

Flame Retardancy and Rearrangement Reaction of Polyphenylene-ether/Polystyrene Alloy

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ABSTRACT: The flame retardancy and the rearrangement reaction of polyphenylene-ether [poly-(oxy-2,6-dimethyl-1,4-phenylene), PPE] and polyphenylene-ether/polystyrene (PS) alloys have been studied. The flame retardancy of PPE blended with phosphates was proportional to PPE content as well as to the phosphates. The surface temperatures of PPE during a combustion was higher than that of PS, whereas PPE is more flammable than PS. The element analysis of the polymer surface showed that carbon was richer compared with the content of the newly synthesized PPE. Four monomeric and eight dimeric scission products were recovered by thermogravimetric-mass (TGA-MASS) analysis at high temperature in inert atmosphere. These structures of the scission products suggested that the rearrangement reaction occurred in combustion at high temperature. Namely, the formation of carbonaceous materials on the surface followed the rearrangement reaction and dehydration which was accelerated by the addition of aromatic phosphates. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1175–1183, 1997

Key words: polyphenylene-ether; PPE/PS alloy; flame retardancy; rearrangement reaction; carbonaceous material

INTRODUCTION

Polyphenylene-ether [poly(oxy-2,6-dimethyl-1,4-phenylene, PPE)] is one of the most important engineering plastics because the glass transition temperature is 211°C, which is much higher than that of other engineering plastics commonly used, such as polycarbonate. PPE is also known as an excellent organic material characterized by relatively low flammability.

On the other hand, many halogenated compounds, which are often used to impart fire retardance to engineering plastics, have been

widely used since World War II. These compounds are about 80% flame retardant. However, international regulations tend to limit the use of these compounds because of their toxic and corrosive combustion effluents. Study on flame retardancy for engineering plastics is becoming one of the most important areas of research.

There have been many studies on flame retardancy without halogenated compounds. For example, Fenimore and Martin introduced the "Oxygen Index," in 1966, by which one can measure the degree of fire retardancy quantitatively.^{1,2} The method provided a novel fire retardancy system of a "carbonaceous structure formation method." van Krevelen proposed the method for calculating the relation between the chemical structure of the polymer and the fire retardancy. His work made a great contribution to the development in this

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Table I List of Aromatic and Miscellaneous Phosphates Used in this Study

Abbreviation	Structure	Abbreviation	Structure
TPP		RBPP	
CDP		BBPP	
TCP		BBCP	
TXP		TNPP	$(C_9H_{19}-\text{C}_6\text{H}_4-O)_3P=O$
XDP		BGPP	$C_9H_{19}-\text{C}_6\text{H}_4-O-P\langle\text{OCH}_2\rangle C\langle\text{CH}_2\text{O}\rangle P-O-\text{C}_6\text{H}_4-C_9H_{19}$
RPP		TPOP	$(\text{C}_6\text{H}_4-O-CH_2CH_2O)_3P=O$

field of introducing a parameter by which one can calculate how much carbonaceous material is produced during combustion.³⁻⁵ Since then, many studies on carbonaceous materials have been also achieved.⁶⁻¹⁰ This included studies on phosphates

to form the surface layer made by the carbonaceous materials¹¹⁻¹⁶ and on "an intumescent structure," which is highly porous.¹⁷⁻²⁰

Mechanistic studies have shown that combustion and fire retardance in polymeric materials

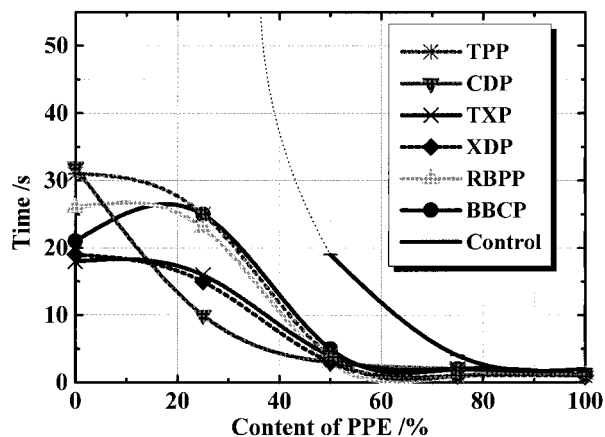


Figure 1 Flame extinguishment times of PPE blended with red-P and various phosphates at the first flaming as a function of PPE contents.

are closely related to their thermal degradation behavior. However, this understanding is still unsatisfactory because of the complexity of the degradation and other chemical reactions occurring in combustion. This research is concerned with the mechanism of flame retardancy of PPE and its alloys by approaching rearrangement, dehydration, degradation, crosslink and other miscellaneous reactions occurring in combustion on the surface of polymeric materials.²¹

EXPERIMENTAL

Polymers and Phosphates

2,6-Dimethylphenol (DMP) was synthesized by the reaction of phenol and methanol on the catalyst and distilled. The purity was 99.3%, and *o*-cresol (0.094%) was a major impurity in the DMP.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.22 g), 35% HCl (0.98 g), methylalcohol (300 g), di-*n*-butylamine (2.88 g), and *N,N,N',N'*-tetramethyl-1,3-diaminopropane (7.62 g) were fed into a 1.5 L reactor equipped with a stirrer, oxygen inlet tube, and jacket. Xylene (551 g) and DMP (286 g) were added while oxygen was fed at 40°C. The slurry was recovered from the reactor, successively washed with methanol, and dried at 120°C for 1 h.

Asahi Chemical Co. Ltd., supplied polystyrene (PS, "Polystyrene-685"), and organic phosphates were supplied by Daihachi Chemicals and Toho Chemicals (Table I). Two types of phosphates

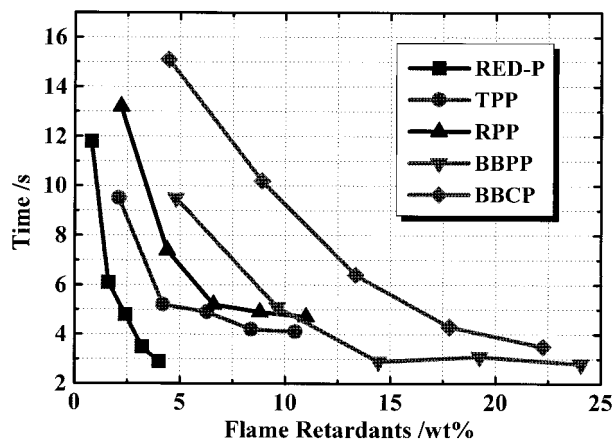


Figure 2 Flame extinguishment time as a function of phosphates and red-P contents for the PPPE65/PS35 alloy.

were used in this study. They were aromatic phosphates (from TPP to BBCP in Table I) and miscellaneous phosphates, which include oxyethylene and aromatic rings.

Measurements of Flame Retardancy, Thermal Degradation, and Other Characteristics

The specimens of PPE/PS alloy were molded by an extruder (Ikegai, PCM-30) at 280°C and subjected to the Underwriters' Laboratory UL-94 test. In the UL-94 vertical burn test, a sample was exposed vertically to a Bunsen burner flame for 10 sec. If the flame extinguished within 30 sec, another 10 sec application was made. The flame

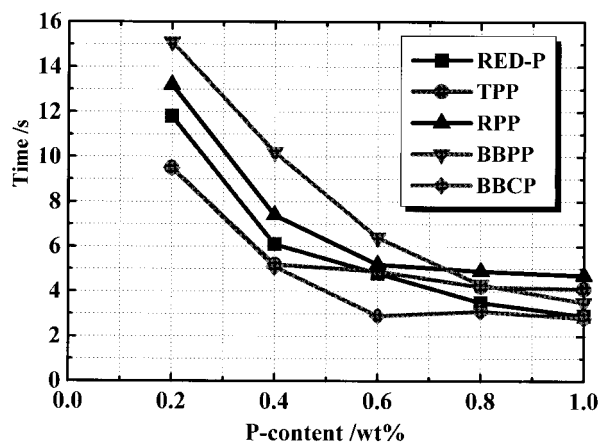


Figure 3 Flame extinguishment time of PPE65/PS35 alloys as a function of P content included in phosphates.

Table II Flame Extinguishment Time of PPE/PS with Red-P and Phosphates

Phosphate	Organic PPE : PS Frequency	1/8 50 : 50 First	1/8 50 : 50 Second	1/8 65 : 35 First	1/16 65 : 35 First
Control	Control	19	42	23.8	40.5
	red-P	—	—	3.5	7.8
Aromatic	TPP	4	8	4.2	4.9
	CDP	3	6	4.5	5.3
	TCP	—	—	4.1	5.5
	TXP	4	11	3.2	6.1
	XDP	3	5	—	—
	RPP	—	—	4.3	5.5
	RBPP	4	7	4.3	5.1
	BBPP	3	7	3.8	6.5
	BBCP	5	12	3.7	5.4
Miscellaneous	TPOP	—	—	31.1	38.1
	TNPP	—	—	4.2	5.6
	BGPP	—	—	6.8	26.1

extinguishment times and surface temperatures during the combustion were observed by thermography (JTG-3210, Nippon Denshi).

Thermogravimetric analyses (TGA-50, Shimazu-seisakusyo) were achieved with a heating rate of 40°C/min from room temperature to 800°C. The thermal degradation products were analyzed by GC-CP (gas chromatography; Perkin Elmer, Autosystem GC) with a Curie point pyrolyzer (Nippon Bunseki, JHP-22). The GC column was a capillary type, 0.25 mm in diameter, 30 cm in length, with 5% phenylmethylsiloxane as a liquid phase. The pyrolyzer could make the temperature of the speci-

men elevate at a rate of 3,720°C/sec. The fractions at 590°C were analyzed with a TGA-MASS spectrometer by GC-CP (Rigaku, TGA-MS).

RESULTS AND DISCUSSION

Red phosphorus (red-P) and various organic phosphates were selected as flame retardant and were classified into two groups, one of which was a group of aromatic phosphate and the other was miscellaneous phosphates including aliphatic and oxyethylene units. Three dimeric phosphates,

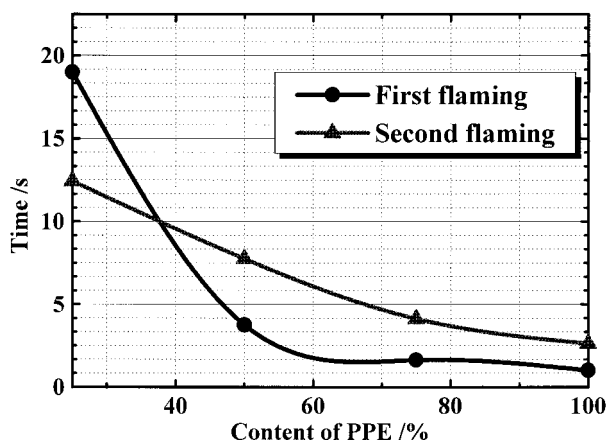


Figure 4 Average flame extinguishment time at the first and the second flamings in the case of aromatic phosphates for the PPE50/PS50 alloy.

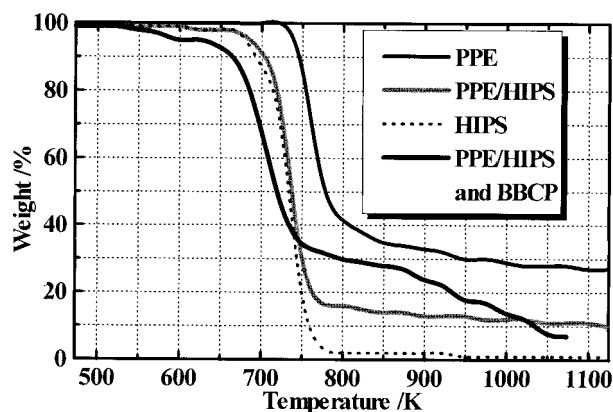


Figure 5 TGA curves and carbonaceous residues at elevated temperature in inert atmosphere. (HIPS: high impact polystyrene)

Table III Surface Temperature, 50% Degradation Temperature, and Carbonaceous Residue

P (%)	PPE (%)	Surface Temperature (°C)	50% Degradation Temperature (°C)	Carbonaceous Residue at 750°C (%)
0	0	587	435	0
0	65		455	13.5
0	100	704	508	29.8
0.8	65		491	27.2

(RBPP, BBPP, and BBCP), were used as high-boiling-point flame retardants. The higher boiling points are desirable because they play a role when the polymer is heated to above 500°C in combustion. If the boiling point or the thermal degradation temperature of the flame retardant is low, it is volatilized or decomposed before it acts as a flame retardant.

Figure 1 shows the flame extinguishment times of one-eighth-inch-thick test specimens of PPE/PS alloy at first flaming. The flame was not extinguished at up to at least 25% PPE contents without phosphate. The fire was out within about 20–50 sec by phosphate addition to PS, and the times decreased with an increase in PPE content in the polymer alloy. We recognized that PPE in the PPE/PS alloy and organic phosphates had a strong effect on the flame retardancy.

The flame extinguishment time at the second flaming of PPE65/PS35 alloys decreased with an increase of the flame retardant, as shown in Figure 2. The effects of red-P and TPP on flame retardancy were appreciable with 10% weight concentrations. It is one of the reasons that red-P and TPP are known as the best flame retardants to many aromatic plastics.

However, the flame extinguishment times of the same specimens are shown in Figure 3 as a function of P content included in the various phosphates. The effects of red-P and TPP on the time were indistinguishable compared with other phosphates. It suggested that phosphorus contents were more essential.

Results from the UL tests for the blends of $\frac{1}{8}$ and $\frac{1}{16}$ inch specimens in this study are listed in Table II. PPE contents were 50 and 65%. The times of PPE-rich alloy (PPE, 65%; PS, 35%) were 23.8 sec for $\frac{1}{8}$ inch specimens and 40.5 sec for $\frac{1}{16}$ inch specimens.

Aromatic phosphates had almost the same effect on flame retardancy, and those times were between 3.2 to 4.5 sec. For miscellaneous phos-

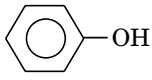
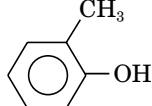
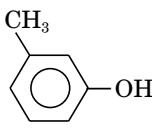
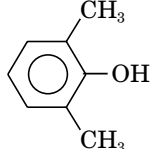
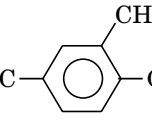
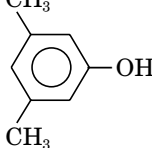
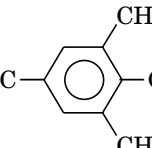
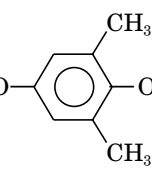
phates like TPOP and BGPP ($\frac{1}{16}$ inch specimens), however, the times were much larger than those for aromatic phosphates.

Figure 4 shows the average times for the blends with aromatic phosphates at the first and second flammings. The surface of the specimen was ignited by exposure to a Bunsen burner flame; it was then immediately covered with carbonaceous materials on the polymer surface after the first flaming. The carbonaceous materials played a role as a heat shield and protected the polymer from an external heat flux. The specimen was also ignited by exposure to the burner at the second flaming, whereas the surface had been already covered with the carbonaceous materials. The sizes of the flame observed were smaller at the second flaming than at the first flaming. The reaction rates were slower and the flame extinguishment times were larger at the second flaming than at the first flaming.

As mentioned above, the flame extinguishment times of specimens which blended aromatic phosphate compounds were between 3 and 6 sec and the time increased by several times when decreasing the content of PPE from 60 to 30%. It is well known that some kinds of aromatic polymers such as polycarbonate (bisphenol-A type) and PPE form a carbonized layer on the surface during combustion. The high temperature at the oxidation reaction site in gas phase, which is several millimeters from the surface of the polymer, heats the polymer surface.²² The degradation of the polymer near the surface proceeds in inert atmosphere because oxygen is consumed by reactions with fuels at the oxidation reaction site and cannot reach the polymer surface. At the polymer surface, hydrogen in the polymer is "pulled out" by oxygen, which is inherently included in the polymer. The residue is rich in carbon, and the carbon-rich layer protects the fire because it is difficult to burn.

TPP and other aromatic phosphorous com-

Table IV Monomeric Scission Products of PPE by Thermal Degradation

	Structure	Degradation Temperature		
		590°C	670°C	764°C
A1		0.89	3.84	3.26
B1		17.06	26.26	25.02
C1		1.55	4.40	3.76
D1		28.59	21.03	24.07
E1		25.25	27.22	25.04
F1		0.14	0.07	0.12
G1		25.28	16.19	17.96
H1		1.22	0.98	0.77
Sum		100.00	100.00	100.00

pounds accelerated the dehydration near the polymer surface. Figure 5 shows the TGA curves of PPE/PS alloy, PS, and PPE with and without phosphates. The experiments on thermal degradation in inert atmosphere provide useful infor-

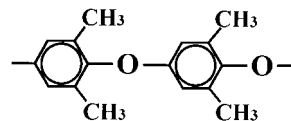
mation regarding combustion. The carbonaceous residue in the TGA curve increased with increasing the PPE content and with adding P compound.

The environmental oxygen concentration is effective in continuing the combustion, in contrast to a conventional diffusion flame, where the rate of fuel supply represents another independent parameter.^{23,24} Because the combustion site is apart from the polymer surface, the temperature of the polymer surface is expected to be much lower than that of the combustion site. The enthalpy of the reaction at the combustion site where oxygen reacts with hydrocarbon is large, and the reaction is exothermic. On the contrary, the reactions in the polymer surface region, which are degradation reactions of polymers, are endothermic.

In Table III, the surface temperatures during the combustion and the residue amounts of TGA tests are listed. The temperature of the combustion site was 1,000°C or more, but the surface temperatures were about 600–700°C in the two cases. This implied that the temperature did not depend on combustion (heat capacity, enthalpy, and so on) but on the degradation temperature of polymer. Although the flame extinguishment time of PPE was shorter than that of PS, the higher the content of PPE in the alloy, the higher the surface temperature was.²⁵

Carbonaceous residues at 750°C are also listed in Table III. Their tendencies were the same as the surface temperature in combustion. The larger the carbonaceous materials formed, the shorter the combustion times were.

It is important to know the reaction route by which the carbonaceous materials form in combustion. However, the experiments for elucidating the mechanism are difficult because the combustion reaction completes within several seconds. In this study, the thermal degradation in the pyrolyzer was selected as the model combustion reaction. The Curie point pyrolyzer, which can heat the sample at a rate of 3,720°C/sec, was used for this purpose because it is much faster than the rate of combustion. The scission products in the

**Figure 6** Chemical structure of PPE just after polymerization.

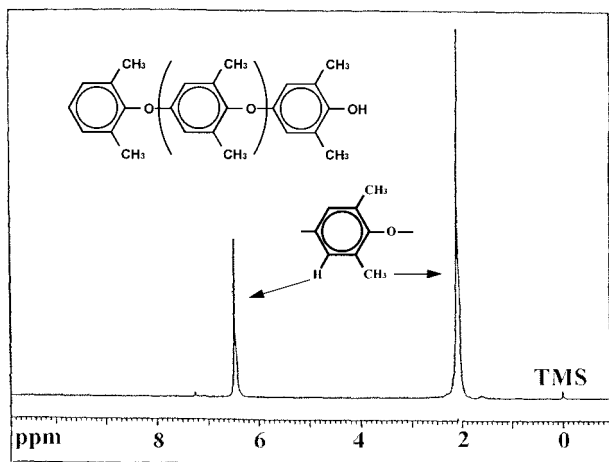


Figure 7 ^1H nuclear magnetic resonance chart of PPE. (TMS: trimethylsiloxane)

Curie point pyrolyzer were introduced to mass spectroscopy and gas chromatography and measured quantitatively. The results are listed in Table IV. 2,6-Dimethylphenol, which is the raw material for the synthesis of PPE, was found in the scission products. However, the content was only one-fourth among the monomeric scission products. *o*-Cresol, 2,4-dimethylphenol, and 2,4,6-trimethylphenol were also recovered in the same amounts as 2,6-dimethylphenol.

Although *o*-cresol could be thought to be the scission product from 2,6-dimethylphenol by demethylation, 2,4-dimethylphenol and 2,4,6-trimethylphenol were not the scission products by the direct degradation of the PPE chain. The chemical structure of PPE (Fig. 6), which was observed by ^1H nuclear magnetic resonance²⁶ was simple, as is shown in Figure 7. The rearrangement reaction from the ether bridge between benzene rings to the methylene bridge was supposed to occur by heating. The model structure after the rearrangement is shown in Figure 8.^{27,28}

The calculated values of four major scission products in Table IV were about 25% under the assumption that the PPE chain rearranged and that the methylene bridges in the rearranged polymer chain underwent cleavage in the same probability. Comparing the values in the columns of "Content Observed" the rearrangement reaction is considered to occur before thermal degradation.

The results by elemental analysis of the burnt

samples are listed in Table V. The hydrogen atom ratio to carbon and oxygen ratio to carbon were 1.00 and 0.12, respectively, in the untreated polymer, which were the same values as the calculated. The values of the residue at 850°C in the nitrogen atmosphere were 0.44 and 0.01, which showed that almost all of the oxygen reacted with hydrogen or carbon. The ratios of the combustion surface char (carbonaceous materials) were 0.69 and 0.08, respectively, which were smaller than the ratio of untreated polymer and were larger than that of the residue in nitrogen atmosphere.²⁹ The dehydration and dehydrogenation seemed to occur on the surface of the polymer in combustion, and this led to polyaromatic species the hydrogen content of which is lower than that of PPE.

The combustion reaction of polymeric materials is one of the rapid and complicated reactions. The oxidizing reaction site is apart from the surface of the polymer, so the polymer is thermally decomposed under the inert atmosphere, like thermal degradation experiments by GC-CP.

CONCLUSION

When the alloy is exposed to the Bunsen burner flame, PPE and PS polymer chains underwent cleavage to lower molecular compounds and successively decompose to various volatile compounds, which release from the surface of the alloy and reach the oxidation site. The high enthalpy of the reaction elevates the temperature of the site, and it heats the surface of the polymer and continues to decompose. At the same time, part of the polymer chain is converted to carbona-

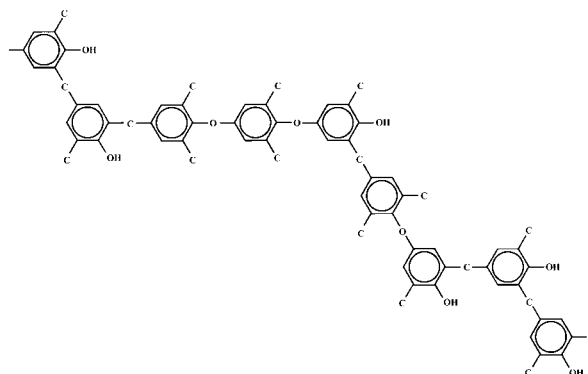


Figure 8 Chemical structure of PPE rearranged just before degradation.

Table V Elemental Analysis of Polymer and Polymer Surface

Parameter	Sample		Element Analysis			Element Ratio	
			C	H	O	H/C	O/C
			(wt %)			(g atoms/g atoms C)	
Untreated		obs. ^a	80.2	6.7	13.1	1.00	0.12
		cal.	80.0	6.7	13.3	1.00	0.12
Treated	TGA (at 850°C in N ₂)	obs.	94.6	3.5	1.8	0.44	0.01
	Combustion surface	obs.	84.5	4.9	9.3	0.69	0.08
	Under surface	obs.	81.5	6.1	12.7	0.89	0.12

^a obs., observed; cal., calculated.

ceous materials, which cover the polymer surface. Because the carbonaceous materials can be ignited in 65% or more oxygen concentration, the combustion is difficult to continue.

If oxygen could reach the surface of the polymer surface in combustion, PPE might not be converted to carbonaceous materials, as shown in the results of the TGA. However, PPE converts to carbonaceous structure materials under the inert atmosphere. The carbonaceous materials with irregular macrovoids reduce the rate of heat transfer, and the dehydration reaction occurring on the surface in combustion is endothermic. They reduce the heat flux.

The main chain of PPE in the PPE/PS alloy rearranges to the other kind of polymer in which the methylene bridge bonds adjacent benzene rings in place of the ether bond. It accelerates the dehydration reaction, which is catalyzed by phosphates. Combustion leads to constant charring, although the reactions are very furious and complicated. The flame extinguishment times at the first and the second flamings and the content of elements in the carbonaceous layer keep constant.

There have been many discussions on the effects of phosphates as flame retardants. For example, the effect of TPP, which is one of the volatile compounds, is considered to be flame inhibition in the flame by the evaporation-degradation of TPP.³⁰ However, the char formation on the surface of PPE and its alloys and the effect as a barrier of heat transfer could account for the rearrangement reaction before combustion and the dehydration due to organic phosphates.

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