

Combustion and Fire Retardance of Poly(2,6-dimethyl-1,4-phenylene ether)–High-Impact Polystyrene Blends.

II. Chemical Aspects

A. B. BOSCOLETTO,¹ M. CHECCHIN,¹ L. MILAN,¹ P. PANNOCCIA,¹ M. TAVAN,¹ G. CAMINO,² M. P. LUDA²

¹ EniChem, Centro Ricerche, Via della Chimica 5, 30175 Porto Marghera (Venezia), Italy

² Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università, Via P. Giuria 7, 10125 Torino, Italy

Received 28 April 1997; accepted 3 September 1997

ABSTRACT: The chemical reactions occurring during the intumescent process taking place in the combustion of the poly(2,6-dimethyl-1,4-phenylene ether)–high-impact polystyrene blends (PPE–HIPS) are studied in detail through the chemical characterization of the burnt and original material by infrared, pyrolysis–gas chromatography–mass spectrometry, and direct insertion probe spectrometry. Evidence is given of thermal rearrangement in the blend of the polyether PPE chains to polybenzylic structures occurring in the heating conditions of pyrolysis or combustion, as previously shown, to take place in thermal degradation of PPE. The rearranged chain segments are shown to give a larger contribution to the intumescent char, while volatile blowing products are mostly formed by polystyrene and polybutadiene components. From PPE–HIPS blends, the volatilization of the fire-retardant triphenyl phosphate (TPP), which when heated alone volatilizes at a temperature below that of PPE–HIPS degradation, is delayed probably by hydrogen bonding with PPE. This allows TPP to play the typical flame inhibition role of volatile phosphorus compounds. Moreover, it is found that TPP favors the PPE rearrangement and henceforth increases the char yield of the burning blend, which is a typical condensed phase fire-retardant action. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2231–2240, 1998

Key words: fire retardance; combustion; polyphenylene ether–high-impact polystyrene blends; thermal decomposition; fire retardants

INTRODUCTION

The study of morphological aspects in the thermal degradation on burning of the blend poly(2,6-dimethyl-1,4-phenylene ether)–high-impact polystyrene (PPE–HIPS) was carried out in the first part of this article. It was shown that the thermal degradation of the blend occurs with simultaneous formation of a carbonized material and evolu-

tion of gaseous products, which blow the viscous charring mass (intumescence). The resulting thermally stable residue is a foamed multicellular intumescent char that protects the underlying material from the action of heat and flames.¹

The chemistry of the intumescence process, including blowing and charring steps, is examined here through the analysis of the composition of the blend on burning.

Intumescence is kinetically controlled and depends therefore on the conditions in which it occurs. Combustion, as it takes place in the Underwriters Laboratories UL 94 vertical test,^{2,3} is con-

Correspondence to: G. Camino.

sidered here because, so far, this is the most widely used test in trading specifications of fire-retardant polymeric materials.

An effective fire-retardant additive for PPE-HIPS blends is triphenyl phosphate (TPP),^{4,5} which was shown to modify the shape and size of the voids formed in the burning material by thermal degradation.¹ The physicochemical aspects of the fire-retardant action of TPP are discussed.

EXPERIMENTAL

Materials and Combustion

Industrial samples of PPE-HIPS 65/35 w/w (Enichem, Marghera, Italy) with and without 16.6% TPP (Reomol, Ciba Geigy, Switzerland), previously described in detail elsewhere,¹ were burned in the UL 94 test, in which vertical small bar specimens are burned upon bottom ignition.^{2,3}

Fourier Transform Infrared Spectrometry

All Fourier transform infrared (FTIR) spectra were collected at room temperature with a Nicolet 740 spectrophotometer equipped with a CsI beam-splitter and DTGS detector. Each spectrum in the wavenumber range 5000–250 cm^{-1} was the average of 64 scans at a resolution of 8 cm^{-1} . Absorption spectra were obtained either from films cast from CHCl_3 solution or the KBr pellet technique. Diffuse reflectance infrared Fourier transform (DRIFT) spectra from the surface of UL94 specimens as burned were recorded with 20–70° off-normal beam by using a Spectra Tech DRIFT attachment. The DRIFT spectra were transformed in equivalent absorbance units by using the Kubelka-Munk function.⁶

Pyrolysis-Gas Chromatography-Mass Spectrometry

Pyrolyses of thin-cut and powder samples were performed on a CDS Pyroprobe Model 1000 using approximately 1 mg of a sample, a heating rate of 100°C/s, pyrolysis temperatures in the range of 300–1000°C, and a total pyrolysis time of 9 s. The probe was inserted into the gas chromatography (GC)-interface, held at 250°C, connected to a Hewlett-Packard Model 5890 gas chromatograph. The pyrolysis products were separated by HP-1 Hewlett-Packard chromatographic column of 12.5

m \times 0.2 mm i.d., with a film 0.33 mm thick, directly connected with the mass spectrometer. The helium carrier gas flow was 0.56 mL/min. The gas chromatograph oven was heated from 35 to 300°C at a heating rate of 10°C/min and maintained at the highest temperature for 13.5 min. In the pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS) configuration, the injector and the transfer line of gas chromatograph were held at 300°C.

In some experiments, direct insertion probe (DIP) was utilized inserting the samples directly into the mass source. The samples, about 1 mg, thin-cut from unburned or scraped from the burned surface of UL94 test specimens, were heated from 40 to 300°C at heating rates of 8 and 20°C/min. The formation of volatile products on heating was monitored as a function of time by means of the total ion current (TIC) produced by electron impact.

Mass spectra of Py-GC and of DIP products were collected by using a Hewlett-Packard Model 5988A quadrupole mass analyzer. The following parameters were used for the analyses: source temperature, 200°C; electron impact energy, 70 eV; emission current, 300 mA; and source pressure, 2×10^{-6} Torr. The samples were analyzed in the mass range between 20 and 500 or 1050 amu in the case of Py-GC-MS and DIP-MS analysis, respectively.

RESULTS

Infrared

PPE-HIPS Blend

In the infrared spectrum of PPE-HIPS [Fig. 1(a)], the absorptions (Table I) are due to the chemical structures of the two following major components of the blend: polyphenylene ether (PPE) and polystyrene (PS), which overlap those of the polybutadiene rubber phase (PBU; ca. 3%).¹ Specific PPE absorptions are at 1188 cm^{-1} (C—O—C stretching mode) and at 1379 with its overtone at 2734 cm^{-1} (CH_3). Similarly, the PS chains are responsible for the absorptions of the typical doublet at 698 and 755 cm^{-1} and for the CH aromatic stretching at 3078, 3058, and 3025 cm^{-1} .^{7,8} The contribution of PBU (CH_2 , CH, CH=CH), although not distinguishable, should be relatively more important in the region of aliphatic C—H stretching (2800–3000 cm^{-1}) owing to the relative concentration of these groups in

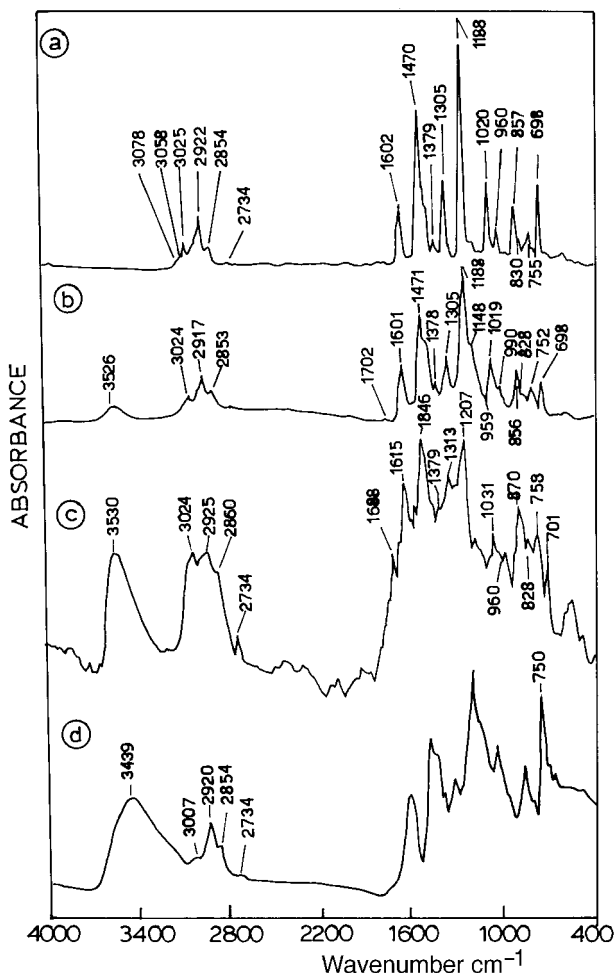


Figure 1 Infrared spectra of PPE-HIPS blend: (a) original sample, film on KBr disc; (b) combustion residue from UL 94 test, KBr pellet; (c) DRIFT of charred material; and (d) residue of combustion after extraction with CHCl_3 , film on KBr disc.

the three polymers. Thus, the degradation of the three molecular structures during burning can be specifically examined by the evolution of these infrared absorptions.

The surface of specimens burned in the UL 94 test was carefully scraped avoiding collecting the unaltered material underlying the charred surface. The FTIR spectrum of the residue of combustion in Figure 1(b) is compared with that of the original blend [Fig. 1(a)]. It can be seen that the most evident difference between the two spectra is a broad absorption centered at 3526 cm^{-1} due to OH vibration mode, which appears for the burned material. This modification is accompanied by growth of two shoulders at 990 and 1148 cm^{-1} . The three absorptions together are indicative of formation of phenolic groups in the material as

observed in the thermal degradation of pure PPE carried out under inert atmosphere or vacuum.⁹⁻¹² A simultaneous decrease of intensity ratio of the ether band at 1188 cm^{-1} to the CH_3 band (1379 cm^{-1}) is seen in the spectrum of the combustion residue, indicating that phenol groups result from scission of ether bonds of PPE.

Another difference between spectra 1(a) and 1(b) concerns the relative decrease in the latter of the typical absorption of PS at 698 cm^{-1} . The decrease of the "twin" weaker band at 755 cm^{-1} [Fig. 1(a)], which should correspondingly become very small, is apparently masked by a band at 752 cm^{-1} [Fig. 1(b)], which increases on heating (see below).

The DRIFT-FTIR spectrum of the charred surface layer produced on burning the specimen in the UL 94 test [Fig. 1(c)], shows further features as compared to that of the overall burned material [Fig. 1(b)]. Taking into account that the relative intensity of the bands in different regions of the spectrum may depend on the morphology of charred surface, owing to different contribution of specular or diffuse reflectance, a most noticeable difference is the presence in the spectrum of Figure 1(c) of an absorption at 1698 cm^{-1} due to carbonyl groups not visible in the spectrum of Figure 1(b). Furthermore, three absorptions at 701 , 758 , and 870 cm^{-1} , attributed to aromatic C-H bonds typical of chars obtained from pyrolysis of C, H, and O polymers,¹³ are more evident from the surface spectrum.

The PS fraction not volatilized on burning remains completely soluble.

The residue of combustion of Figure 1(b), after four repeated extractions with CHCl_3 , indeed shows the spectrum reported in Figure 1(d) in which the typical absorptions of PS at 698 and 3078 , 3058 , and 3025 cm^{-1} [Fig. 1(a) and (b)] are absent. After the extraction, the residue reveals the growth of a strong absorption at 750 cm^{-1} , which overlaps the CH absorption of PS at 755 cm^{-1} present in the residue prior to extraction [Spectrum 1(b)].

Fire-Retarded PPE-HIPS Blend

All the relevant absorptions of the fire-retardant additive TPP overlap absorptions of the blend PPE-HIPS. However, Figure 2(a) shows that the intensity of the band at 960 cm^{-1} of the blend is significantly increased in the presence of TPP by contribution due to the P-O-C (phenyl) bond in pentavalent phosphorus compounds.⁸

Table I Infrared Absorptions of PPE–HIPS Blend: Spectra of Figures 1(a) and 2(a)

Wavenumber (cm^{-1})	Vibration Description	Structure
3080–3000	CH aromatic, unsaturated aliphatic	PPE, PS, PBu
3000–2800	CH aliphatic	PPE, PS, PBu
2734	CH in aromatic CH_3	PPE
1602	Aromatic ring, $\text{C}=\text{C}$	PPE, PS, PBu
1470	CH_2 , CH_3 , aromatic ring	PPE, PS, PBu
1379	CH_3	PPE
1305	na ^a	PPE
1188	C—O—C aromatic ether	PPE
1020	Aromatic ring	PPE
960	P—O—C (aromatic)	TPP
857 and 830	Aromatic CH	PPE
755	Aromatic CH	PS
698	Aromatic ring	PS

^a na = not attributed.

The chemical modifications of the blend upon burning seem not to depend on the presence of the fire-retardant, as shown by comparison of the spectra of Figure 1(b) and (c) with 2(b) and (c), respectively. Moreover, in spite of the fact that TPP volatilizes completely on heating between 220–350°C,¹⁴ the concentration of TPP in the combustion residue appears comparable to that of the original sample as shown by the relative intensity of the absorption at 960 cm^{-1} in the spectra reported in Figure 2(a) and (b). Artifacts due to scraping of the burnt specimen, which might include some unburnt material, are excluded by the presence of the 968 cm^{-1} band also in the surface DRIFT spectrum of Figure 2(c). The absorption disappears upon extraction of the combustion residue with CHCl_3 in which TPP is soluble so that the spectrum of the insoluble fraction in Figure 2(d) results similar to that of Figure 1(d). This indicates that most of TPP should not be kept in the blend by strong chemical bonds.

DIP–MS

PPE–HIPS and Fire-Retarded Blend

The TIC curve of Figure 3(a), relative to the PPE–HIPS blend heated up to 300°C that is below the temperature of thermal degradation (>350°C),¹⁴ shows that volatile products are evolved as soon as the PPE–HIPS is heated in high vacuum in the mass spectrometer ion source with a maximum at 60°C due to the presence of

processing aid additives. Above 160°C, the TIC curve increases because of volatilization of trace amounts of oligomeric products present in PPE and PS.

Indeed, the mass spectrum [Fig. 4(a)] of the products evolved at the maximum heating temperature (approximately 300°C) shows the typical oligomeric fragments deriving from both PS (for example, $m/z = 104$, styrene; 207/208, dimers; 312, trimer) and PPE (for example, $m/z = 242$, dimer; 362, trimer; 482, tetramer), which might either be present in the original polymers or be formed by limited degradation in the blending process.

The presence of TPP modifies the TIC curve of the blend, as reported in Figure 3(b). The signal that is one order of magnitude larger than that in absence of TPP shows a small maximum at 90°C followed by a much larger one at 190°C. Accordingly, the mass spectrum of the products evolved at 300°C [Fig. 4(b)] mainly shows the presence of TPP ($m/z = 77, 94, 170, 233, \text{ and } 326$) and PPE species. The evolution of TPP, which when heated alone in DIP/MS conditions extensively evaporates upon insertion into the source at 40°C, is strongly retarded in the polymer matrix as shown by the maximum at approximately 240°C of the TPP specific ion current profile of Figure 5(c). Moreover, it is observed that the TPP presence determines the anticipation of styrene evolved with shifting of the rate maximum from 210 to 140°C as shown by the ion ($m/z = 104$) curve profiles of Figure 5(a) and (b). Thus, from

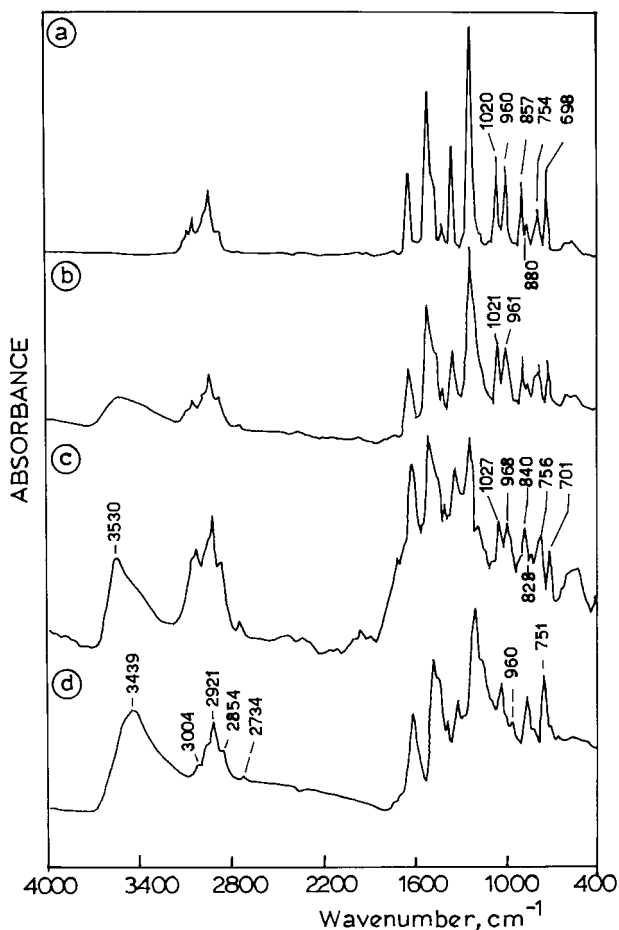


Figure 2 Infrared spectra of PPE-HIPS fire-retarded with TPP (16.6%): (a) original sample; (b) combustion residue; (c) charred material; and (d) combustion residue after extraction with CHCl_3 . Conditions as for respective spectra in Figure 1.

these data, it appears that blending of PPE with HIPS in the presence of TPP might increase the evolution of PS and PPE oligomers.

Combustion Char

The results of DIP-MS experiments carried out on the residues of combustion scraped from the surface of burnt UL94 specimens after repeated CHCl_3 extraction are shown in Figures 6 and 7. Small amounts of PS and PPE oligomeric products are evolved from the burnt PPE-HIPS blend [Fig. 7(a)]. Whereas a much larger signal is seen in the case of the fire-retarded blend, which is essentially due to TPP [Fig. 7(b)].

This, on one hand confirms infrared (IR) data on retention of TPP in the polymer blend during combustion. On the other hand, it indicates that

at least part of TPP, although small, cannot be extracted by CHCl_3 from the burnt material, suggesting that chemical bonds could be formed with the matrix. This was not evident from IR data, probably owing to its lower sensitivity.

Py-GC-MS

PPE-HIPS and Fire-Retarded Blend

In Figures 8 and 9, TIC chromatograms of UL94 unburnt PPE-HIPS blends specimens, without and with TPP, respectively, pyrolyzed stepwise at increasing temperatures of 300, 400, and 500°C, are reported. The chemical assignments relative to the numbered peaks, as revealed from mass fragmentation patterns, are given in Table II.

At 300°C, the PPE-HIPS blend is stable; whereas, in the case of the fire-retarded blend, the release of TPP (peak 61) and of trace amounts of styrenic oligomers (peak 62–65) and PPE fragments (peaks 70, 71) are detected, with these last being likely impurities in the material in agreement with above DIP-MS results.

At 400°C, the styrene monomer evolution (peak 7) from both blends due to beginning of polystyrene degradation becomes evident. The further temperature increase to 500°C of both blends gives rise to the evolution of PS fragments, such as styrene, α -methyl-styrene (peak 12), toluene (peak 3), ethylbenzene (peak 4), and oligomers (peaks 36, 37, and 62), and of dimeric butadiene (peak 5) oligomers from PBU rubber domains of HIPS as results of the extensive thermal degradation. Moreover, a reduction of the TPP peak relative intensity is observed, which is mainly due to prolonged heating throughout the experiment. In

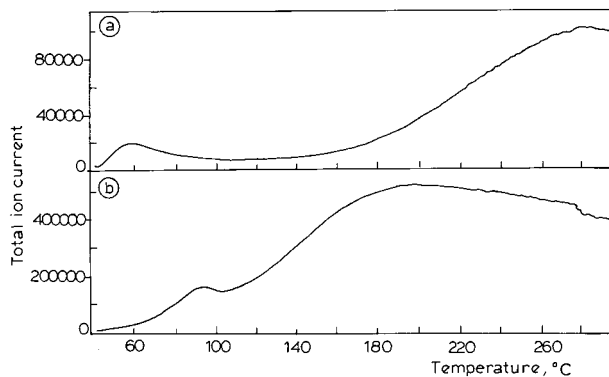


Figure 3 Total ion current curve in DIP/MS of (a) PPE-HIPS blend and (b) PPE-HIPS added with TPP (8°C/min heating rate).

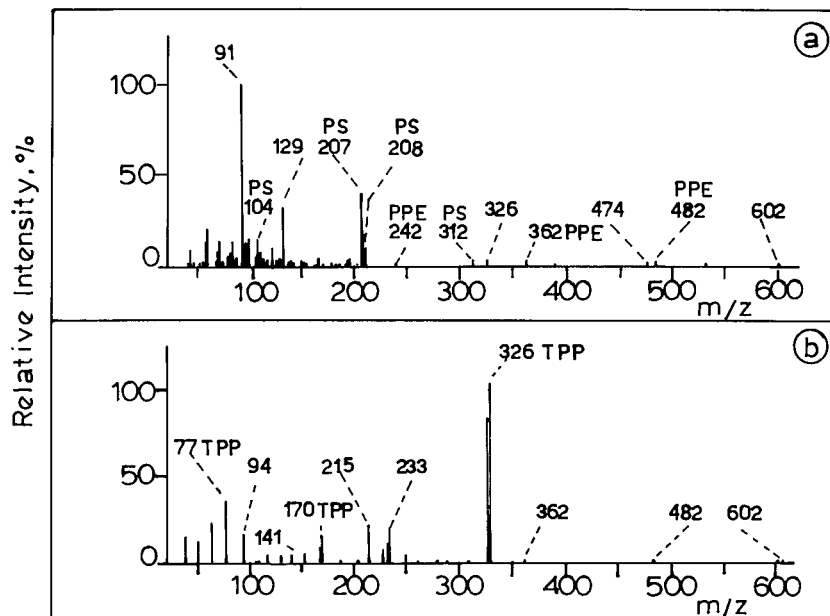
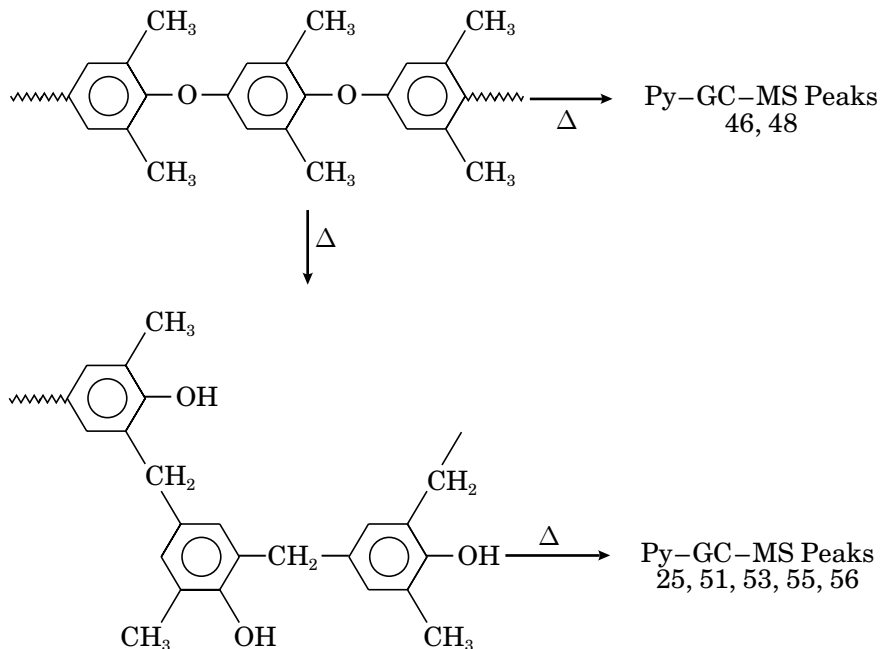


Figure 4 Electron impact mass spectra of products evolved at 300°C in DIP-MS of blends of Figure 3(a) and (b), respectively.

these experimental conditions, the PPE typical fragments, such as xylene (peak 24) and 2,4,6-trimethylphenol (peak 25), from both blends, were detected only in traces, starting from 500°C, pointing out the good PPE thermal stability.

The TIC chromatograms from pyrolysis directly performed at 700°C on the blends reveal the presence of typical fragments for both PS and PPE (Fig. 10) besides that of TPP (peak 61) from

the fire-retarded blend. The observed species from PPE (Table II) are explainable on the basis of scission of the PPE chains that have undergone a partial Fries-type rearrangement reaction.^{9,10,15} In particular, two types of product are obtained, respectively, derived from substituted phenylene ether (for example, peaks 46 and 48; Table II) or benzylic structures (for example, peaks 25, 51, 53, 55, and 56; Table II), as follows:



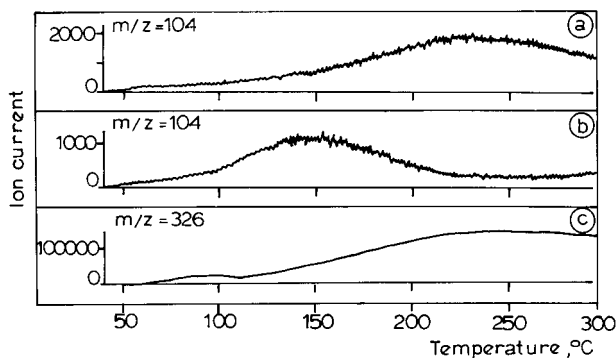


Figure 5 Single ion profile curves of ions from DIP-MS of (a) PPE-HIPS blend and (b) and (c) fire-retarded blend.

If, on one hand, the presence of TPP doesn't seem to have any influence on the type of fragments, on the other hand, in the presence of TPP, there is a change of relative yield of PPE fragments deriving from rearranged chain segments (Table III).

Weight-normalized chromatographic data (averaged over four repeated experiments) referred to weight-normalized styrene evolved, usually taken for the evaluation of blend composition,^{7,16} show that in the presence of TPP, the concentration of the benzylic-type fragments from rearranged PPE chains significantly increases apart from peak 55, which is not clearly detectable in the presence of TPP, whereas the concentration of the ether-type fragments from original PPE does not change, as compared to the PPE-HIPS blend. Since the area of the weight-normalized styrene peak (peak 7) practically does not change upon introduction of TPP in the blend (5.3 compared to 6.6 arbitrary units; standard deviation 0.4), the ratioed data of Table III can also be compared as absolute values.

The overall area ratio between peaks corresponding to fragments from benzylic (25, 51, 53, 55, and 56) and ether structures (46 and 48) increases from 5.6 to 8.1. Therefore, TPP seems to favor Fries-type rearrangement of PPE chains (reaction 1), resulting in a larger amount of polybenzylic type fragments on pyrolysis.

Combustion Char

The burnt residue from the UL 94 test on the fire-retarded blend, sampled from the charred surface and extracted with CHCl_3 was successively examined in Py-GC-MS at 700 and 1000°C [Figs. 11(a) and (b), respectively].

It can be seen that the peak 61 corresponding to TPP is present in Figure 11(a), confirming DIP-MS data, which show the presence of unextracted TPP in the charred residue of combustion. However, in contrast to the DIP-MS experiment, Figure 11(a) shows much larger signals due to PPE fragments (for example, 18, 21, 23, 25, etc.; Table II), indicating that the char is built with PPE structures, which are broken down by pyrolysis at 700°C. In fact, DIP-MS above reveals only volatile products that can be desorbed from the char by heating to 300°C. Also in this case, it appears that the fraction of benzylic fragments from PPE chains (for example, 51, 53, 55, and 56) is larger than that of ether fragments (for example, 46 and 48). However, as shown in Figure 11(a), it is observed a higher contribution of 2,4,6-trimethylphenol (peak 25) with respect to the overall benzylic and ether fragments from the previous pyrolysis experiments performed on the blends [Figs. 9 and 10(b)]. This result points out that an extensive chain rearrangement is occurred on combustion.

The subsequent char breakdown by pyrolysis at 1000°C indicates that the most stable structures in the char are due to aromatic residues decomposing to benzene (peak 2; Table II), toluene (peak 3), xylene (peak 6), methyl phenol (peak 18), etc.

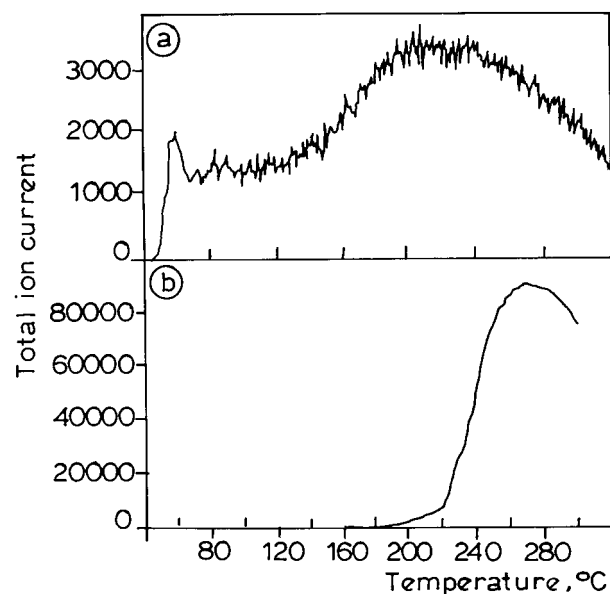


Figure 6 Total ion current curve in DIP-MS of the combustion residue after extraction with CHCl_3 : (a) PPE-HIPS blend and (b) fire-retarded blend (20°C/min heating rate).

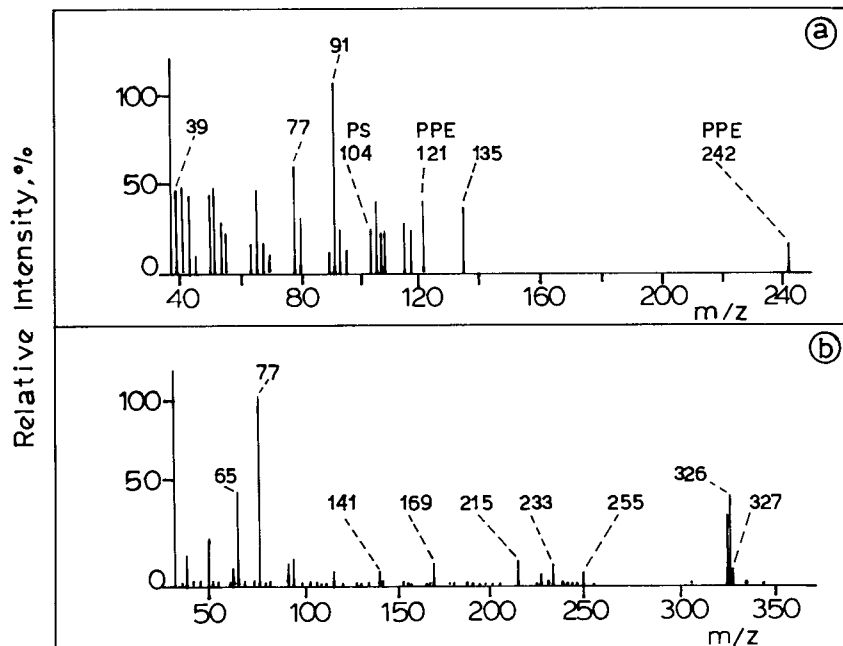


Figure 7 Electron impact mass spectra of products evolved at 300°C in DIP-MS of blends of figure 6(a) and (b), respectively.

The CO₂ evolved by pyrolysis of the char at 1000°C [Figure 11(b)], as well as the carbonyl groups of Figures 1(c) and 2(c), might be products of the phenol-formaldehyde like structures of the rearranged polybenzylic chains, which have been shown to undergo auto-oxidation and form CO₂ on thermal degradation under vacuum.¹⁷

DISCUSSION

The thermal decomposition to volatile compounds of the polystyrene and polybutadiene components of the PPE-HIPS blend precedes that of PPE on progressive heating of the PPE-HIPS blend [Figures 8 and 10(a)]. This is in agreement with the

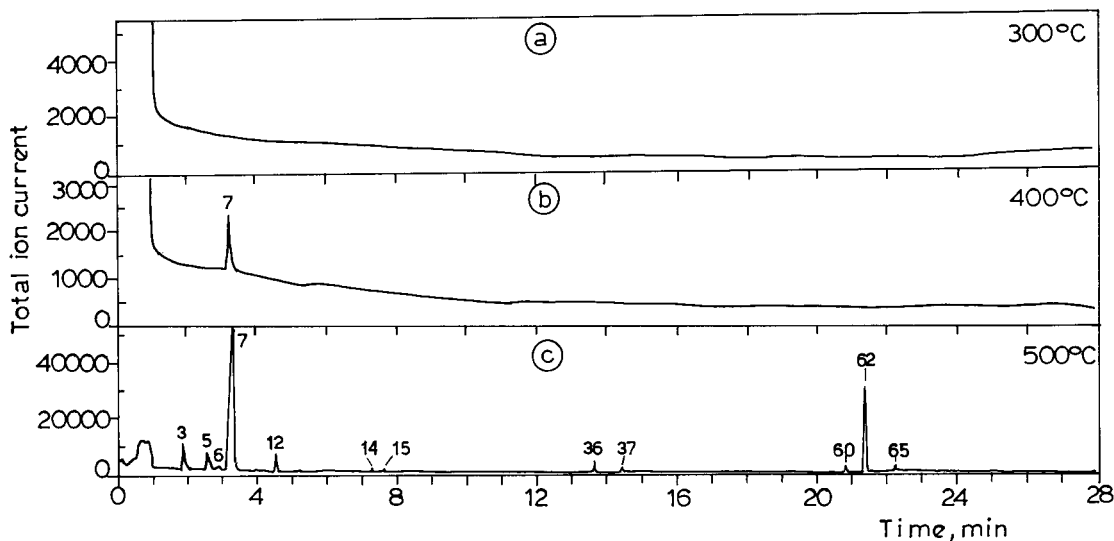


Figure 8 Total ion current curves in Py-GC-MS at sequential temperature steps of 300, 400, and 500°C of PPE-HIPS blend. The assignments of labeled peaks are reported in Table II.

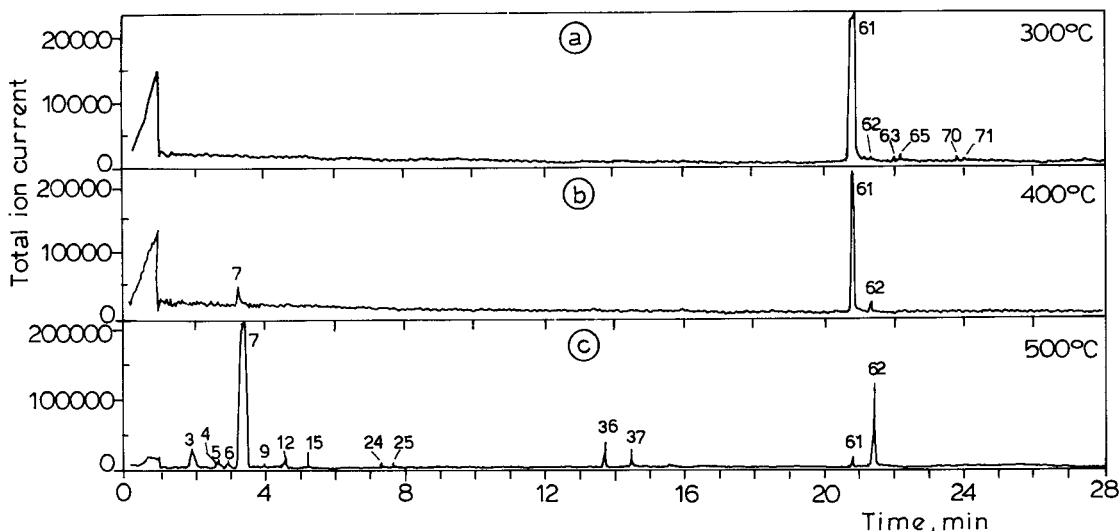


Figure 9 Total ion current curves in Py-GC-MS at sequential temperature steps of 300, 400, and 500°C of fire-retarded blend. The assignments of labeled peaks are reported in Table II.

thermal stability of the three polymers and with conclusions from our previous morphological study.¹

PPE undergoes partial thermal rearrangement from a polyether to a linear phenol-formaldehyde type polybenzylic structure,^{8,9,14} even on a rapid heating, as shown by pyrolysis fragments of Figure 10(a).

Infrared (Fig. 1) shows that the PPE rearrangement also occurs during combustion in the UL 94 test and that rearranged segments contribute to the chemical structure of the char. This char shows a high concentration of IR-detectable chemical functional groups similar to that the original material, apart from the IR modifications due to the thermal volatilization of the PS structures, which are the least stable.

As far as IR characterization of char is concerned, production of char by thermal degradation of organic polymers was shown to proceed through three main steps, as follows¹³: low-temperature chars, intermediate chars, and graphite structures.

Low temperature chars, which are obtained on heating up to about 400°C, while mostly gases evolve, are characterized by high concentration of functional groups, similar to those of the starting material.

Intermediate chars, which are obtained between 450–650°C, at the end of the evolution of high boiling products (tars), are generally opaque to IR radiations and must be analyzed by surface

IR techniques. The chemical nature of the charred surface in which aliphatic residues are eliminated or converted to aromatics ones is mostly independent from the original structure of the starting material. Above 700°C, on prolonged heating, graphite structures are obtained with low surface functionality.

Thus, combustion of the PPE-HIPS blend in the UL 94 test produces a low-temperature char type, indicating that a temperature around 400°C should be reached by the burning surface of the material.

The volatility of the fire-retardant TPP is strongly reduced upon addition to the PPE-HIPS blends [Figs. 3(b), 4(b), and 5(c) and thermogravimetry in¹⁴]. This behavior could be explained on the basis of the studies of Djordjevic and Porter¹⁸ on an intermolecular interaction between PPE/PS, indicating that the driving force in the formation of the blend is the hydrogen bonding between the electron-deficient methyl group of PPE and π orbitals of the aromatic ring in PS. Thus, the evaporation of TPP may be delayed by quite similar interactions between methyl groups of PPE and aromatic rings of TPP. The TPP found in the combustion char [Figure 2(b)] suggests that the interaction is strong, contrasting the effect of temperature up to 400°C, (combustion charring temperature) as confirmed by sequential pyrolysis of Figure 9. Moreover, the presence of unextracted TPP in the char [Figures 6(b), 7(b), 11(a) and 11(b)] might indicate that fire-re-

Table II Assignment of TIC Chromathograms of Figures 8–11

Peak	Retention Time (min)	Polymer	Compound	Chemical Formula	Mass Weight
1	0.44	PBu	Butadiene	C ₄ H ₆	54
2	1.05		Benzene	C ₆ H ₆	78
3	1.78		Toluene	C ₇ H ₈	92
4	2.50		Ethyl–benzene	C ₈ H ₁₀	106
5	2.54	PBu	Dimeric butadiene	C ₈ H ₁₂	108
6	2.90		Xylene	C ₈ H ₁₀	106
7	3.34		Styrene	C ₈ H ₈	104
8	3.78		Isopropyl–benzene	C ₉ H ₁₂	120
9	4.01	PS	2-Methyl styrene	C ₉ H ₁₀	118
10	4.16		Propyl–benzene	C ₉ H ₁₂	120
11	4.54	PS	Phenol	C ₆ H ₆ O	94
12	4.56	PS	α-Methyl–styrene	C ₉ H ₁₀	118
13	4.64	PS	β-methyl–styrene	C ₉ H ₁₀	118
14	5.15		2,3-dihydro–1H-indene	C ₉ H ₁₀	118
15	5.19			C ₁₀ H ₁₀	130
16	5.36		1-Ethynyl–4-methyl–benzene	C ₉ H ₈	116
17	5.42		3-Butenyl–benzene	C ₁₀ H ₁₂	132
18	5.61		2-Methyl–phenol	C ₇ H ₈ O	108
19	5.66	PS	α-Ethyl–styrene	C ₁₀ H ₁₂	132
20	5.97		4-Methyl–phenol	C ₇ H ₈ O	108
21	6.34	PPE	2,6-Xylenol	C ₈ H ₁₀ O	122
22	6.62			C ₁₀ H ₁₄	134
23	7.06	PPE	Xylenol	C ₈ H ₁₀ O	122
24	7.35	PPE	Xylenol	C ₈ H ₁₀ O	122
25	7.44	PPE	2,4,6-Trimethylphenol	C ₉ H ₁₂ O	136
26	7.84	PPE	Trimethylphenol	C ₉ H ₁₂ O	136
27	8.10			C ₁₂ H ₁₄	158
28	8.20			C ₁₂ H ₁₄	158
29	9.54		Phenyl–cyclohexene	C ₁₂ H ₁₄	158
30	9.73	PPE	5-Methyl–benzenediol	C ₇ H ₈ O ₂	124
31	9.82			C ₁₃ H ₁₆	172
32	10.16		1,1'-Biphenyl	C ₁₂ H ₁₀	154
33	10.85		Diphenyl–methane	C ₁₃ H ₁₂	168
34	12.05		1,2-Diphenyl–ethane	C ₁₄ H ₁₄	182
35	12.48			C ₁₅ H ₁₆	196
36	13.63		1,3-Diphenyl–propane	C ₁₅ H ₁₆	196
37	14.54		1,4-Dephenyl–2-butene	C ₁₆ H ₁₆	208
38	14.63	PPE		C ₁₇ H ₁₈	222
39	15.49	PS	1,4-diphenyl–1-butene	C ₁₆ H ₁₆	208
40	16.04		(3,2',6'-trimethyl–4'-hydroxy) diphenylether	C ₁₅ H ₁₆ O ₂	228
41	16.31	PS	3-Methyl–1-styrene–indene	C ₁₈ H ₁₈	234
42	16.48	PPE	(2,6,3',5'-Tetramethyl–4-hydroxy) diphenylether	C ₁₆ H ₁₈ O ₂	242
43				C ₁₇ H ₁₈	220
44	16.95		Phenyl–naftalene	C ₁₆ H ₁₂	204
45	idem			C ₁₇ H ₁₆	220
46	17.04	PPE	(2,4,6,3'-Tetramethyl–4'-hydroxy) diphenylether	C ₉ H ₁₈ O ₂	242
47	17.16			C ₁₇ H ₁₆	220
48	17.45	PPE	(2,4,6,3',5'-pentamethyl–4'-hydroxy) diphenylether	C ₁₇ H ₂₀ O ₂	256
49	17.43	PS	1,4-Diphenyl–1,4-dimethyl–1,3-butadiene	C ₁₈ H ₁₈	234
50	17.99	PPE			238
51	18.27	PPE	(2,4'-Dihydroxy–3,3'-dimethyl) diphenyl–methane	C ₁₅ H ₁₆ O ₂	228
52	18.49		Benzyl–naftalene	C ₁₇ H ₁₄	218

Table II. Continued

Peak	Retention Time (min)	Polymer	Compound	Chemical Formula	Mass Weight
53	18.69	PPE	(2,4'-dihydroxy-3',5',6-trimethyl) diphenyl-methane	C ₁₆ H ₁₈ O ₂	242
54	18.87				
55	19.07	PPE	(2,4'-Dihydroxy-3,5,3'-trimethyl) diphenyl-methane	C ₁₆ H ₁₈ O ₂	242
56	19.43	PPE	(2,4'-Dihydroxy-3,5,3',5'-tetramethyl) diphenyl-methane	C ₁₇ H ₂₀ O ₂	256
57	19.96			C ₂₂ H ₂₂	286
58	20.04	PPE		C ₁₆ H ₁₆ O ₂	240
59	20.17				
60	20.74	PPE		C ₁₇ H ₁₈ O ₂	254
61	20.85	TPP	Triphenylphosphate	C ₁₈ H ₁₅ PO ₄	326
62	21.40	PS	Oligomer	C ₂₄ H ₂₄	312
63	22.03	PS	Oligomer	C ₂₄ H ₂₄	312
64	22.18	PS	Oligomer	C ₂₄ H ₂₄	312
65	22.31	PS	Oligomer	C ₂₄ H ₂₄	312
66	22.62	PS	Oligomer	C ₂₄ H ₂₄	312
67	22.94	PS	Oligomer	C ₂₄ H ₂₄	312
68	23.36	PS	Oligomer	C ₂₄ H ₂₄	312
69	23.68	PS	Oligomer	C ₂₄ H ₂₄	312
70	23.79	PPE	Oligomer	C ₂₄ H ₂₆ O ₃	362
71	24.04	PPE	Oligomer	C ₂₅ H ₂₈ O ₃	376

tardance may establish chemical bonds with the matrix.

The complexity of the chemical-physical interactions among components within the fire-retarded blend is pointed out also by the lowering of the temperature of styrene release in the pres-

ence of TPP [Figure 5(b)] as if competition was occurring between TPP and styrene in forming hydrogen bonds with PPE.

These results are in agreement with the condensed phase component of the fire-retardant action previously proposed for TPP,¹⁴ which could

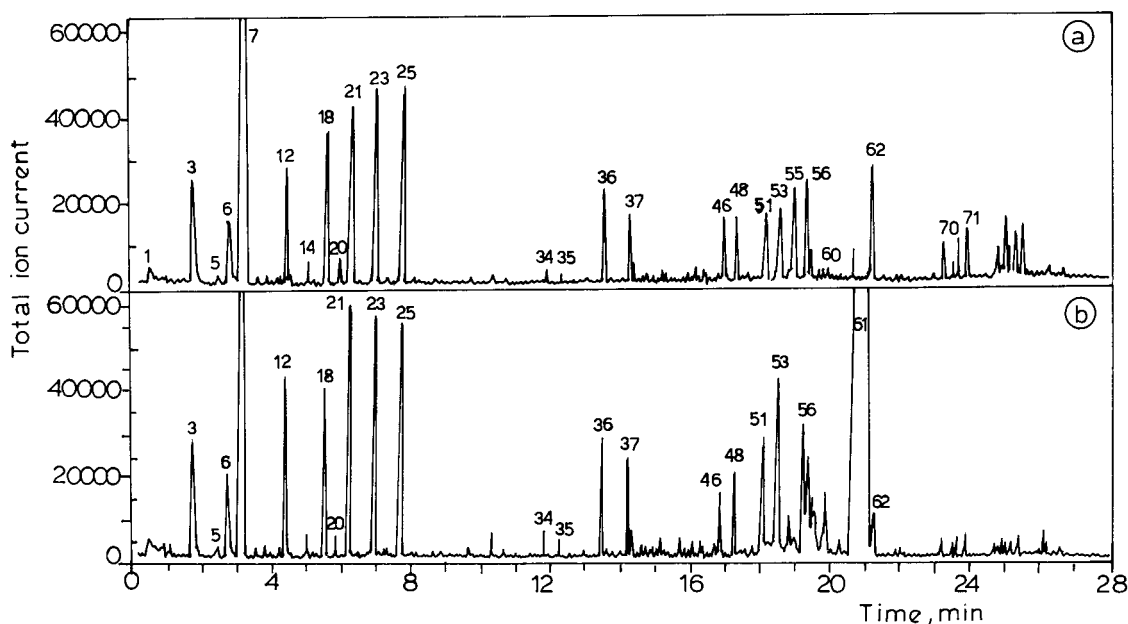


Figure 10 Total ion current curves in Py-GC-MS at 700°C of (a) PPE-HIPS blend and (b) fire-retarded blend.

Table III Py-CG-MS Analyses of PPE-HIPS Blends with and without TPP and Weight-normalized Peak Area Ratio of TIC Chromatograms Between Different PPE Fragments and Styrene

Structure	Peak Area Ratio (TPP, Wt. %)	0%		16.6%	
		Mean Value	St. Dev.	Mean Value	St. Dev.
Benzylic-type	25/7	0.0396	0.0026	0.0604	0.0061
Benzylic-type	51/7	0.0156	0.0026	0.0264	0.0030
Benzylic-type	53/7	0.0160	0.0026	0.0402	0.0021
Benzylic-type	55/7	0.0198	0.0042	—	—
Benzylic-type	56/7	0.0172	0.0031	0.0326	0.0084
Ether-type	46/7	0.0091	0.0025	0.0080	0.0006
Ether-type	48/7	0.0101	0.0008	0.0118	0.0008

not take place if TPP evaporated from the blend at 220–350°C, as it does when heated alone.

The condensed phase action of TPP might be attributed to its promotion of rearrangement of PPE chains to polybenzylic structures [Figures 9(b); Table III; Fig. 10]. Because the phosphoric ester (C_6H_5O)₃P=O can form hydrogen bonds,¹⁹ it could be thought that another strong TPP interaction with the matrix involves hydrogen bonding between TPP and the acidic species, such as the phenol functional groups formed on PPE rearrangement. On this basis, further stabilized polybenzylic structures should give a larger contribution to charring than original polyether segments.

Indeed, as far as the correlation between polymer charring, chemical structure and flammability is concerned, Van Krevelen²⁰ proposed a two-step degradation process for charring in which a primary char (equivalent to the above intermediate char) is formed on heating to 550°C with evolution of gas and high boiling products (tar). On further heating to 800–1000°C, a secondary decomposition would give the final or secondary char with elimination of gas rich in hydrogen. Linear correlation was found²⁰ between amount of secondary char measured from pyrolysis of polymers under nitrogen at 850°C (char residue, CR) and their fire retardance, as measured by the oxygen

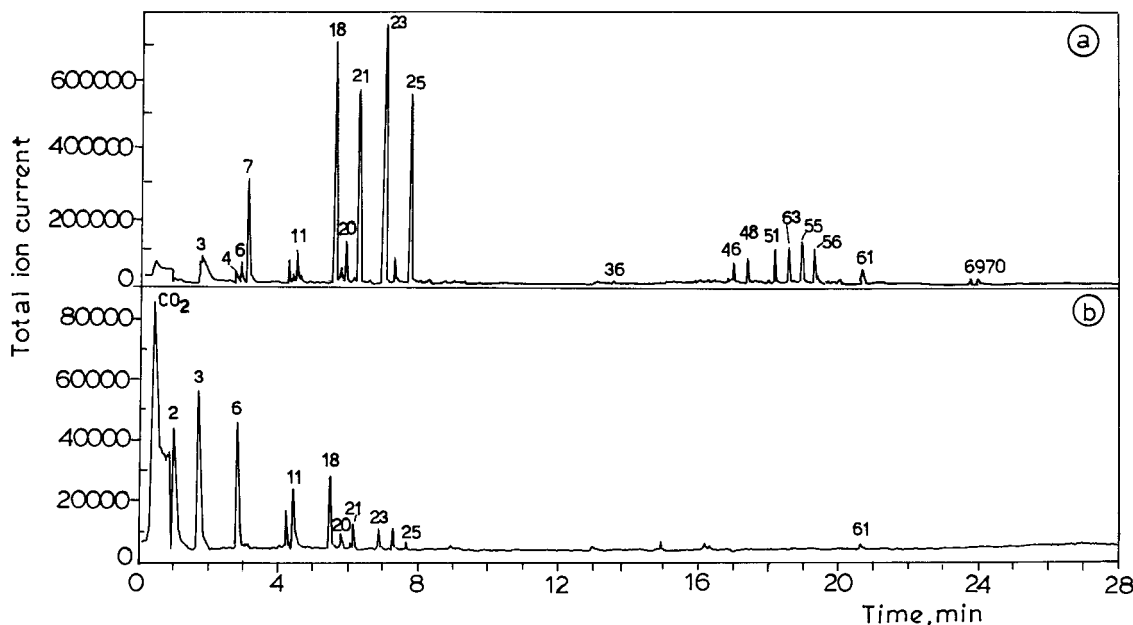


Figure 11 Total ion current curves in Py-GC-MS of PPE-HIPS fire-retarded combustion residue after extraction with $CHCl_3$ at the sequential temperatures of (a) 700°C and (b) 1000°C.

Table IV Oxygen Index (OI) and Char Residue Data at 800°C (Wt %) of PPE-HIPS Blend at Different TPP Content

TPP phr Content	0	5	10	20
OI	28	37	39	41
Residue	21	23	20	22
Residue calculated for 100 parts of neat PPE-HIPS blends	21	24	22	26
Residue calculated for 100 parts of neat PPE	32	37	34	41

index (OI) method, which gives the minimum oxygen concentration required for sustaining combustion.²¹

Moreover, it is proposed that the char forming tendency (CFT) of a polymer be an additive property, which may be calculated from group contribution typical of the constituents in the repeating unit. The calculation of CR based on CFT, as reported by Van Krevelen,²⁰ gives 30% of char from original PPE structures and 35% from the rearranged ones. Thus, the condensed phase action of TPP appears to be confirmed.

Experimental support is presented in Table IV, in which the residue obtained in thermogravimetry under nitrogen flow at 800°C from the blend with and without TPP is reported. Since, at 800°C, HIPS thermally decomposed, leaving no residue, and TPP was completely lost (Fig. 3(b) and 11(a) and 11(b)], the residue obtained from the material was due only to charring of PPE; so its yield could be calculated referring to neat PPE (Table IV). Thus, for example, in the absence of TPP, the residue was 21% w/w, which corresponds to the yield of 32% referred to the neat PPE in the blend (Table IV). In the case of the fire-retarded blends, the amount of residue can be referred to either the neat PPE-HIPS or neat PPE (Table IV). It can be seen that fraction of PPE that chars increases from 32 to 41% by the addition of 20 phr TPP to the PPE-HIPS blend. Apart from the absolute values for char yields of neat PPE, which is larger than calculated above, there is a fair agreement with Van Krevelen's data, which explain the increasing CR trend in the presence of TPP, as expected for CFT values from polybenzylic structure.²⁰

The PPE charring increase correlates with that of OI, as predicted by Van Krevelen, although also a contribution from gas phase flame inhibition effect was shown to be present particularly for TPP content $\leq 5\%$.¹⁴

This char increase from PPE would give a better contribution to the fire-retardant action, owing to its higher thermal stability and intumescent insulating structure.²²

Therefore, a relevant action of organophosphorus TPP compound in condensed phase by promotion of the rearrangement of the polymeric matrix with char enhancement has to be called upon.

It is worth noticing that our findings are not in contrast with the work of Carnahan et al.,²³ reporting a predominant gas phase fire-retardant activity for TPP in PPE-HIPS blends with high PS content (65 wt %). The above results indicate that the condensed phase action of TPP concerning the PPE component of the blend is discernible in the case where the blend is PPE rich, but it may become negligible with PPE poor blends.

CONCLUSIONS

Thermal degradation of the polystyrene and polybutadiene components of PPE-HIPS blends are the major contributors to combustible gases to the flame of the blend burning in the UL 94 test. Whereas PPE provides the combustion char, which is foamed by the gases evolved by thermal degradation (intumescent char). The IR spectrum of the combustion char shows that the temperature reached by the surface of the burning UL 94 specimen is about 400°C. During combustion, partial thermal rearrangement of polyether PPE chains to polybenzylic, phenol-formaldehyde resin type structures occurs, which gives a char yield on thermal degradation larger than the polyether ones.

In fire-retarded formulations, TPP, of which volatilization is delayed probably by hydrogen bonding with PPE, seems to promote the rearrangement, which, in turn, increases the char yield. Thus, a dual fire-retardant action is displayed by TPP. The gas phase chemical inhibition of the flame, typical of volatile phosphorus-containing compounds and a condensed phase charring effect.

REFERENCES

1. A. B. Boscoletto, M. Checchin, M. Tavan, G. Camino, L. Costa, and M. P. Luda, *Appl. Polym. Sci.*, **53**, 121 (1994).
2. American National Standard 1979, Standard for

- Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriters Laboratories, 1285 Walt Whitman Rd., Melville, NY 11747.
3. J. Troitzsch, *International Plastics Flammability Handbook*, Hanser, Munchen, 1983.
 4. W. R. Haaf, U.S. Pat. 3,639,506 (1972).
 5. H. Feldmann and P. Steinert, *Kunststoffe Germ. Plast.*, **80**, 36 (1990).
 6. A. M. P. Fuller and P. R. Griffiths, *Anal. Chem.*, **50**, 1906 (1978).
 7. A. K. Mukherji, M. A. Butler, and D. L. Evans, *J. Appl. Polym. Sci.*, **25**, 1145 (1980).
 8. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, Boston, 1990.
 9. A. Factor, *J. Polym. Sci.*, **A-1**, 363 (1969).
 10. J. Jachowicz, M. Kryszewski, P. Kowalski, *J. Appl. Polym. Sci.*, **22**, 2891 (1978).
 11. S. Takayama, *Polym. Degrad. Stab.*, **50**, 277 (1995).
 12. K. Takeda, *J. Appl. Polym. Sci.*, **64**, 1175 (1997).
 13. C. Morterra and M. J. D. Low, *Mater. Lett.*, **2**, 289 (1984).
 14. M. Checchin, A. B. Boscoletto, G. Camino, M. P. Luda, L. Costa, *Makromol. Chem., Macromol. Symp.*, **74**, 311 (1993).
 15. J. Jachowicz, M. Kryszewski, *Polymer*, **19**, 93 (1978).
 16. G. J. Mol, R. J. Gritter, G. E. Adams, *Application of Polymer Spectroscopy*, Academic Press, 1978, pp. 257–277.
 17. G. Camino, M. P. Luda di Cortemiglia, L. Costa, L. Trossarelli, in *Thermal Analysis*, Vol. 2, B. Miller, Ed., Wiley, New York, 1987, p. 1137.
 18. M. B. Djordjevic and R. S. Porter, *Polym. Eng. Sci.*, **23**, 650 (1983).
 19. E. Cherbuliez, in *Organic Phosphorus Compounds*, G. M. Kosolapoff and L. Maier, Eds., Wiley-Interscience, 1973, pp. 344–345.
 20. D. W. Van Krevelen, *Polymer*, **16**, 615 (1975).
 21. C. P. Fenimore and F. J. Martin, *Combust. Flame*, **10**, 135 (1966).
 22. A. B. Boscoletto, M. Checchin, L. Milan, G. Camino, L. Costa, and M. P. Luda, *Makromol. Chem., Macromol. Symp.*, **74**, 35 (1993).
 23. J. Carnahan, W. Haaf, G. Nelson, G. Lee, V. Abolins, P. Shank, *Proceedings of the 4th International Conference on Flammability and Safety*, San Francisco, CA, Jan. 15–19, 1979.