

# Influence of the Molecular Weight of PPO Resins and Char-Forming Behavior of Polymeric Additives on the Flame Retardancy of EPDM Formulations

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Received 20 November 1996; accepted 31 May 1997

**ABSTRACT:** The influence of the molecular weight of poly(2,6-dimethylphenylene oxide) (PPO) on the flame retardancy of ethylene-propylene-diene-modified elastomer (EPDM) formulations containing melamine, kaolin, and PPO formulations was studied. The influence of the molecular structures of various char-forming polymers on their flame-retardant effect was also investigated. PPO resins having number-average molecular weight ( $M_n$ ) from 3200 to 24,800 and weight-average molecular weight ( $M_w$ ) 9000 to 58,400 affected the oxygen index (OI) values and UL 94 ratings of EPDM formulations, and the preferable molecular weight was found to be about  $M_n$  13,300 and  $M_w$  29,200. Among the char-forming polymeric additives studied, PPO was most effective in providing flame retardancy. The concept of char-forming rate is proposed to explain the variation in the observed flame retardancy. Higher char-forming rate (in contrast to char yield) correlated well with higher OI and better UL 94 ratings in these systems. The melting-before-charring character of char-forming polymers was another important factor that appeared to control char morphology and thus flame retardancy. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1405–1414, 1998

**Key words:** flame retardancy; oxygen index; UL 94 test; char-forming polymer; char-forming rate; EPDM polymer

## INTRODUCTION

The admixture of char-forming polymers with less-char-forming polymers has become an important approach for creating useful flame-retardant systems. These char-forming polymers are in most cases polymers containing aromatic ring structures, such as poly(2,6-dimethylphenylene oxide) (PPO), polyphenylene sulfide (PPS), polyimide (PI), and poly(ether ketone ketone) (PEKK). They typically have high heat resistance and thermal stability due to their aromatic backbones.<sup>1,2</sup> Upon burning, these polymers tend to generate a

substantial amount of char, which may serve as a heat- and mass-transfer barrier to retard fire propagation. Therefore, these polymers have inherently a certain degree of flame retardancy.<sup>3–5</sup>

The flame retarding of less charrable or non-charrable polymer by incorporation of a char-forming polymer has been reported in a number of patents and is represented by some commercial examples. One of these examples is a blend of high-impact polystyrene (HIPS) and poly(2,6-dimethylphenylene oxide) (PPO).<sup>6–10</sup> High-impact polystyrene is flammable and leaves nearly no char upon burning, while PPO is a good char-forming polymer. This blend, which normally contains more than 40 wt % PPO, has been commercialized by General Electric Co. under the trademark of NORYL. To attain a stringent flame retardancy such as a UL 94 V-0 rating, an organo-

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Contract grant sponsor: Electric Power Research Institute.

*Journal of Applied Polymer Science*, Vol. 67, 1405–1414 (1998)

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CCC 0021-8995/98/081405-10

phosphorus flame retardant (e.g., a triaryl phosphate or a tetraaryl arylene diphosphate) is usually used in a NORYL formulation. Our Laboratory developed a flame retardant system for a poorly charrable polyamide by using PPO as a char-forming polymer.<sup>11</sup> In this novel composition, polyamide formulations containing 5–10% PPO, 4–8% iron oxide, and 5% zinc borate exhibited satisfactory flame retardancy with OI above 30 and UL 94 V-0 ratings. No halogen and phosphorus flame retardants were used. Examples of using a phenolic resin as a char-forming polymer in acrylonitrile–butadiene–styrene copolymer (ABS) have been reported by German and Japanese groups, respectively.<sup>12,13</sup> These formulations also require an organophosphorus flame retardant to achieve the desired level of flame retardancy.

It seems feasible to employ barrier-forming additives together with vapor phase flame retardants as flame-retardant systems. Using this design principle, we developed a ternary system of PPO–melamine–kaolin to flame retard EPDM polymer and other polyolefins.<sup>14</sup> In this system, PPO undergoes charring to help build a partly-char partly-mineral barrier in the condensed phase upon burning, while melamine acts mainly as a vapor phase flame retardant through several possible endothermic effects of sublimation, vapor dissociation, and ammonia release, as well as by adding a nitrogenous residue to the char. One of the useful characteristics found in this system is a demonstrable synergistic flame retardancy involving all three components.

In the present research, we investigated the effects of molecular weight and particle size of PPO resins on the flame retardancy of EPDM formulations. We also tested a number of char-forming polymers to try to gain insight into some aspects of charring behavior, other than char yield, which correlate to the flame retardancy contribution. The concept of char-forming rate was developed to correlate the flame retardancy characterized by the oxygen index and UL 94 vertical burning test.

## EXPERIMENTAL

### Materials

Ethylene–propylene–1,4–hexadiene terpolymer (EPDM, NORDEL 2722, DuPont), polyphenylene sulfide (regular grade RYTON, Phillips 66), poly-

imide (a polymer prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,4-phenylenediamine, Aldrich, Milwaukee, WI), poly(ether ketone ketone) (Eastman Chemical), glycidyl ether of cresol formaldehyde novolac (epoxy novolac resin, EPON DPS 164, Shell), melamine (superfine grade, Melamine Chemicals), silane-treated calcined kaolin (TRANSLINK 37, Engelhard), dicumyl peroxide (DCP, PERKADOX BC, Akzo Nobel), benzoyl peroxide (Aldrich), and 4,4'-isopropylidenediphenol (Aldrich) were used as received. Three poly(2,6-dimethyl-1,4-phenylene oxide) resins (PPO resins, General Electric's BLENDX products) were also used. They were HPP 821 (IV = 0.28, in CHCl<sub>3</sub>, 25°C), HPP 820, (IV = 0.40), and HPP 823 (IV = 0.49).

PPO resins of lower molecular weight were prepared in this laboratory by modification of HPP 821 using a published method,<sup>15</sup> and the results are listed in Table I.

### Polymer Sample Preparation

EPDM polymer and other ingredients were mixed in a Brabender PLASTICORDER (Brabender Co.) at 115°C for 5–10 min, followed by molding at 180°C and 10,000 psi in a Carver press, and cured at 180°C for 20 min. The resulting sample plate was cut into test specimens of specific sizes required for ASTM D-2863 and UL 94 tests.

### Testing

Oxygen index (OI) was determined by ASTM D-2863 using a Stanton Redcroft FTA Flammability Unit (Tarlin Scientific). The UL 94 vertical burning test was done by the standard procedure developed by Underwriter Laboratories. The thickness of the sample for the UL 94 test was 1/8 in. (3.2 mm).

The TGA measurements were done using a DuPont 951 thermogravimetric analyzer at a heating rate of 20°C/min and in 1% oxygen in nitrogen with a flow rate of 50 mL/min. The DSC experiments were done on a DuPont DSC 910 differential scanning calorimeter at a heating rate of 20°C/min and under 1% oxygen in nitrogen with a flow rate of 30 mL/min. The FTIR spectra were run on a Perkin–Elmer 1600 FTIR at a resolution of 2 cm<sup>-1</sup>. The molecular weight of PPO resins was measured on a Waters GPC I model 590 with a STYRAGEL column and a differential refractometer. The eluent was THF at a flow rate of 1.0 mL/min. Polystyrene samples with known molec-

**Table I Preparation of Low MW PPO Resins**

Exp. No.	PPO	4,4'-Isopropylidenediphenol (g)	Benzoyl Peroxide (g)	Product Yield (g)
1	PPOM1	0.6	0.6	58.1
2	PPOM2	1.8	1.8	59.0

In each preparation, 60 g of HPP 821 was used.

ular weight were used as standards. Optical microscopy was performed with a Nikon OPTIPHOT microscope and a high intensity fiber optic illuminator (FIBER-LITE 3100, Dolan-Jenner Industries, Inc.).

The char-forming rate and char yield of EPDM formulations were determined by our combustion analysis method, the procedure and rationale of which were reported elsewhere.<sup>16</sup> The sample size for these measurements was  $30 \times 6.5 \times 3$  mm (about 700–750 mg weight).

## RESULTS AND DISCUSSION

### Preparation of Low Molecular Weight PPO and Properties of PPO Resins

Poly(2,6-dimethyl-1,4-phenylene oxide) resins of low molecular weight ( $M_n \leq 8500$ ) were prepared by the reaction of a commercial PPO resin ( $M_n$  13,300) with 4,4'-isopropylidenediphenol and benzoyl peroxide in toluene at 95°C for 1 h, followed by precipitation in methanol. Two modified PPO resins (PPOM1 and PPOM2) were obtained through this method, essentially the method of Chao and Whelan.<sup>15</sup>

Table II lists some properties of the commercial and modified PPO resins. These data indicated

that higher molecular weight PPO gave higher thermal transition temperatures ( $T_g$  and  $T_m$ ) on DSC and higher residue yield of TGA residues. In TGA under 1% oxygen in nitrogen, PPO resins decomposed in a first step to give temporary residues at about 510°C. All five temporary residues then further underwent a smaller loss of weight to produce final residues, and the TGA curves were very similar. The molecular weight of PPO seemed to have little influence on the decomposition temperature.

### Effect of the Molecular Weight of PPO on the Flame Retardancy of EPDM Formulations

The cured EPDM formulations containing PPO, melamine, and kaolin were employed to investigate the influence of PPO molecular weight on the flame retardancy. The technique was as described above.

Results in Table III show that the flame retardancy of EPDM form was affected by the molecular weight of PPO resins, and the best flame retardancy was obtained with the formulation containing HPP 821, which has  $M_n$  13,300 and  $M_w$  29,200. The OI values of the EPDM formulations were influenced by the choice of the PPO resin. HPP 821 gave the highest OI, followed by PPOM2

**Table II Properties of PPO Resins**

PPO Resin	$M_n$	$M_w$	$M_w/M_n$	$T_g$ (°C)	$T_m$ (°C)	$\Delta H^a$ (J/g)	Temp. at 1 wt % Decomposition (°C)	Temp. at Max DTG Peak (°C)	TGA Residue at 510°C (%)	TGA Residue at 700°C (%)
HPP 823 <sup>b</sup>	24800	58400	2.4	210 <sup>c</sup>	247	16.7	403	467	60.4	37.4
HPP 820 <sup>b</sup>	22700	48000	2.1	210 <sup>c</sup>	246	18.3	416	476	57.2	35.7
HPP 821 <sup>b</sup>	13300	29200	2.2	205 <sup>c</sup>	242	11.1	438	469	46.8	31.1
PPOM1	8500	17400	2.0	196	229	7.1	441	467	44.8	27.2
PPOM2	3200	9000	2.8	178	213	5.9	426	468	46.4	28.2

<sup>a</sup>  $\Delta H$ , endothermic enthalpy of melting.

<sup>b</sup> General Electric BLENDEX products.

<sup>c</sup> Data from General Electric technical data sheet (August 30, 1993).

**Table III Flame Retardancy of EPDM Formulations Containing Different Molecular Weight PPO**

Formulation	PPO in the Formulation	OI	UL 94 Rating at 1/8 in.
1	HPP 823	29.8	Burning
2	HPP 820	30.4	V-0
3	HPP 821	33.7	V-0
4	PPOM1	31.7	V-0
5	PPOM2	31.9	V-0

All formulations contain 100 parts per hundred resin (phr) of EPDM, 100 phr of melamine, 60 phr of kaolin, 30 phr of PPO resin, and 3 phr of dicumyl peroxide.

( $M_n$  3200), PPOM1 ( $M_n$  8500), and HPP 820 ( $M_n$  22,700). HPP 823, which had the highest molecular weight ( $M_n$  24,800), resulted in the poorest flame retardancy. All formulations except that containing HPP 823 reached a UL 94 V-0 rating at a sample thickness of 1/8 in. (3.2 mm).

Although formulations 1 and 2 had almost similar OI values, their UL 94 ratings were significantly different. Formulation 1 was rated burning (indicating that the sample burned during the test), while formulation 2 attained a V-0 rating (self-extinguishing and the highest flame-retardant rating in the test). Therefore, their overall flame retardancy based on both OI and UL 94 rating was different and affected by the molecular weight of PPO resins used in the formulations.

We previously indicated that the use of a PPO resin to form a ternary system of PPO–melamine–kaolin in EPDM appeared to show a cooperative (“synergistic”) action requiring the presence of each of the three additives to afford satisfactory flame retardancy.<sup>14</sup> We also suggested, based on microscopic study of the burning residues from EPDM formulations, that the PPO resin might act as a char former, a fluxing agent, and a binder for the combustion residues. These functions of the PPO helped generate the coherent barrierlike residue that is responsible for the flame retardancy of EPDM formulations.

Table III indicates the influence of the molecular weight of PPO resins on the flame retardancy, and Table II evidences the effect of molecular weight of PPO resins on the yields of TGA residues. We speculated that the flame retardancy of EPDM formulations containing PPO of different molecular weights might be affected by the burning and thermal behavior of the formulations. We applied our methodology of char-forming rate (as

discussed further below) to evaluate the burning behavior, because we found previously that the char-forming rate was useful in explaining the flame retardancy of polyolefins containing melamine phosphates and aminomethylphosphonate ester.<sup>16</sup>

The TGA method was also used to evaluate the thermal behavior of the EPDM formulations.

#### Char-Forming Rate and Char Yield by Combustion Analysis of Cured EPDM Formulation Containing PPO Resins of Differing Molecular Weights

The char-forming rate and char yield were determined through our combustion analysis method, which was performed with an FTA flammability unit used to measure oxygen index (OI). In this combustion analysis method, the specimen supported on a needle was vertically positioned, ignited on the top, and burned downward at the oxygen concentration (in volume percentage) of 3.0% above OI of the specimen. The weight of specimen, of char, and burning time were recorded. The whole procedure resembles that of measuring OI except that the combustion analysis method requires the specimen to be burned completely. The rationale and methodology of the combustion analysis have been discussed in our previous publication.<sup>16</sup>

Both char-forming rate and char yield were related to the term “char.” We define the char in this study as the burning residue containing PPO char, melamine condensation polymer, and kaolin clay. In this study, we use the term “char” to not only signify the residue of carbonaceous structures alone but to also include any residual nitrogen–carbon products and the mineral.<sup>16,17</sup>

Table IV lists the data of char-forming rate and char yield for EPDM formulations. Formulation 1, containing the highest molecular weight PPO (HPP 823) in the series, had the lowest char-forming rate but the highest char yield, and this formulation showed the poorest flame retardancy (see Table III). Formulation 3, which contains HPP 821, the PPO resin of  $M_n$  133,00 and  $M_w$  29,200, gave the highest char-forming rate among these five formulations. It also had the best flame retardancy, as shown in Table III. Formulation 5 had the second highest char-forming rate, and its flame retardancy was also ranked second (Table III). Both formulation 2 and formulation 4 seemed to have the same char-forming rate, although formulation 4 had slightly higher OI than formulation 2. Notably, the char yield values in

**Table IV Char-Forming Rate and Char Yield of EPDM Formulations Containing PPO of Differing Molecular Weights**

Formulation	PPO Used	Char-Forming Rate (mg/min)	Char Yield (%)
1	HPP 823	90 <sup>a</sup>	25.3 <sup>b</sup>
2	HPP 820	94	24.6
3	HPP 821	103	22.8
4	PPOM1	94	21.8
5	PPOM2	96	22.9

For information on the formulations, see Table II.

<sup>a</sup> Average char-forming rate from four runs with a standard deviation ( $S_{n-1}$ ) of 1.9 mg/min.

<sup>b</sup> Average char yield from four runs with a standard deviation ( $S_{n-1}$ ) of 0.4%.

the series were not useful in explaining the ranking of the flame retardancy, but the char-forming rate was useful.

A substantially linear relation between OI and char-forming rate [CFR] of EPDM formulations in Table IV was obtained as follows:

$$OI = 2.84 + 0.30[CFR]$$

and the correlation coefficient for the equation was 0.95. Moreover, char-forming rate and char yield data were reproducible. In the case of formulation 1, the standard deviations ( $S_{n-1}$ ) of four runs were 1.9 mg/min for char-forming rate and 0.4% for char yield. We have shown that the combustion analysis results were not affected by the oxygen concentration of 0.5 to 4.0% above OI and by the sample weight within a 20% variation.<sup>16</sup>

It should be pointed out that the above equation is valid only for these EPDM formulations in Table IV, which contain the same loadings of PPO, melamine, and kaolin, because we found that char-forming rate was related to the total loading levels of additives in a formulation.<sup>16</sup>

All chars (or burning residues) from the combustion analysis were dark, cementlike, and coherent. Two typical chars obtained from burning formulations 1 and 3 were analyzed to determine the content of carbon, hydrogen, and nitrogen. An elemental char composition was calculated from these elemental analysis data (Table V).

An FTIR spectrum of char from formulation 3 showed the evidence of PPO char and melon (the thermoset condensation product of melamine) by comparison with our previous work<sup>14</sup> and with IR spectra of PPO TGA residues reported by Factor.<sup>18</sup> Such evidence further indicated that the char obtained from burning of an EPDM formulation contained carbon and nitrogen residues.

The above combustion analysis indicates that the flame retardancy of cured EPDM–PPO–melamine–kaolin formulations was generally correlated with their char-forming rate, but not with char yield. The variation of the flame retardancy from different molecular weight PPO resins may be explained by the char-forming rate. Two typical examples are formulations 1 and 3, which had different char-forming rates while their OI and UL 94 ratings were also significantly different. The high char-forming rate might suggest that the char formation is sufficiently fast to cover the burning surface of the polymer. Thus, the fuel generation from the burning polymer is reduced, and the heat and fire propagation is effectively impeded. The high char yield does not necessarily correlate to sufficiently fast char formation, and hence, may not result in high flame retardancy.

Formulation 1 generated more char than formulation 3 upon burning (Table IV), but the former had poorer flame retardancy than the latter (Table III). Both formulations gave fairly continuous and coherent chars as observed by optical microscopy. Therefore, the morphology of char was not the evident reason for the difference in flame retardancy. The elemental analysis indicated that the char from formulation 3 contained slightly more kaolin clay than the char from formulation 1. The presence of the kaolin clay is essential to constitute coherent, cementlike char. However we showed previously that the kaolin alone did not provide satisfactory flame retardancy for EPDM, and high loadings of kaolin in the PPO–melamine–kaolin system gave little or no benefit to the flame retardancy.<sup>14</sup> Thus, the kaolin content in the char was not useful in explaining the flame retardancy. We conclude at this point that char yield, char morphology, and char composition may not be the variables that

**Table V Elemental Contents and Calculated Compositions of Chars**

Formulation	Experimental Data			Calculated Composition <sup>a</sup> (wt %)			
	C%	H%	N%	Kaolin	Melon <sup>b</sup>	PPO Char	C/H in PPO Char
1	13.43	0.49	6.45	81.0	10.3	8.7	2.4
3	10.88	0.40	3.92	89.9	6.1	4.0	2.3

<sup>a</sup>The following provides an example of calculating the char composition: In formulation 1, the char yield is 25.3%. 6.45% N content in the char is equivalent to 10.3% melon, because it has a molecular formula of C<sub>6</sub>H<sub>3</sub>N<sub>9</sub>, which contains 62.67% N. The kaolin clay has 20.5% in the original formulation. It should consist of 81% in the char assuming that kaolin remains constant during the combustion. Therefore, the remaining 8.7% is PPO char assuming that EPDM burned off completely during the combustion.

<sup>b</sup>Melon is the crosslinked melamine condensation polymer. The term as used here is not meant to imply a specific structure. The structure of melon is somewhat unresolved.

correlate well to the different flame retardancy in formulations 1 and 3. Only the char-forming rate appears to correlate well to the variation in flame retardancy. The greater importance of char-forming rate is supported by the experimental data of this and one other system<sup>16</sup> that we have studied; at this point, we do not know whether this relationship will be found in other systems. This measurable feature of burning polymer systems probably deserves attention in other systems. In contrast to the extensive and well-accepted work especially of Van Krevelen on the relation of char yield to flammability,<sup>19</sup> very little has been reported on char formation rate except in cellulosic systems.

#### Thermogravimetric Analysis of EPDM Formulations

The purpose of thermogravimetric analysis (TGA) was to compare the results with data from the combustion analysis. The TGA technique has been used to study the flame retardancy of various polymers, and some correlations between TGA residue and OI have been found.<sup>19,20</sup> In this research, TGA experiments were carried out under 1% O<sub>2</sub> in N<sub>2</sub>.

In selecting this atmosphere, we were influenced by Steutz et al. who published a remarkable correlation of bottom-burn OI to the reciprocal of the rate of oxidative breakdown at 1% O<sub>2</sub> under this atmosphere.<sup>21</sup> This atmosphere represents an oxygen-depleted atmosphere that is plausible in the critical zone controlling flame propagation.

Some informative results were obtained from TGA (Table VI). First, the thermodecomposition of the EPDM formulations seemed to have little to do with the molecular weight of PPO resins. Second, two major weight loss stages were observed. The first stage of weight loss, which started at 250°C and ended at about 420°C, is

likely to be due to the evaporation of much of the melamine. The subsequent stage of weight loss is likely to be mainly the degradation of EPDM and PPO. Third, after these two major stages of weight loss, a temporary residue was formed at about 510°C. All temporary residues underwent a similar further degradation to the final residues at 700°C, because the TGA curves for this process looked almost identical for the five formulations. The molecular weight of PPO resins did not affect the process, and did not affect residues at 510°C and at 700°C. Fourth, neither the residues at 510°C nor at 700°C were correlated with the flame retardancy of the corresponding formulation, because formulation 3, which had the best flame retardancy, failed to produce the highest residue yield. Furthermore, formulations 1 and 4 had almost the same TGA residue yield, but their flame retardancies were significantly different.

The TGA results showed that the molecular weight of PPO had little effect on the thermal behavior of EPDM formulations. Because the TGA residues obtained at 510 and 700°C could not be used to correlate the flame retardancy of

**Table VI TGA Results of EPDM-PPO-Melamine-Kaolin Formulations**

Formulation <sup>a</sup>	Temp. at	Residue at 510°C (%)	Residue at 700°C (%)
	1 wt % Decomposition (°C)		
1	250	30.0	21.8
2	257	32.0	23.3
3	253	28.2	22.1
4	253	30.0	21.2
5	254	30.5	22.1

<sup>a</sup> For information on the formulations, see Table III.

**Table VII Effect of the PPO Particle Size on Flame Retardancy**

Formulation <sup>a</sup>	PPO Particle Size Used in the Formulation (Diameter in $\mu\text{m}$ )	OI	UL 94 Rating at 1/8 in.
6	$d \leq 45$	35.5	V-0
7	$45 < d \leq 75$	34.5	V-0
8	$75 < d \leq 125$	34.7	V-0
9	$125 < d \leq 180$	35.0	V-0
10	$180 < d \leq 250$	34.2	V-0
11	$d > 250$	33.1	V-0
12	regular	33.7	V-0

<sup>a</sup> All formulations contain 100 phr of EPDM, 100 phr of melamine, 60 phr of kaolin, 2.5 phr of dicumyl peroxide, and 60 phr of HPP 820 of different particle sizes as indicated in the table.

these formulations, we must revert to the char-forming rate as the determinable parameter best correlated to the flame retardancy, at least in this particular study.

#### Influence of Particle Size of the PPO Resin on the Flame Retardancy

One PPO resin (HPP 820) was chosen to study the particle size effect on the flame retardancy. The particles of different sizes were separated through several molecular sieves with sizes ranging from 45 to 250  $\mu\text{m}$  (325 mesh to 60 mesh). For comparison, the regular unsieved HPP 820 obtained from General Electric was also used. Both OI and UL 94 tests were conducted to characterize the flame retardancy. Results were included in Table VII.

From data in Table VII we observed that the particle size of PPO resins had little effect on flame retardancy, although formulation 11, which contains the coarsest PPO resin, gave the lowest OI value. The particle size of PPO resins affected the surface appearance of the formulations, and these formulations having finer PPO resins showed much smoother surface, a matter of some significance in wire and cable manufacture.

The PPO particle size did not affect the morphology of the burning residue, because both formulations 6 and 11 generated similar-appearing coherent chars upon combustion, as observed under the optical microscope. This observation is consistent with the belief that the PPO melted and flowed somewhat before charring.

#### Effect of Different Char-Forming Polymers on the Flame Retardancy of EPDM Formulations

The synergistic combination of PPO–melamine–kaolin in providing necessary flame retardancy for EPDM polymer led us to evaluate other char-forming polymers, including polyphenylene sulfide, a polyimide, poly(ether ketone ketone), and an uncured epoxy resin derived from a cresol formaldehyde novolac (epoxy novolac resin). The same methodologies in studying EPDM–PPO–melamine–kaolin formulations were used to prepare and characterize EPDM samples containing different char-forming polymers. All samples showed good dispersion uniformity by microscopic examination.

Table VIII summarizes the flame-retardant performance of formulations containing these char-forming polymers along with melamine and kaolin. Formulation 13, which contains a PPO resin (HPP 821), showed superior flame retardancy over the four other formulations. It had the highest OI, followed by the PPS formulation 14, the aromatic polyimide formulation 15, the PEKK formulation 16, and the epoxy formulation 17. Only the PPO formulation 13 gave a UL 94 V-0. All other formulations were not self-extinguishing in the UL 94 vertical burning test. By judging the OI and UL 94 ratings, we concluded that the order of the effectiveness in providing the flame retardancy by char-forming polymers was poly(2,6-dimethylphenylene oxide) (PPO)  $\gg$  polyphenylene sulfide  $\approx$  polyimide  $\geq$  poly(ether ketone ketone)  $>$  epoxy novolac resin.

The investigation on char morphology with an optical microscope showed that the PPO formulation 13, the PPS formulation 14, and the epoxy formulation 17 produced coherent and continuous chars upon burning, while the polyimide formulations 15 and the PEKK formulation 16 did not.

We can interpret these observations from our EPDM-char former-melamine–kaolin formulations by postulating that melting and substantial flowing before charring is essential for a char-forming polymer to generate coherent char. The char thus formed plays an important role in providing flame retardancy. In our control experiment to burn char-forming polymers in air with a Bunsen burner, we observed that PPO, polyphenylene sulfide, poly(ether ketone ketone), and epoxy novolac resin melted before charring, but polyimide did not melt, which might account for the coherent and noncoherent chars that resulted from these polymers. Melting produced a fluxing

**Table VIII Flame Retardancy of EPDM Formulations Containing Different Char-Forming Polymers**

Formulation <sup>a</sup>	Char-Forming Polymer used in the Formulation (40 phr)	OI	UL 94 Rating at 1/8 in.
13	Poly(2,6-dimethylphenylene oxide) <sup>b</sup>	33.4	V-0
14	Polyphenylene sulfide	25.7	Burning
15	Polyimide	25.3	Burning
16	Poly(ether ketone ketone)	24.6	Burning
17	Epoxy novolac resin	23.5	Burning

<sup>a</sup> All formulations contain 100 phr of EPDM, 80 phr of melamine, 60 phr of kaolin, and 3 phr of dicumyl peroxide in addition to the char-forming polymers indicated in the table.

<sup>b</sup> The PPO resin used is HPP 821.

effect for binding the combustion residue. Although poly(ether ketone ketone) appeared to melt somewhat before charring, it did not exhibit much flow, which may be the reason that it was relatively ineffective in barrier formation with the kaolinite. Another simple experiment was conducted to test the melting-before-charring hypothesis. A PPO resin (HPP 820) was heated in air at 200°C for 5 h to give a yellowish product (HPP 820-5). This (presumably) oxidatively cross-linked product did not melt when burning in air. It showed a much smaller endothermic melt peak (melting point 247°C, enthalpy 7.3 J/g) on DSC than HPP 820 (melting point 246°C, enthalpy 18.3 J/g). The EPDM formulation containing HPP 820-5, melamine, and kaolin gave an OI of 25.7 and burning rating in UL 94 vertical burning test, a much poorer flame retardancy than formulation 2 (in Table III). This formulation failed to produce coherent char upon burning. Our interpretation is that HPP 820-5 did not have enough fluxing ability to ensure the formation of coherent char.

To further explain the difference in flame retardancy in Table VIII, we measured char-forming rate and char yield for these formulations (Table IX). The PPO formulation 13 had the highest

char-forming rate, but not the highest char yield. The order of char-forming rates for the other formulations was PPS formulation 14 = polyimide formulation 15 > PEKK formulation 16 > epoxy novolac formulation 17. This order was almost the same one as observed in the flame retardancy of these formulations (see Table VIII).

Formulations 13-17 generated a certain amount of char upon burning. The polyimide formulation 15 gave the highest char yield, while the epoxy novolac formulation 17 resulted in the lowest char yield. By comparing the flammability data in Table VIII, we found no general correlation between the char yields and flame retardancy of the formulations, in contradiction to what would have been expected from Van Krevelen's predictive rules.<sup>19</sup>

PPO, polyphenylene sulfide, polyimide, and poly(ether ketone ketone) produce high-residue yields under TGA conditions.<sup>3,19</sup> We also observed the formation of chars after burning the above char-forming polymers in air in a control experiment. Our elemental analysis and FTIR spectrum indicated early in this article that the PPO char is one component of the final char residue of the EPDM-PPO-melamine-kaolin formulation. Therefore, we may reasonably suggest that

**Table IX Char-Forming Rate and Char Yield of EPDM Formulations Containing Different Char-Forming Polymers**

Formulation <sup>a</sup>	Char-Forming Polymer used in the Formulation (40 phr)	Char-Forming Rate (mg/min)	Char Yield (%)
13	Poly(2,6-dimethylphenylene oxide) <sup>b</sup>	126	25.2
14	Polyphenylene sulfide	72	28.3
15	Polyimide	72	31.1
16	Poly(ether ketone ketone)	53	27.3
17	Epoxy novolac resin	49	23.9

<sup>a</sup> For information on the formulations, see Table IX.

<sup>b</sup> The PPO resin used is HPP 821.



polyphenylene sulfide, polyimide, poly(ether ketone ketone), and epoxy novolac resin contribute to the final char residues. The difference in char yield of Table IX might be due to the char yield of individual polymers upon burning.

It seemed that the concept of char-forming rate, instead of char yield, better explained the different flame retardancy in formulations 13–17 of Table VIII, because char-forming rate values were best correlated with OI and UL 94 ratings. The PPO (HPP 821) formulation 13 and the PPS formulation 14 are two examples sharply illustrating the correlation of char-forming yield with the flame retardancy. PPO and polyphenylene sulfide have related molecular structures in that they both have chains of *p*-phenylene groups linked by chalcogens. Thermal analyses of polyphenylene sulfide in this study showed a TGA residue of 39.0% at 700°C by TGA and a melting point of 285°C with an endothermic enthalpy of 58.5 J/g. In the light of the teachings of Van Krevelen, we would have expected that the PPS formulation 14 would give flame retardancy similar to that offered by the PPO formulation 13 offered, because polyphenylene sulfide and PPO possess structural similarities, and moreover, polyphenylene sulfide has an even higher TGA (char) residue yield. The results that we experimentally obtained did not agree with this prediction. In our experimental series, we observed that the char yield from burning EPDM formulations is not the critical factor to control the flame retardancy.

The fact that the char-forming rate in this study is related to the structures of char-forming polymers and the molecular weight of the PPO resin might indicate the relation between the char-forming rate and thermooxidative degradation of char-forming polymers. We suggest the mechanism and kinetics of the thermooxidative degradation to be possible factors governing the char-forming rate. The structural effect of char-forming polymers on char-forming rates might be due to different mechanisms of the degradation. For example, PPO and polyphenylene sulfide behaved differently in providing flame retardancy for EPDM. One of the major reasons for this flame-retarding behavior might be their different mechanisms of the degradation,<sup>3,22</sup> which could control the char-forming rate. On the other hand, a kinetic influence can probably be seen in studying the molecular weight of PPO on the char-forming rate of EPDM formulations (Table IV). The kinetics of PPO degradation might be affected by PPO molecular weight, because these PPO poly-

mers are assumed to degrade via the same reaction scheme. The different kinetics involved in PPO degradation might result in different char-forming rates of EPDM formulations containing these PPO resins. It may be possible to control the char-forming rate by changing the mechanism and kinetics of the polymer degradation, such as using catalytic approaches to alter the degradation process. The above suggested reasons for char-forming rate are hypothetical. The mechanism and kinetics of the polymer degradation are known to be complicated, and the study of these topics was beyond the scope of this research.

## CONCLUSIONS

We have shown that the molecular weight of the PPO resin affected the flame retardancy of EPDM formulations containing PPO, melamine, and kaolin. The preferable molecular weight of PPO was found to be  $M_n$  13,300 and  $M_w$  29,200. The molecular structure of char-forming polymers also had a significant influence on the flame retardancy contribution. The PPO resin was the best char-forming polymer among these investigated. It has been experimentally suggested (and reasonable *a priori*) that melting and flowing before charring is an essential feature of a char-forming polymer if it is to provide coherent and continuous char.

In this particular study, the concept of the char-forming rate instead of the char yield was shown to be useful to explain the different flame retardancy affected by molecular weight and molecular structure of char-forming polymers. The char-forming rate correlated with OI and UL 94 ratings of EPDM formulations, whereas the char yield did not. This suggests that more attention should be paid to charring kinetics in flammability studies.

The authors wish to thank the Electric Power Research Institute, and in particular Mr. Bruce S. Bernstein, Technical Advisor, for support and for permission to publish these results. They also thank Prof. Eli M. Pearce for help and support in our research.

## DISCLAIMER

The small-scale flammability tests performed in this research do not necessarily reflect the hazard of a real fire.

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