

Flame Retardancy of Polypropylene and Impact Polystyrene: Phosphonium Bromide/Ammonium Polyphosphate System

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Synopsis

The individual and the combined effects of the phosphonium salt Cyagard RF-1 and ammonium polyphosphate on the oxygen index of polypropylene and high-impact polystyrene have been studied. The synergistic action of the two flame retardant components is evaluated quantitatively, and a correlation between char yield and synergism is discussed. The chars are characterized in terms of their elemental composition.

INTRODUCTION

Flame retardation of organic polymers by phosphorus compounds is assumed to involve, in most cases, condensed phase reactions of the flame retardant/polymer system that occur during the course of combustion.¹ In many instances, flame retardation by way of condensed phase action can be inferred from an increase in char yield during burning.

Mixtures of thermally stable phosphonium salts such as Cyagard RF-1 {ethylene-bis[tris(2-cyanoethyl)]phosphonium bromide} with ammonium polyphosphate (APP) have been reported to be effective condensed-phase flame retardants for thermoplastic polymers such as polypropylene² (PP) and high-impact polystyrene³ (HIPS). The present report gives a quantitative treatment of the oxygen index effects, the char yields, and the char compositions for the flame retardant system Cyagard RF-1 flame retardant/APP in both PP and HIPS.

EXPERIMENTAL

Materials

Cyagard RF-1 flame retardant {ethylene-bis[tris(2-cyanoethyl)]phosphonium bromide} was manufactured by American Cyanamid, ammonium polyphosphate, Phos-Chek P/30, by Monsanto. Polypropylene was Profax 6401 by Hercules, stabilized with 0.1% pentaerythrityl tetrakis[3(3,5-di-*t*-butyl-4-hydroxyphenyl)]propionate and 0.2% Cyanox STDP (3,3'-distearyl thiodipropionate) antioxidant from American Cyanamid. Polystyrene by Cosden Oil Co. was impact grade 825 TV.

Sample Preparation

The polymer was dry blended with the additive and extruded through a melt index apparatus at a temperature of 280°C in the case of polypropylene and 235°C in the case of impact polystyrene.

Test Methods

The flammability of the samples was determined in terms of the oxygen index according to ASTM D-2863. The measurements were carried out with a General Electric flammability gauge.

Determination of Char Yields

The preweighed sample was placed in the oxygen index (OI) tester in an oxygen atmosphere with an oxygen content slightly above the OI for this particular sample. The sample was then ignited and burned until about 50% of it had been consumed. The oxygen flow was then cut off and the burned sample was left to cool in nitrogen. The sample was then weighed and the char layer was removed mechanically. From the weight loss of the sample before and after removal of the char, the char yield could be calculated. Each char yield determination was done in duplicate. The elemental composition of the char was determined according to conventional microanalytical methods.

RESULTS AND DISCUSSION

Effect of RF-1 and APP on the Oxygen Index of PP and HIPS

Figure 1 shows plots of OI versus concentration of APP in PP and HIPS, re-

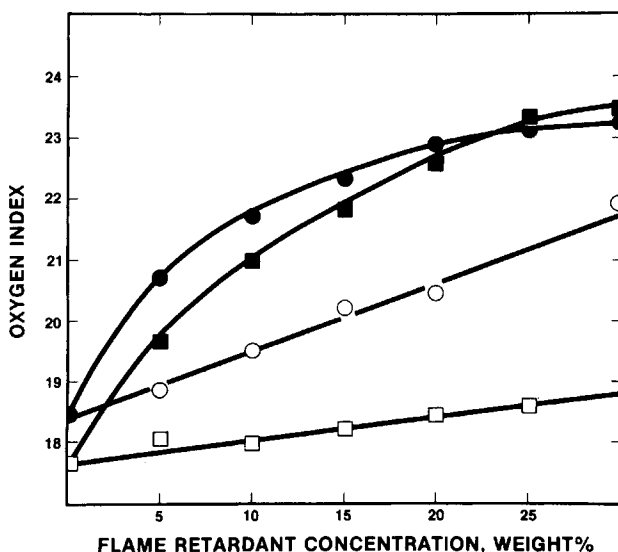


Fig. 1. Plots of oxygen index vs. concentration. (○) APP in polypropylene; (□) APP in high-impact polystyrene; (●) RF-1 in polypropylene; (■) RF-1 in high-impact polystyrene.

spectively. One sees that the efficiency curves for APP are linear in both polymers; they are described by eqs. (1) and (2), respectively;

$$\text{OI (PP)} = 18.4 + 0.11 \times \% \text{ APP} \quad (1a)$$

$$\Delta \text{OI (PP)} = 0.11 \times \% \text{ APP} \quad (1b)$$

$$\text{OI (HIPS)} = 17.6 + 0.043 \times \% \text{ APP} \quad (2a)$$

$$\Delta \text{OI (HIPS)} = 0.043 \times \% \text{ APP} \quad (2b)$$

The intercepts in eqs. (1a) and (2a) correspond to the OI values of the pure polymers, while the slopes give the increase of the OI per wt % APP present in the polymer. It should be noted that the flame retardant efficiency of APP in PP is higher by a factor of ~ 2.5 . The effect of RF-1 on the OI of PP and HIPS is likewise shown in Figure 1. In the case of the phosphonium salt, the efficiency curves are nonlinear for both polymers and tend to level off at high additive concentrations. To linearize this type of relationship, the data are replotted in double reciprocal coordinates according to Figure 2. The plots are linear with the reciprocal intercepts representing the OI for infinite flame retardant concentrations, while the reciprocal slopes signify the efficiencies at low concentrations. The equations of the efficiency curves for RF-1 are given by the following equations:

$$1/\Delta \text{OI (PP)} = 0.156 + 1.36/\% \text{ RF-1} \quad (3a)$$

$$\Delta \text{OI (PP)} = \frac{\% \text{ RF-1}}{0.156 \times \% \text{ RF-1} + 1.36} \quad (3b)$$

$$1/\Delta \text{OI (HIPS)} = 0.096 + 2.04/\% \text{ RF-1} \quad (4a)$$

$$\Delta \text{OI (HIPS)} = \frac{\% \text{ RF-1}}{0.096 \times \% \text{ RF-1} + 2.04} \quad (4b)$$

In PP, a high concentration of RF-1 results in an OI increase of $\Delta \text{OI}_{C \rightarrow \infty} = 6.4$, while in the case of HIPS, the high concentration limit amounts to $\Delta \text{OI}_{C \rightarrow \infty}$

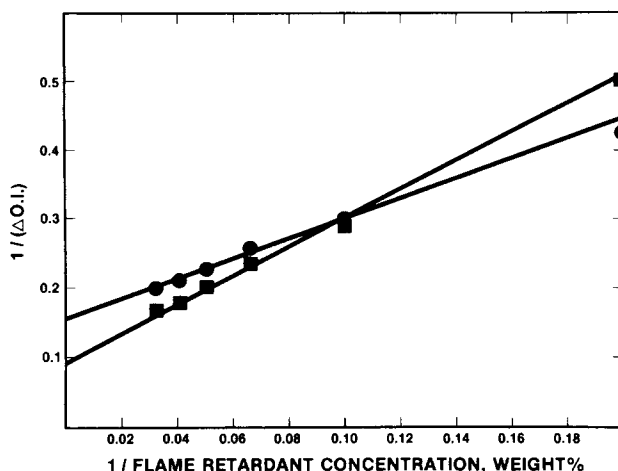


Fig. 2. Double reciprocal plots of the oxygen index increase vs. RF-1 concentration in polypropylene (●) and high-impact polystyrene (■).

= 10.4. The flame retardant efficiencies at low concentrations are $(\Delta\text{OI}/\% \text{RF-1})_{C \rightarrow 0} = 0.74$ for PP and $(\Delta\text{OI}/\% \text{RF-1})_{C \rightarrow 0} = 0.49$ for HIPS; this means that at low concentrations, the addition of 1% RF-1 results in an OI increase of 0.74 for PP and of 0.49 for HIPS. The qualitatively different type of efficiency curve for APP and RF-1 that is encountered in both PP and HIPS indicates that the two flame retardants operate by different mechanisms. While APP has been shown to be mainly a condensed-phase flame retardant,² the mode of action of RF-1 is likely to involve inhibition in the gas phase.

The quantitative differences in activity of APP and RF-1 in the two polymer systems are probably related to their different thermal degradation mechanisms: while PP is known to degrade entirely by way of random chain scission,⁴ a major degradation pathway of HIPS involves monomer formation by way of unzipping of the polymer chains.⁵

Synergistic Effects in PP and HIPS for Mixtures of RF-1 and APP

If mixtures of RF-1 and APP are added to either PP or HIPS, the reduction of flammability is in both cases greater than one would expect from the additive effects of the two individual components. One has, therefore, to conclude that RF-1 and APP act synergistically as flame retardants in both polymers. Figure 3 shows the OI of mixtures containing RF-1 and APP in different proportions at a constant additive level of 30% by weight in both PP and HIPS. By adding the equation of the efficiency curves, eqs. (1b) and (3b) for PP and eqs. (2b) and (4b) for HIPS, efficiency curves can be calculated that represent the additive

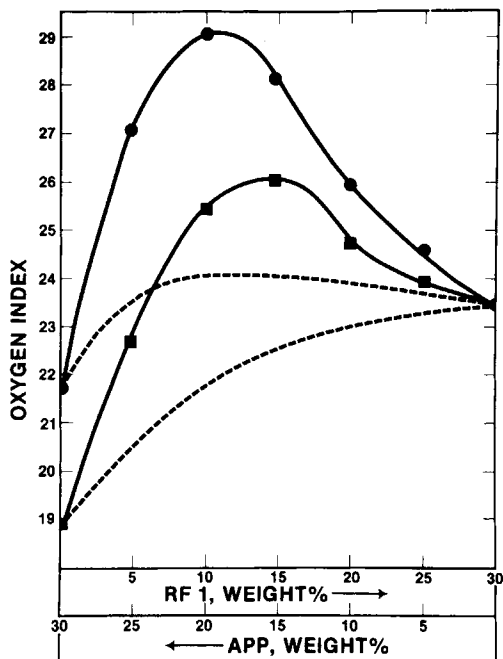


Fig. 3. Plots of oxygen index vs. composition of RF-1/APP mixtures in polypropylene and high-impact polystyrene at a total additive concentration of 30%. Solid line: measured values; broken line: calculated values; (●) polypropylene; (■) high-impact polystyrene.

effects of the individual components of the RF-1/APP mixtures in the absence of any synergistic interactions. These curves are also shown in Figure 3.

The degree of synergism, $\Delta(\Delta\text{OI})$, is given by the difference between the measured and the calculated increase in OI. As shown in Figure 4, maximum synergism is observed for a ratio of RF-1/APP \approx 1:1. In terms of phosphorus content, this corresponds to a ratio $[\text{P}]_{\text{RF-1}}/[\text{P}]_{\text{APP}} \approx 0.3$. The maximum synergism as expressed by $\Delta(\Delta\text{OI})$ is higher for PP than for HIPS. This difference in activity of the RF-1/APP system in the two polymers is in agreement with the results of the flammability rating according to the UL 94 test: While in the case of PP, a total loading of 20% is sufficient to yield a V-O rated polymer sample, as much as 40% of the RF-1/APP mixture is required in order to obtain a V-O rating in HIPS.

Char Formation and Flame Retardance

PP burns with a hot, smokeless flame, while the burning of HIPS is accompanied by ample soot formation; both polymers burn without leaving any appreciable char residue. Char formation is also absent for PP and HIPS samples that contain RF-1 or APP alone. However, samples of the two polymers that contain RF-1/APP mixtures form large amounts of porous char when combusted in an atmosphere with an oxygen content slightly above the OI of the particular formulation.

As we have shown earlier,⁶ the char layer formed during combustion of PP, flame retarded by the system phosphine oxide/APP, acts as an effective thermal barrier and thus reduces the flammability by impeding the pyrolysis of the unburned polymer. There is little doubt that the char formed during the combustion of samples containing RF-1/APP mixtures exerts a similar insulating effect.

Figure 5 shows the gravimetrically determined char yields for PP and HIPS

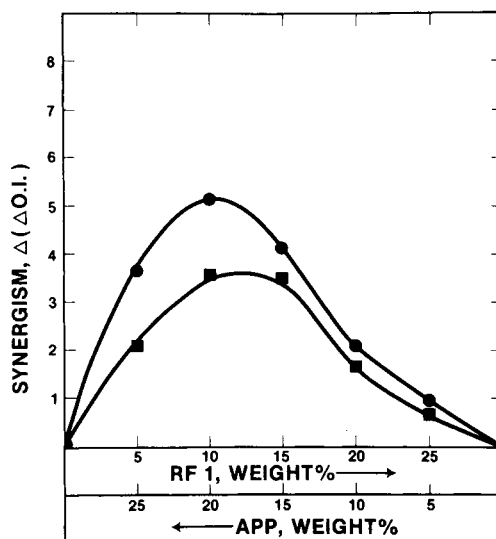


Fig. 4. Plots of synergism vs. composition of RF-1/APP mixtures in polypropylene and high-impact polystyrene at a total concentration of 30%. (●) Polypropylene; (■) high-impact polystyrene.

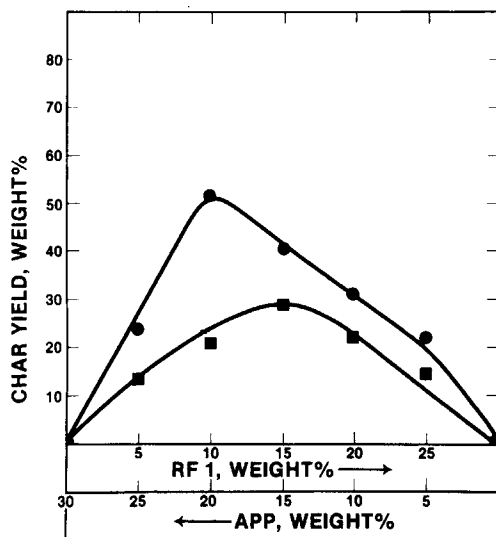


Fig. 5. Plots of char yield vs. composition of RF-1/APP mixtures in polypropylene and high-impact polystyrene at a total concentration of 30%. (●) Polypropylene; (■) high-impact polystyrene.

containing RF-1/APP mixtures of different compositions at a total additive concentration of 30%. For all compositions, the char yield is higher in the case of PP. Since for some mixtures the char yield exceeds by far the amount of flame retardant additive that is present in the formulation, the polymer itself must contribute to the formation of the char. In the case of HIPS, where the char yields are always lower than the concentration of the additive in the sample, a participation of the polymer in the charring process cannot be inferred *a priori*.

A comparison of Figures 4 and 5 shows that maximum char formation occurs for the same compositions in which the highest degree of synergism is encountered. This suggests a possible correlation of char yield and synergism. Figure

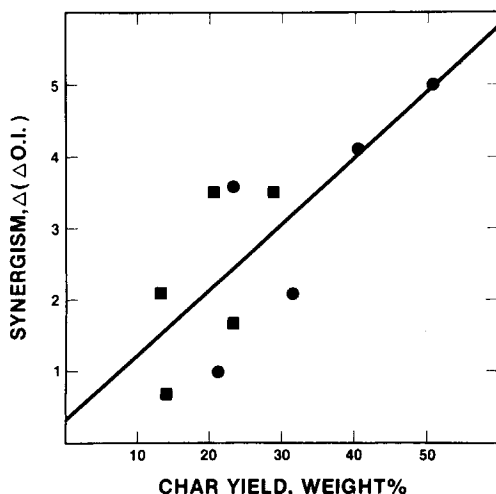


Fig. 6. Correlation of synergism with char yield in (●) polypropylene and (■) high-impact polystyrene.

6 shows a plot of $\Delta(\Delta\text{OI})$ vs. % char yield. One sees that the points representing measurements in both PP and HIPS scatter around the same least-squares line. This implies that the flame retardant properties of the char are similar for the two polymers. A char yield of $\sim 9\%$ corresponds to a synergism of $\Delta(\Delta\text{OI}) = 1.0$. However, the correlation depicted in Figure 6 is only moderately good with a correlation coefficient of $r = 0.752$ and can therefore be considered only as a first approximation. Aside from the quantity of the char, other factors must contribute to the degree of flame retardancy.

An obvious additional parameter is the composition of the char, which in turn should depend on the RF-1/APP ratio in the flame retardant mixture. Table I shows the quotient percent char/ $\Delta(\Delta\text{OI})$ for different RF-1/APP ratios. One sees that for corresponding compositions, similar results are obtained in PP and in HIPS. If the composition of the flame retardant mixture is expressed in terms of the molar fraction of organic phosphorus, $[P]_{\text{RF-1}}/([P]_{\text{RF-1}} + [P]_{\text{APP}})$ in the flame retardant mixture, the data of Table I can be plotted according to Figure 7. This correlation with $r = 0.982$ is very good, and the following conclusions can be drawn:

The flame retardant properties of equivalent amounts of char are the same for PP and HIPS. The flame retardant efficiency of a given amount of char is a function of the composition of the RF-1/APP mixture, and the efficiency decreases as the weight fraction of RF-1 increases. Since the properties of the chars that are formed in PP and HIPS, respectively, are similar, one may infer that the chars for the HIPS system likewise require the participation of the polymer for their formation.

Elemental Composition of the Combustion Chars

As already shown, the flame retardant properties of the combustion chars depend on the composition of the RF-1/APP mixture originally present in the polymer sample. This suggests that the elemental compositions of the char should be an important parameter.

Table II gives the analytical results for the composition of chars from PP

TABLE I
Char Yield and Synergism for Different RF-1/APP Ratios in Polypropylene and High-Impact Polystyrene

Sample			$\frac{[P]_{\text{RF-1}}}{([P]_{\text{RF-1}} + [P]_{\text{APP}})}$	% Char	$\Delta(\Delta\text{OI})$	% Char/ $\Delta(\Delta\text{OI})$
70% PP	+ RF-1	+ APP				
	5%	25%	0.062	23.7	3.7	6.41
	10%	20%	0.145	51.7	5.1	10.14
	15%	15%	0.251	40.6	4.1	9.90
	20%	10%	0.403	31.4	2.1	14.95
	25%	5%	0.625	21.8	1.0	21.80
70% HIPS	+ RF-1	+ APP				
	5%	25%	0.062	12.9	2.1	6.14
	10%	20%	0.145	21.1	3.6	5.86
	15%	15%	0.251	28.9	3.5	8.26
	20%	10%	0.403	23.3	1.7	13.70
	25%	5%	0.625	14.0	0.7	20.00

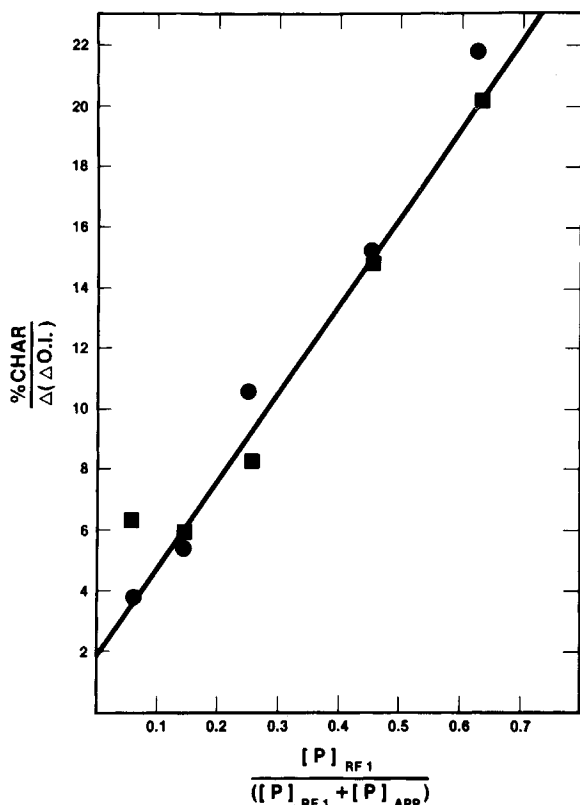


Fig. 7. Plot of char yield/synergism vs. mole fraction of organo-phosphorus in RF-1/APP mixture. (●) Polypropylene; (■) high-impact polystyrene.

samples containing RF-1/APP mixtures in different ratios at a total additive concentration of 30%. Qualitatively, one sees that all chars contain high concentrations of phosphorus. On the other hand, most of the nitrogen is lost to the gas phase during combustion. However, in all cases a small amount of nitrogen remains in the char. As one would expect, none of the bromine contained in the RF-1 component is retained.

Table II also shows the empirical molecular formulas for the different chars. To facilitate comparisons, the calculated molecular compositions are normalized for phosphorus, and the calculated amount of oxygen in the char is assumed to be present in the form of H₂O. The H/C ratio is, in most cases, close to one, which

TABLE II
Elemental Composition of Combustion Chars

70% PP	Sample		Char composition					Empirical formula
	+ % RF-1	+ % APP	% C	% H	% P	% N	% O	
	5	25	52.04	7.78	9.00	3.60	27.58	C _{14.9} H _{14.9} N _{0.9} P × 5.9 H ₂ O
	10	20	52.31	8.81	12.43	2.92	23.53	C _{10.9} H _{14.7} N _{0.5} P × 3.7 H ₂ O
	15	15	35.91	7.07	14.54	3.56	38.92	C _{6.4} H _{4.7} N _{0.5} P × 5.2 H ₂ O
	20	10	39.55	8.16	16.78	3.13	32.38	C _{6.1} H _{7.7} N _{0.4} P × 3.7 H ₂ O
	25	5	28.12	7.04	14.35	2.89	47.60	C _{5.1} H _{2.5} N _{0.5} P × 6.4 H ₂ O

TABLE III
Phosphorus Retention in Combustion Chars

70% PP	Sample		% Phosphorus		Char yield, %	Phosphorus retention, %
	+ % RF-1	+ % APP	In sample	In char		
	5	25	8.54	9.00	23.7	25.0
	10	20	7.48	12.43	51.7	85.9
	15	15	6.42	14.54	40.6	92.0
	20	10	5.36	16.78	31.4	93.3
	25	5	4.30	14.35	21.8	72.8

may suggest the presence of aromatic structures, since a ratio of two would be required for aliphatic polymer fragments. The C/P ratio increases with an increase of the ratio APP/RF-1. In all char samples a nearly constant ratio of N/P ≈ 0.5 is observed, which may suggest the presence of heat stable P—N bonds in all cases.

From the char yields of Table I and the analytical data of Table II, it is possible to calculate the total amount of P in the char; with the original P content of the unburned sample, one can then obtain the percent phosphorus retained in the solid phase. The data in Table III shows that the RF-1/APP ratios which exhibit high phosphorus retention are the same that provide the best flame retardant activity.

SUMMARY AND CONCLUSIONS

(1) The oxygen index of polypropylene and high-impact polystyrene is increased by the individual addition of the phosphonium salt Cyagard RF-1 flame retardant and ammonium polyphosphate. The efficiency curves for APP are linear for both polymers, while the efficiency of RF-1 levels off at high concentrations.

(2) Mixtures of RF-1 and APP act synergistically in both polypropylene and high-impact polystyrene. The degree of synergism is higher in the case of polypropylene. The maximum of synergistic action occurs at a weight ratio of APP/RF-1 ≈ 1 in both polymers.

(3) The char yield after combustion increases with the degree of synergism in both polymer systems. However, the flame retardant properties of the char vary with the RF-1/APP ratio in the sample.

(4) Elemental analysis shows the presence of C, H, P, O, and of small amounts of N in all chars; no Br is retained.

(5) The retention of phosphorus in the char is highest for RF-1/APP ratios that show strong synergism.

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