracking was quite evident (Fig. 12). The cured chlorinated polymer appeared excellent, giving a hard, tightly adhering char layer (Fig. 13). A char depth of about 0.2 in. and a surface regression of less than 0.01 in. were observed with samples of this type. The use of either silica or carbon fibers produced comparable results.

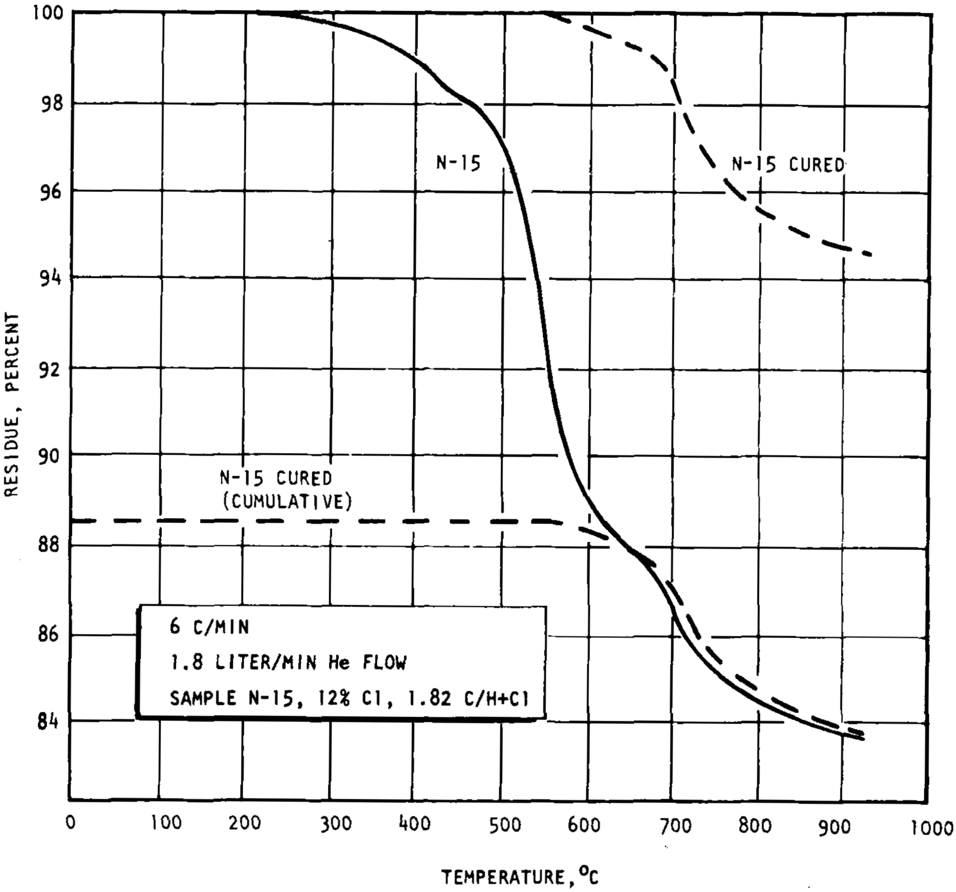

Fig. 10. TGA of polyphenylene N-15 prior to and after 30-min cure at 550°C.

Table 1. Analysis of Cured Polyphenylene, Sample N-36

Temperature °C	Weight loss, %	Cl, %	C/H + Cl	Cross-link sites per ring
Ambient	–	5.55	1.57	–
450	3.9	2.64	1.61	0.11
500	5.3	1.21	1.65	0.18
550	6.6	0.78	–	–
600	7.1	0.16	1.73	0.36

Fig. 11. Oxyacetylene torch test, sample N-1 (0.8% Cl, 1.50 C/H + Cl) unfilled, uncured.

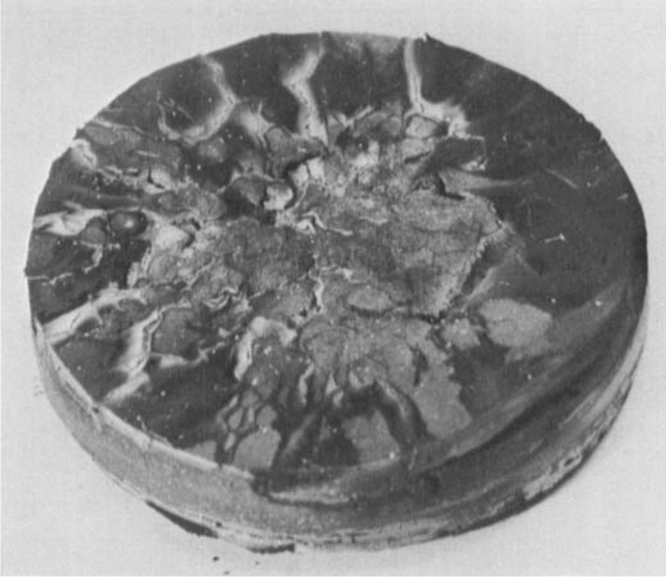

Fig. 12. Oxyacetylene torch test, sample N-34 (4.2% Cl, 1.83 C/H + Cl) + 4 pph chopped quartz fiber, uncured.

Fig. 13. Oxyacetylene torch test, sample N-44 (4.6% Cl, 187 C/H + Cl) + 4 pph chopped quartz fiber, cured.

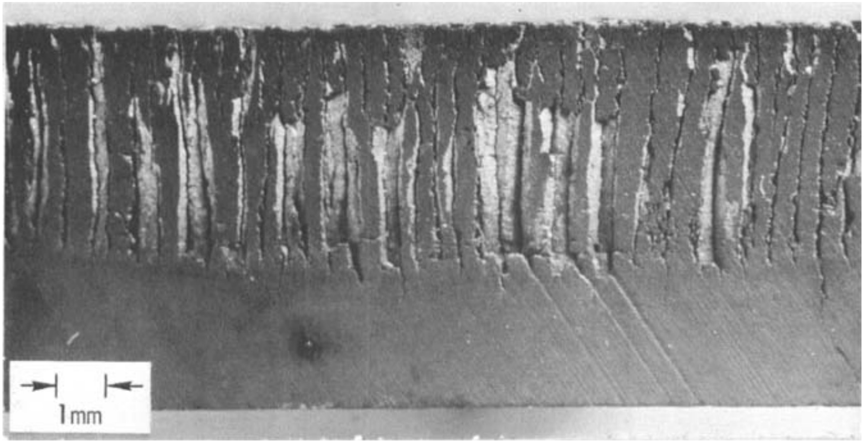

Fig. 14. Cross section of charred sample.

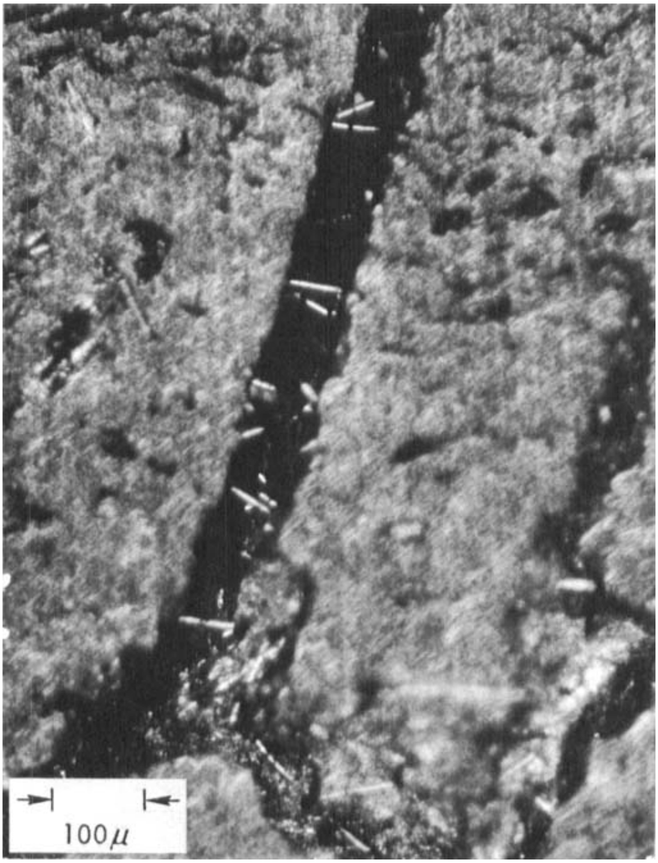

Fig. 15. Cross section of char.

Microscopic examination of the sectioned test specimens revealed a honeycomb pattern of cracks running perpendicular to the char surface (Fig. 14). Under higher magnification (Fig. 15) it can be seen that the fibers of the filler span these cracks and reinforce the char. Thus, under ablative conditions, a hard and very stable char structure is formed. The presence of the myriad of micro-cracks in the char serves as an escape route and, perhaps, a catalytic cracking bed, for the gaseous degradation products forming at the polymer-char interface.

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