

Flame-Retardant Properties of Phenol–Formaldehyde-Type Resins and Triphenyl Phosphate in Styrene–Acrylonitrile Copolymers

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ABSTRACT: The thermal and flame-retardant properties of phenol–formaldehyde-type resins (crosslinked and noncrosslinked) in mixtures with triphenyl phosphate and styrene–acrylonitrile resins were evaluated. The mixtures show a synergistic effect between triphenyl phosphate and novolacs. Those containing phenol–formaldehyde novolac resins are found to be most flame retardant. There does not seem to be a relationship between the oxygen index (OI) and UL 94 tests. Scanning electron microscopy analysis show a surface structure with cavities and stratification, very similar to that of intumescent additives. Evidence was found indicating that this flame-retardant system works in both the gas and condensed phase. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1067–1076, 1998

Key words: flame retardants; phenol–formaldehyde resins; novolacs; styrene–acrylonitrile resin; triphenyl phosphate

INTRODUCTION

A number of studies have been carried out to study the thermal degradation of phenol–formaldehyde polycondensate.^{1–12} In our previous work¹³ the thermal behavior of three different novolacs was analyzed in the absence of flame. Here, the same resins have been studied in the presence of a flame in order to understand and compare their flame-retardancy mechanism. These resins have been tested together with triphenyl phosphate (TPP) as coflame retardants in mixtures with a styrene–acrylonitrile (SAN) polymer. We use SAN not for its importance itself (although it does have applications requiring flame retardancy),

but to have a simple model for ABS, wherein the role of the rubber could be avoided.

Previously, studies have focused on TPP and other phosphorus compounds, to find out whether these phosphorus compounds act primarily in the gas phase or in the solid phase or both. Both gas- and solid-phase mechanisms were shown to occur.^{14–17} Gas-phase effects are due to flame inhibition by phosphorus compounds introduced by the volatilization of TPP and/or its degradation products.^{15–17} Condensed phase activity is due to interaction with other flame-retardant additives or with the polymer.^{14–17} This interaction delays the evaporation of TPP, which therefore undergoes thermal degradation.¹⁸ Earlier studies have been reported on aryl phosphate novolac combinations in ABS,¹⁹ and such combinations are also mentioned in various patents.

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EXPERIMENTAL

Materials

Three different types of novolacs were used: phenol–formaldehyde (PH-F), *m*-cresol–formaldehyde (MC-F), and *p*-cresol–formaldehyde (PC-F), which were either laboratory samples (PH-F/S, MC-F/S, PC-F/S, S = synthesized) or commercial samples (PH-F/C, MC-F/C, PC-F/C, C = commercial).

The commercial samples were supplied respectively by Oxychem, Durez Division, New York; Durez 22091, $M_n \approx 8000$ – $10,000$ a.m.u. (PH-F/C) and by Schenectady International, Inc., New York; HRJ-2729, $M_n \approx 4000$ – 5000 a.m.u., m.p. $\approx 168^\circ\text{C}$ (MC-F/C) and HRJ-2900, $M_n \approx 50,000$ a.m.u., m.p. $\approx 120^\circ\text{C}$ (PC-F/C).

The synthesis of laboratory samples was based on Japanese Patent JP 02,127,461 [90,127,461].²⁰ The phenols were added to an aqueous solution of formaldehyde (7% formaldehyde by weight) (phenol–formaldehyde molar ratio 0.95). This solution was added slowly (1.5 h) with stirring to an aqueous HCl solution (20% HCl by weight) preheated to 70°C . When the addition was completed, the precipitated resins were filtered, milled, washed in hot water, and then dried under pump vacuum at room temperature overnight. Using this method, we obtained resins that were easy to mill and to compound with polymeric materials. Owing to the treatment under vacuum and from the results of TG analysis¹³ we can exclude the presence of low molecular compounds.

The commercial and laboratory samples gave the same IR spectra but the latter were insoluble in typical solvents for novolacs (acetone, methanol, *N,N*-dimethylformamide, 1,4-dioxane, tetrahydrofuran, 1-butanol, methyl ethyl ketone, chloroform, methylene chloride, and dimethyl sulfoxide), showing that they were crosslinked. Likewise, they did not melt below 320° on the hot stage microscope. These results are in agreement with the literature that shows when strong acid is used as the catalyst, a crosslinked resin is obtained.²¹

Both commercial and laboratory samples were sieved to 200 mesh (75 micron) to facilitate obtaining uniform mixtures with the polymer.

The flammability tests for these phenolic resins were carried out on mixtures of each of them with the copolymer styrene–acrylonitrile (SAN) combined with triphenylphosphate (TPP) as a second

flame retardant and with an antioxidant. SAN was supplied by DSM Kunststoffen, The Netherlands, acrylonitrile 27%, styrene 73%; melt flow index (220°C , 10 kg) = 3.5 g/min. TPP (commercial name Phosflex TPP) was supplied by Akzo Nobel Chemicals Inc., Chicago, IL, and the antioxidant Irganox 1076 was from Ciba.

The mixtures were processed in a Brabender Plasti-Corder (type PL-V302) mixer at 210 – 220°C and 60 rpm for 15 min and were subsequently pressed at 190°C to prepare the samples for the OI and UL 94 tests.

Thermogravimetry (TG)

Each sample (6–10 mg) was examined both under nitrogen and air flow on a DuPont 2950 thermobalance with either platinum or ceramic sample holders, at a heating rate of $10^\circ\text{C}/\text{min}$ to 800°C .

Oxygen Index (OI) Determination

OI (ASTM D2863) measures the ease of extinction of materials, and is the minimum percent of oxygen in an oxygen/nitrogen atmosphere that will just sustain combustion in a candle-like configuration of a top-ignited vertical test specimen. The apparatus used was by Stanton Redcroft and the deviation standard was ± 0.4 unit. The char produced by the samples was characterized with FTIR spectrophotometry in KBr pellets, and in some case with P analysis.

UL 94 Testing

The vertical test was used, in which a specimen held vertically is ignited by the flame of a gas burner applied twice for 10 s to the bottom, following the procedure reported in the literature.²¹ Materials are classified depending on time of extinguishment of the flame after each ignition and on whether combustion occurs with dripping of flaming particles, capable of igniting surgical cotton placed underneath the specimen.

Time of flame extinguishment decreases from class V-1 to V-0. Ignition of the cotton leads to a V-2 classification independently of the extinguishment time if it is shorter than or equal to that of class V-1; otherwise, the material is nonclassified. Thus, fire retardance is considered to improve in the sequence V-2, V-1, V-0. The soot carried by the smoke developing from the burning samples

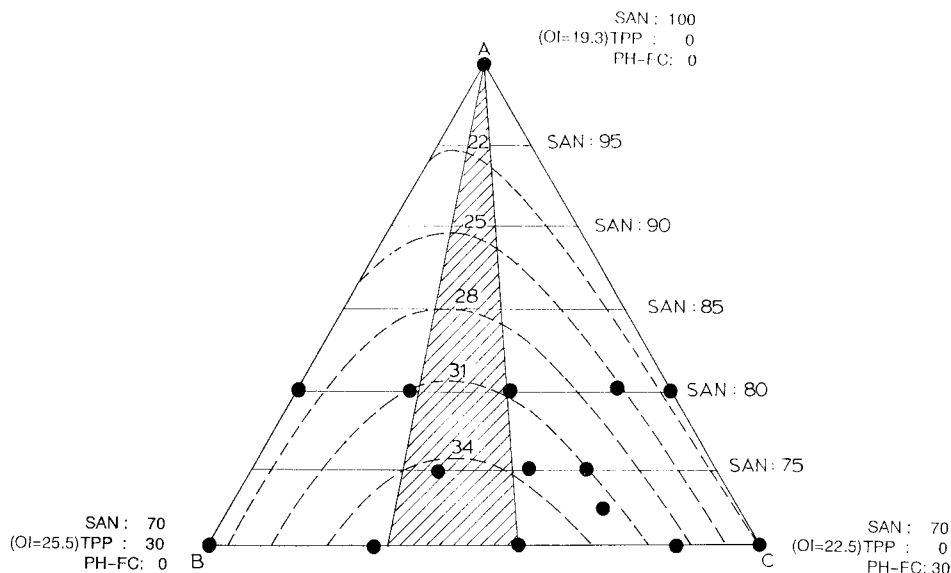


Figure 1 Iso-OI curves of SAN + TPP + PH-F/C mixtures. Composition as wt % is indicated at vertices. Figures on the curves are OI values.

was collected on a microscope glass and characterized with FTIR spectrophotometry in KBr pellets.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy of the surface of the char obtained from three or more OI test of each sample was carried out using a Leica Stereoscan 420 instrument. The specimens were previously coated with graphite to reduce surface charging effects. The magnification used was 1750.

RESULTS AND DISCUSSION

Evaluation of Flammability of Various Compositions

To select the mixture composition with the highest flame retardancy a study was conducted and 15 samples were prepared containing the PH-F/C in various concentrations. These samples were tested for OI and UL 94 values. This research was based on the ternary diagram shown in Figure 1 where A, B, and C correspond, respectively, to these concentrations: A = (1,0,0) 100% SAN; B = (0.7,0.3,0) 70% SAN + 30% TPP; C = (0.7,0,0.3) 70% SAN + 30% PH-F/C.

On the AB side of the triangle are the SAN/TPP mixtures, which have OI values that increase with increasing TPP concentration, reach-

ing a maximum of 25.3 with 30% of TPP. The AC side represents the SAN/(PH-F/C) novolac blends: also, in this case, OI values increase with increasing PH-F/C concentration but the maximum is only 23.0 with 30% of novolac and the increase is less pronounced. The SAN/TPP mixtures easily have a UL 94 result of V-0 (Fig. 1, AB side), while the SAN/novolac mixtures, with the same composition, only have V-2 (Fig. 1, AC side). Therefore, TPP as a single flame retardant has a higher effect than the PH-F/C resin, as far as the UL 94 test is concerned. It has been noticed that the samples containing both the TPP and the novolac as flame retardants reach higher OI and UL 94 values than the corresponding samples with the same total flame-retardant concentration, but containing only one of the two additives. This indicates the occurrence of synergism between TPP and PH-F/C.

Furthermore, for the mixtures with the same total flame-retardant amount, the best samples are those containing a TPP/novolac ratio between 2.3 : 1 to 1.5 : 1, as is shown in Figure 1 (the outlined area). We expect that the OI behavior of the other novolac would be the same but we did not investigate it.

Guided by the foregoing study, three compositions with different amounts of total fire retardant and with TPP/novolac ratio circa 2 : 1 were chosen for all the novolacs, and they are shown in Table I.

Table I TPP/Novolac Formulations

Sample No.	SAN (%)	TPP (%)	NOV (%)	Total Additive (%)
1	80	14	6	20
2	75	17	8	25
3	70	20	10	30

Oxygen Index and UL 94

The results for each novolac are as in Table II.

The OI and UL 94 classification improve as the amount of total additive increases. However, for the PC-F resins, even through the UL 94 classifications increase, the OI levels remain essentially the same. Also, the burning specimen developed soot and charring material, except for the case of the *p*-cresol-formaldehyde novolacs. Therefore, the PC-F resins do not appear to be good flame-retardant components.

As for the other samples, the PH-F resins have a better flame-retardant activity than the MC-F at the same concentrations because they reach higher OI. Moreover, the commercial novolacs are better than the corresponding laboratory phenolic resins, leading to the conclusion that the absence of crosslinking gives a better flame-retardancy contribution.

There does not seem to be a relationship between the OI and UL 94 tests because the UL 94 values depend only on the amount of TPP added, regardless of the novolac used, while the OI values are clearly dependent on the TPP–novolac synergism and on their ratio. Also, during the study reported in Figure 1, the highest OI values were obtained for a TPP/novolac ratio of 2/1, but this was not true for the UL 94 results. Other studies²³ have already reported that these two tests are not closely comparable to each other except for very high levels of flame retardancy that would produce high OI results and V-0. As a matter of fact, Table II shows that samples with OI > 30.0 have a V-0, but for lower OI values the UL 94 results do not correspond anymore.

Thermogravimetry

For a better understanding of the flame retardancy, the thermal behavior of these mixtures has been studied through TG analysis. This data was compared with that for pure SAN and pure TPP.

For the sample containing the PH-F/S, the composition numbers 2 (Table I) were used; for all the other resins the number 3 mixture was studied. The results concerning the PC-F/S and PC-F/C novolacs will not be reported because they have little or no effect as flame retardants, as demonstrated in the discussion above; therefore, we had little interest in considering their thermal behavior for comparison.

Results Under Inert Atmosphere

Figure 2 shows the TG of pure SAN [Fig. 2(a)], pure TPP [Fig. 2(b)] and of the mixtures containing the PH-F/C [Fig. 2(c)] and the MC-F/C [Fig. 2(d)] under a flow of nitrogen. Pure SAN shows one degradation peak in the DTG (derivative) curve at 393°C, with total weight loss. Pure TPP evaporates almost completely in one step with maximum rate at 235°C; at about 520°C the DTG curve shows another very small peak that can be caused by loss of impurities initially present in the TPP. The behavior of this sample is exactly the same under a flow of nitrogen or of air; therefore, only one thermogram will be used for both in this study.

Table II Flammability Results

Total Additive (%)	A			
	PH-F/C		PH-F/S	
	OI	UL 94	OI	UL 94
20	35.7	V2	26.2	V2
25	38.0	V1	28.8	V2
30	41.0	V0	30.7	V1
	B			
	MC-F/C		MC-F/S	
	OI	UL 94	OI	UL 94
20	28.8	V2	25.0	V2
25	30.2	V1	26.2	V2
30	33.0	V0	27.4	V1
	C			
	PC-F/C		PC-F/S	
	OI	UL 94	OI	UL 94
20	22.8	V2	22.4	V2
25	22.6	V1	23.1	V1
30	23.0	V0	—	—

All the mixtures have very similar behavior with a weight loss of 20% of the initial weight at about 225–238°C, due to volatilization of TPP. Another major weight loss occurs with maximum rate at 390–394°C, caused by degradation of SAN. A comparison has been made for each mixture between the experimental TG curve and another curve obtained by calculation. This calculation was accomplished by linear combination of the individual TG curves of SAN, TPP, and novolac heated in the same conditions but separately, taking into consideration the different amount of each component in the mixture. Figure 2(c) reports the result of this comparison for the mixture containing the PH-F/C; Figure 2(d) reports the same kind of result for the mixture containing the MC-F/C. Only these two novolacs are considered because all the others showed the same results.

In both cases, between 200 and 350°C the experimental curves (1) show more stability than the calculated curves (2), probably because the volatilization of the degradation products in the actual mixture is delayed by the presence of barrier-producing components in the surface of the melted sample. Again, the experimental curve shows more stability also in the second major weight loss, which occurs at higher temperature than for the calculated curve. This is evidence that the synergism between TPP and the novolac delays the degradation process.³ The stabilization is lower for the mixture containing the MC-F/C, which has, in fact, a lower OI value [Table II(B)].

Results Under Air

Figure 3 shows the TG of pure SAN [Fig. 3(a)], pure TPP [Fig. 3(b)], and of the mixtures containing the PH-F/C [Fig. 3(c)] and the MC-F/C [Fig. 3(d)] under a flow of air. The thermogram of pure SAN shows two steps of weight loss—one of about 95% that corresponds to a peak in the DTG at 371°C, followed by another small peak at 521°C. The behaviors of SAN in air and in nitrogen are very similar, with one main step of degradation that occurs at a lower temperature (about 20° less) in air because of some action of oxygen. In this case there is also a second peak in the DTG at a higher temperature, probably due to the effect of oxygen in causing a temporary carbonization, which later gets oxidized. As for TPP, the thermogram is exactly the same as described before.

All the mixtures have the same behavior also in the presence of air with a first step of weight

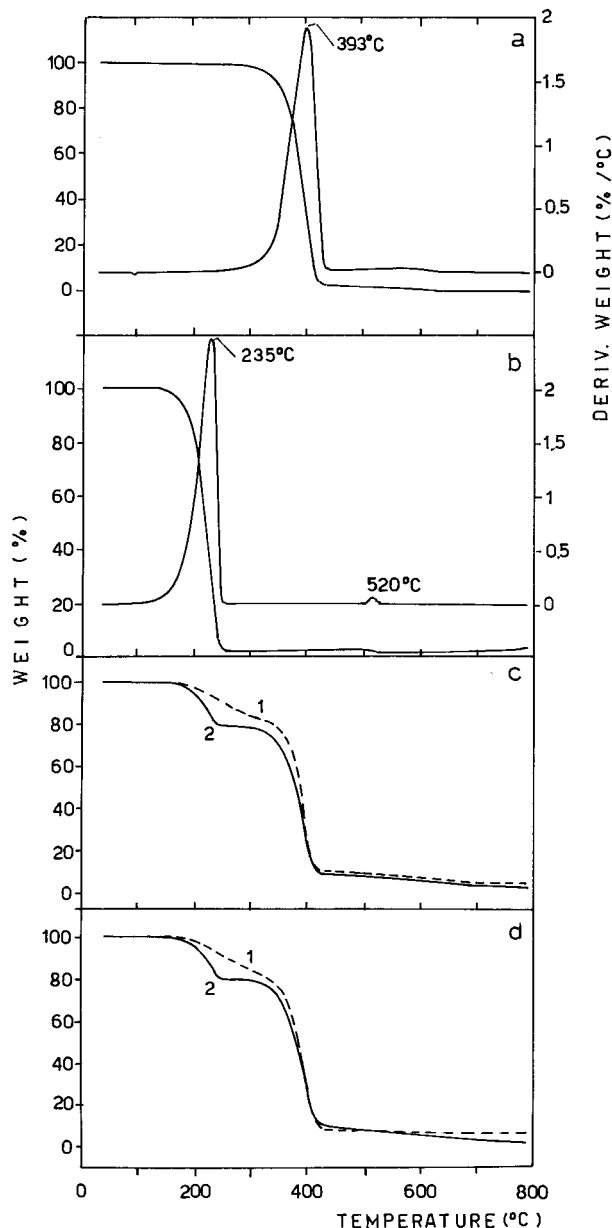


Figure 2 TG curves. Heating rate: 10°C/min under a nitrogen flow of 60 cm³/min. (a) SAN; (b) TPP; (c) 70% SAN + 20% TPP + 10% PH-F/C; (---) experimental, (—) calculated; (d) 70% SAN + 20% TPP + 10% MC-F/C; (---) experimental, (—) calculated.

loss of 20% with maximum rate at 225–238°C, due to volatilization of TPP. Secondly, there is a weight loss of 70% corresponding to a peak at 380–388°C in the DTG, due to loss of SAN, as can be seen from the thermograms of pure SAN in Figure 3(a). There is a third step, which was not present in the thermograms under flow of nitrogen, revealed by a peak at 505–515°C in the DTG.

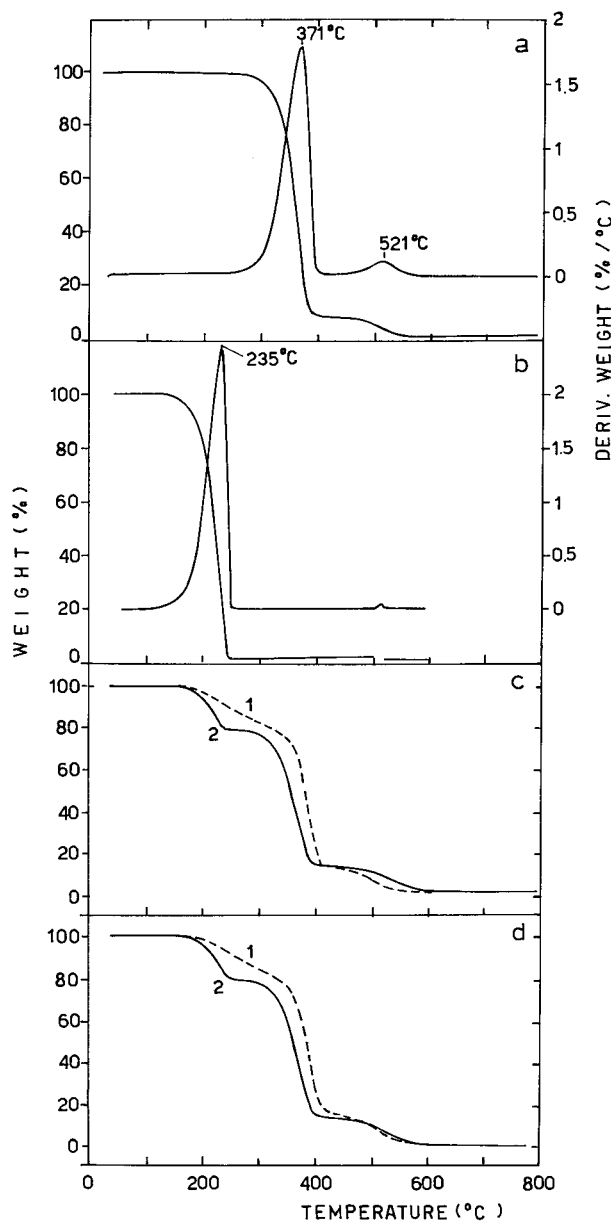


Figure 3 TG curves. Heating rate: 10°C/min under air flow of 60 cm³/min. (a) SAN; (b) TPP; (c) 70% SAN + 20% TPP + 10% PH-F/C; (---), experimental, (—) calculated; (d) 70% SAN + 20% TPP + 10% MC-F/C; (---) experimental, (—) calculated.

This, again, corresponds to the second peak in the thermogram of pure SAN [Fig. 3(a)]. All the weight loss steps occur at lower temperature than in the presence of nitrogen, because of the degradative action of oxygen.

Also, in this case, a comparison has been made between the experimental curves and the calculated curves of the mixtures, and only two are

reported as an example. The results of this study are the same as described for the thermograms in the presence of nitrogen, except for the fact that the stabilization showing by the experimental curves (1) is higher in this case. Phenolic compounds are also known as antioxidants; therefore, it is possible that in the presence of oxygen, some antioxidant activity may be added on to the synergism between the flame retardants further stabilizing the samples below 400°C.

Infrared Analysis

For each sample the char obtained from the OI test and the soot volatilizing during the UL 94 test have been analyzed with FTIR spectrophotometry in KBr pellets. All the mixtures gave the same results; therefore, only one will be reported for all.

Figure 4(a) shows the IR spectrum of the mixture containing the PH-F/S with 30% total additive, as is, for comparison (all the mixtures have

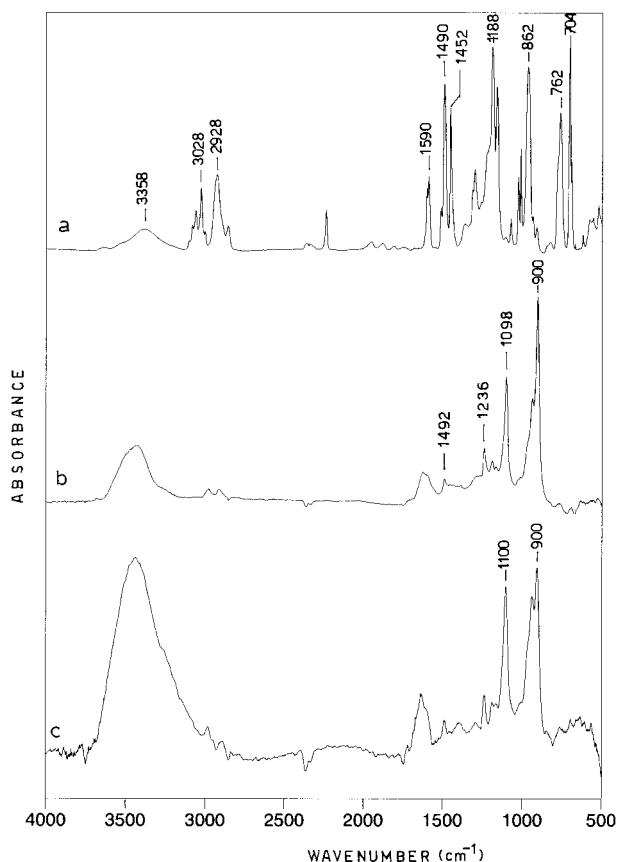


Figure 4 FTIR spectra of 70% SAN + 20% TPP + 10% PH-F/C: (a) original; (b) char; (c) soot.

this same spectrum). Figure 4(b) shows the IR spectrum of the char obtained from the mixture containing the PH-F/C with 30% total additive, and Figure 4(c) reports the spectrum of the soot obtained from the same sample. It can be noticed that the main polymer structure disappeared in the char and in the soot samples, but some phosphorus-containing compound remains, although not TPP; also, peaks due to aromatic rings can be detected.

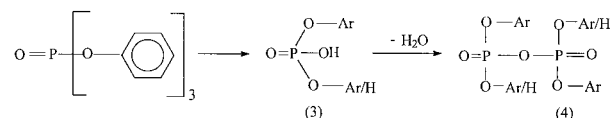
The char and the soot spectra are almost identical except for a different amount of moisture content that is responsible for the broad and intense absorption centered at 3500 cm^{-1} and for the broad band at $1600\text{--}1620\text{ cm}^{-1}$ in Figure 4(c). Therefore, the soot produced during the UL 94 test appears to contain or even mainly comprise char carried by the smoke developing from the burning sample or the reactions are the same in the condensed and gas phase.

The absorption at 3500 cm^{-1} can be due to the stretching OH of P—OH and the absorption at $1600\text{--}1620\text{ cm}^{-1}$ can also be ascribed to the quadrant stretching of aromatic rings, both evident in Figure 4(b,c).

The very weak peak at 1489 cm^{-1} in Figure 4(b,c) may be assigned to semicircular stretching of mono-substituted aromatic rings.²⁴ Phosphorus compounds can be detected by the absorption at 1236 cm^{-1} of weak intensity ascribed to P=O stretching; a 1185 cm^{-1} peak due to PO—Ar stretching²⁴; a strong absorption at 1098 cm^{-1} can be caused by stretching of P=O bonds in POH group containing compounds²⁴; the broad absorption at 900 cm^{-1} is ascribed to asymmetric stretching of P—O—P bonds and also to P—OAr stretching in pentavalent phosphorus compounds.

These spectra belong to phosphorus-containing organic compounds derived from the thermal degradation of TPP. Pure TPP tends to evaporate completely [Fig. 2(b)], but, in the presence of novolacs, part of it must be undergoing a reaction because it is retained in the sample at higher temperature. Similarly to previous related studies, it presumably has undergone interaction with the other additives.¹⁶ In fact, from Figures 2(c,d) and 3(c,d), the first step of weight loss corresponding to loss of TPP occurs at slightly higher temperatures than in the thermogram of pure TPP [Fig. 2(b)]. Therefore, the degrading TPP could produce OH-containing structures (3) that are not stable at the surface temperature of the burning

polymer ($>400^\circ\text{C}$), and they condense to soluble pyrophosphoric esters (4):



The presence of phosphorus in the char has been confirmed with quantitative phosphorus analysis on the samples containing the PH-F/C and the PH-F/S with 30% total additive. About 1.5% of total phosphorus was found, of which about 10% is soluble in water. This also confirms also the fact that part of TPP degrades producing compounds such as structure (4).

Scanning Electron Microscopy (SEM)

Figure 5 shows the photographs of the burned OI samples of the mixtures, taken with the SEM with a magnification of 1750. Pure SAN (OI = 19.3) is represented in Figure 5(a): this burned sample has, to the unaided eye, a smooth brown surface, which, after magnification, looks very rough with small cavities of $5\text{ }\mu\text{m}$ in diameter. By contrast, the burned samples of the mixtures have, to the unaided eye, the appearance of a black charred material, which is soft and sticky.

Figure 5(b,c) show the appearance under magnification of the mixtures containing the PH-F/C (OI = 41.0, UL 94 = V-0) and the PH-F/S (OI = 30.7, UL 94 = V-1), respectively, with 30% of total additive. Both pictures show deep cavities with stratifications, but with different dimensions. In Figure 5(b) the diameters are about $30\text{--}40\text{ }\mu\text{m}$, and the thickness of the separating walls goes from $3\text{ to }13\text{ }\mu\text{m}$. In Figure 5(c), instead, the diameters are smaller, about $20\text{ }\mu\text{m}$, and the walls are $10\text{--}15\text{ }\mu\text{m}$ thick; moreover, in this case there is less stratification and less deepness in the cavities, and the aspect is slightly closer to that of a melted material. As a matter of fact, this sample has much lower OI and UL 94 results.

Figure 5(d,e) belong to the mixtures containing the MC-F/C (OI = 33.0, UL 94 = V-0) and the MC-F/S (OI = 27.4, UL 94 = V-1), respectively, with 30% of total additive. These two samples are very similar one to the other and have the same surface already described, with cavities of $30\text{--}40\text{ }\mu\text{m}$ in diameter and wall thickness from $3\text{ to }14\text{ }\mu\text{m}$. Only, in these cases, the number of

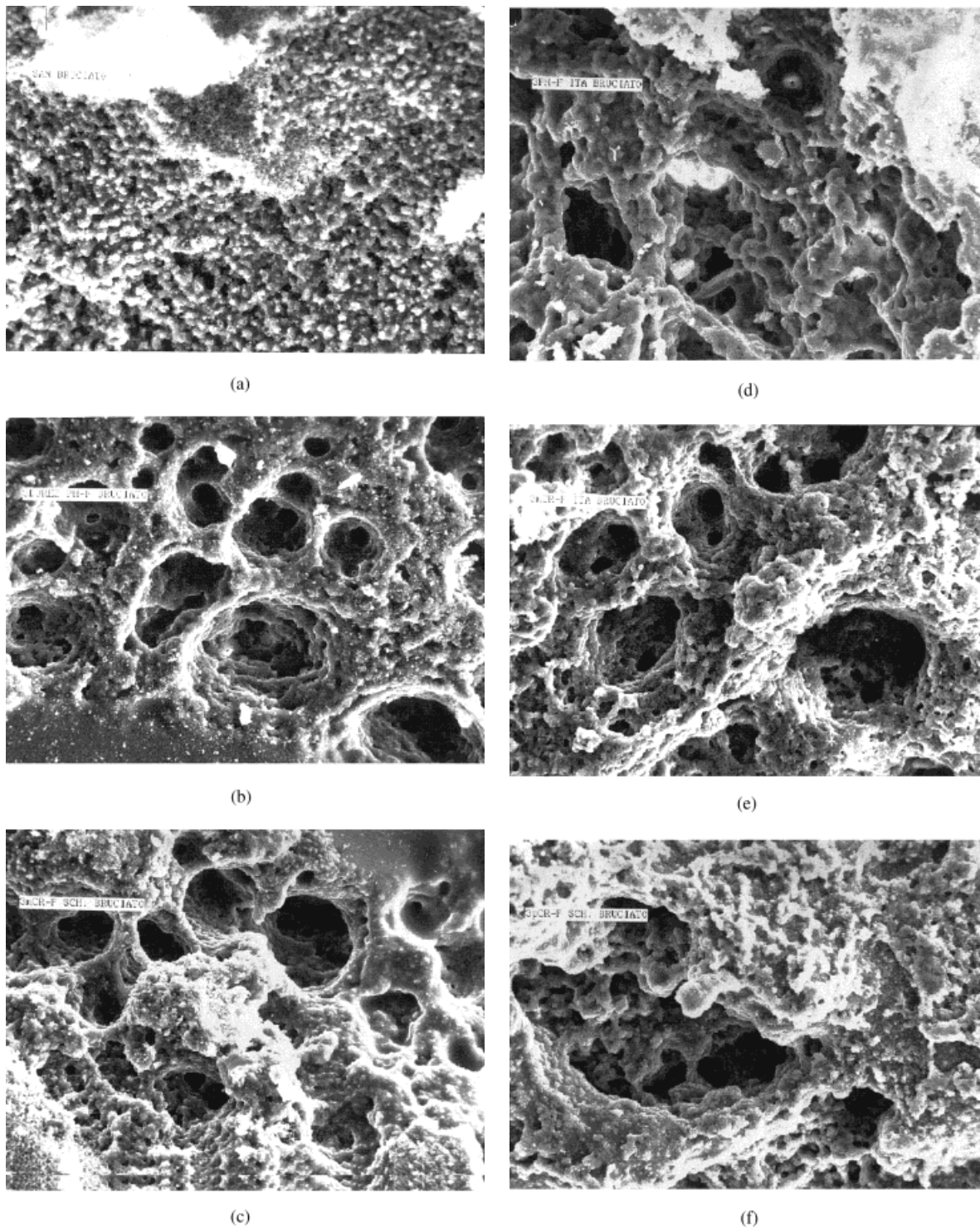


Figure 5 SEM micrograph of burning surface after OI test ($\times 1067.5$). (a) pure SAN; (b) mixtures 70% SAN + 20% TPP + 10% PH-F/C; (c) mixtures 70% SAN + 20% TPP + 10% PH-F/S; (d) mixtures 70% SAN + 20% TPP + 10% MC-F/C; (e) mixtures 70% SAN + 20% TPP + 10% MC-F/S; (f) mixtures 70% SAN + 20% TPP + 10% PC-F/C.

cavities in the same area is lower than for the samples containing the PH-F resins.

The last figure [5(f)] represents the sample containing the PC-F/C (OI = 23.0, UL 94 = V-0). This picture is very similar to Figure 5(a) of pure SAN, and it has very few big cavities with hardly any stratification. It is more the picture of a melted material. The photograph of the sample containing the PC-F/S has been omitted because it shows the same situation as in Figure 5(f).

All these samples, however, do not have a homogeneous surface, but some areas with the cavities as just shown and some with an almost smooth and flat surface; moreover, the dimensions of the cavities may vary from one area to another in the same sample.

It can be concluded that this flame-retardant system has some activity in the surface of the material that is very close to that of intumescent additives. These additives always require the presence of one acid compound, which in this case could be brought by structures like (4), together with a char-forming material like a phenolic resin.

CONCLUSIONS

The mixtures containing the noncrosslinked commercial novolacs must be considered more flame retardant. The level of crosslinking is important when interaction with other additives is concerned as well as activities such as intumescence. Both these aspects involve reactions with other compounds or rearrangements of the main structure that are difficult for a crosslinked polymer because of its rigidity.

Among the different type of novolacs used, the phenol-formaldehyde was best as a flame retardant, because the mixtures containing it reached higher OI and UL 94 values than the others, at the same concentration. The *m*-cresol-formaldehyde novolac came right after, while the *p*-cresol-formaldehyde novolac had almost no effect as a flame retardant. This ranking could even be seen with the crosslinked phenolic resin.

As for the TPP-novolac system, synergism has been proved between these two additives, because OI values tend to increase much more with increasing concentration of the total of the two additives than with increasing concentration of one of the two in binary mixtures with SAN. Also, the comparison between the experimental TG curve of the mixture and the calculated curve confirmed

the fact that these additives are interacting, because the experimental TG shows more stability than the calculated one. It has also been noticed that the volatilization of TPP occurs at higher temperatures when added to the mixtures; consequently, there is also some degradation of TPP because it remains inside the material reaching the degradation temperature. This confirms what others had already found.¹⁶

The results are best explained by considering that this flame-retardant system works both in the gas and in the condensed phase. The gas-phase activity is surmised by the fact that most TPP evaporates, as seen by the TG and by the phosphorus analysis. For the condensed-phase activity instead, both the additives are responsible. This has been observed from the comparison between the experimental TG curve of the mixture and the calculated curve: the experimental TG shows a higher stability of the real material. Moreover, evidence of condensed-phase activity has also been obtained from the SEM analysis, which showed a surface structure with cavities and stratification, very similar to that of intumescent flame retardants, that involves rearrangements of the configuration of the condensed phase.

Therefore, it is further indicated that TPP is active not only in the gas phase but also in the condensed phase.

Although we had not originally intended to study crosslinked phenolics, we now recognize that their utility as possible flame-retardant additives is deserving of study from the standpoint of recycling of waste phenolic plastics; therefore, further comparison of crosslinked and noncrosslinked phenolic resins is of more than academic interest.

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