

Modified Chlorinated Polypropylene as a Polymer Fire Retardant Additive in Polyhydrocarbons

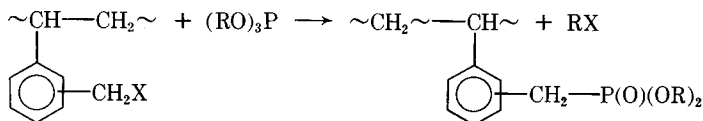
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Synopsis

Partly modified chlorinated polypropylene (CPP) with dimethyl phosphonate side groups was prepared by reacting trimethyl phosphites and CPP at 115°C (Arbuzov type reaction). Products having different phosphorus and chlorine content were obtained, and the reduction of number-average molecular weight \bar{M}_n with the extent of the degree of substitution was studied. The dimethyl phosphonate groups incorporated were studied by IR spectroscopy (P—O—C at 9.6 μ and P → O at 8 μ). All products had a yellow color that may be attributed to double bond formation caused by a side dehydrochlorination reaction. Some differences of thermal stability were observed from the DSC and TGA thermograms, and no significant T_g value changes between phosphorylated products and CPP were indicated in the thermomechanical spectra. The flame retardancy of the phosphorylated products and the blends obtained by the addition of partly phosphorylated CPP to polyhydrocarbons such as polyethylene (PE), polypropylene (PP), and polystyrene (PS) was studied using the oxygen index test. The flame retardancy of these blends was compared with the flammability of the same polyhydrocarbons containing CPP. From this comparison it is concluded that the partly phosphorylated CPP is more effective as a flame retardant additive for PE, PP, and PS than itself.

INTRODUCTION

The reaction of trialkyl phosphites and alkyhalides has been discovered by Michaelis,¹ was studied in detail by Arbuzov,² and is known as a Michaelis–Arbuzov type reaction. Lately, Verizhnikov et al.³ have attempted a study of the reaction of tributyl phosphite and 4-chloro-2-pentene to be used as a model reaction for the phosphorylation of poly(vinyl chloride). From this study it was concluded that, except for phosphorylation, a side dehydrochlorination reaction occurred also. Shayakmetov et al.⁴ prepared phosphorylated PS with a 4% phosphorus content. This preparation was achieved by reacting iodomethylated PS and triethyl phosphite at 100°C and a reaction time of 9 h. Furthermore, the preparation of a phosphorylated PS, by the Arbuzov type reaction, or chloromethylated PS, and of triethylphosphite has been reported.⁵ The above reactions proceed as follows:

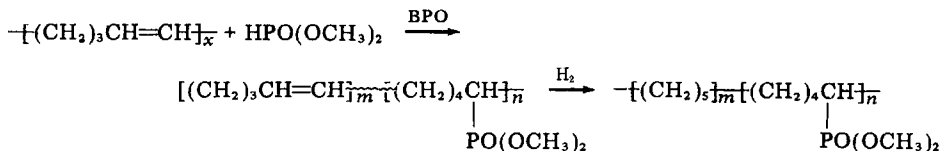


where X = Cl, I.

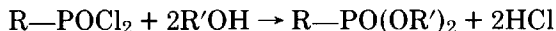
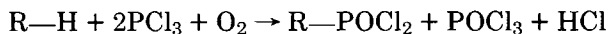
Polymers modified with phosphonate side groups have been prepared by reacting unsaturated polymers (containing double bonds) with dialkyl phosphites

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(hydrogen phosphonates).⁶ Rahrig et al.⁷ prepared phosphonylated polypentenamers followed by hydrogenation of the products obtained; he also reported their dielectric and dynamic mechanical properties. The reaction is shown below:



Recently, MacKnight and co-workers⁸ modified PE by incorporating phosphonate side groups. This was achieved by two reaction steps as follows:



The same authors⁹ also studied the properties and the dynamic mechanical behavior of PE modified with phosphonate side groups.

The incorporation of phosphonate side groups has been attempted by polymerization of vinyl phosphonate monomer with another suitable vinyl monomer. A fire-retardant crosslinked copolymer¹⁰ was obtained by copolymerization of bis(β -chloroethyl) vinyl phosphonate and allyl methacrylate. The product containing 10% phosphorus and 23.2% chlorine was used as a fire-retardant additive in PP. Polypropylene containing 30% of this copolymer gave an oxygen index of 21.7. A fire resistant copolymer was also obtained^{11,12} by copolymerization of vinyl chloride and bis(β -chloroethyl) vinyl phosphonate. Also a fire-resistant polymer obtained by a free radical polymerization mechanism (benzoylperoxide initiator used) of bis(β -chloroethyl) vinyl phosphonate is discussed.¹³

In general it is well known that chlorinated polyhydrocarbons such as, poly(vinyl chloride), chlorinated PE, and polychloroprene have been used in the past as flame retardants.

In this paper the synthesis of partly phosphorylated chlorinated polypropylene (CPP) products and their application as flame-retardant additives in PE, PP, and PS is discussed. Their thermal and dynamic mechanical properties were also studied. This work was undertaken since it was expected that the above-modified polymeric products would be more effective flame-retardant additives than CPP itself. This is based on the consideration of possible synergism between phosphorus and chlorine. In addition, these products would be polymeric and hence more compatible than low-molecular-weight fire-retardant additives.

EXPERIMENTAL

Materials and Methods

CPP in powder form used as a fire-retardant additive as well as a reagent in the phosphorylation reaction, was obtained from EGA CHEMIE Gesellschaft mbH & Co. KG, W. Germany. Trimethyl phosphite was practical grade Fluka AG, Switzerland.

TABLE I
Products of Phosphorylation Reaction of CPP and Trimethyl Phosphite in 120°C without Solvent

Samples	Reaction time (h)	\bar{M}_n	Cl (%)	P (%)	Cl/P	LOI
a	0	45,000	50	0	—	78.0
b	8	47,000	47.3	1.2	39.4	62.5
c	16	35,000	44.4	1.8	24.7	62.5
d	24	29,000	41.0	2.6	15.8	69.5
e	48	—	30.1	4.9	6.1	63.0

Chlorine and Phosphorus content in the starting material and products obtained after phosphorylation reaction were determined by standard procedures.^{14,15}

Phosphorylation Reaction

In a round-bottomed flask equipped with a reflux condenser, 325 mL (2750 mmol) of trimethyl phosphite was added. The liquid was agitated by a magnetic stirrer and 35 g of CPP in powder form was added. The flask was stirred in an oil bath at 115°C. After 8 h of reaction, 80 mL of the reaction mixture was added dropwise in a 370-mL agitated mixture of petroleum ether and methanol 1:1 v/v. The polymer was filtered, washed five times (50 mL each portion), with the above mixture (petroleum ether-methanol) and dried under high vacuum at 40°C for 10 h (sample b; see Table I).

The above procedure was applied using reaction times of 16 h, 24 h, and 48 h, obtaining samples c, d, and e (see Table I), correspondingly.

Number-Average Molecular Weight \bar{M}_n Determination

Number-average molecular weights \bar{M}_n were determined using the membrane osmometer, Knauer & Co. GmbH, W. Germany. All runs were carried out at 45°C using toluene as solvent and regenerated cellulose as membrane material.

IR Spectroscopy

The IR spectra of films having identical thickness and prepared from solutions of polymers in chloroform were obtained using a Perkin-Elmer infrared Spectrophotometer, Model 297.

Flammability

Fire retardancy was determined using the oxygen index test according to ASTM D-2863. Oxygen index is defined as the minimum oxygen concentration which will sustain downward candlelike burning of a supported test specimen.^{16,17}

Thermal Analysis

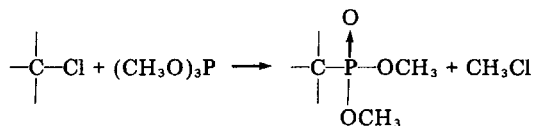
DSC measurements were carried out using a DuPont 910 calorimeter system coupled with a 990 programmer-recorder. Program heating rate was 20°C/min and Indium was used as a temperature calibration standard. All runs were made in an air atmosphere using aluminum closed pans containing about 4 mg of each sample. TGA measurements were carried out using the DuPont 951 Thermogravimetric Analyzer and a heating rate of 20°C/min, in the presence of air.

Dynamic Mechanical Properties

Dynamic mechanical data, loss tangent and complex modulus $|E^*|$ were obtained between -120°C and $+120^\circ\text{C}$ at 110 Hz using the direct reading viscoelastometer, (Rheovibron, Model DDV II-C, Toyo-Baldwin). The correction due to clamp extension was applied.¹⁸ This corrects for the small clamp deformation especially at low temperatures, where the test specimen has high rigidity. The films used were obtained from chloroform solution cast over mercury and dried at 40°C for 3 days. During testing, specimens were heated at 1–2°C/min under dry argon.

RESULTS AND DISCUSSION

The partly modified CPP with dimethyl phosphonate side groups was prepared by reacting CPP and trimethyl phosphite at 115°C in the absence of solvent.



The reaction took place in solution, because after a short time the polymer was dissolved in trimethyl phosphite. The reaction takes place slowly and even more so when toluene and xylene are used as solvents. During the reaction progress dehydrochlorination occurred, imparting a yellow color to the reaction

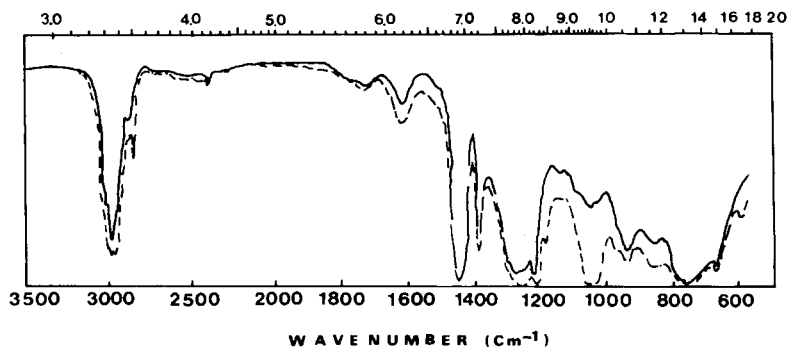


Fig. 1. IR spectra of partly phosphorylated CPP (---) compared with IR spectra of CPP (—).

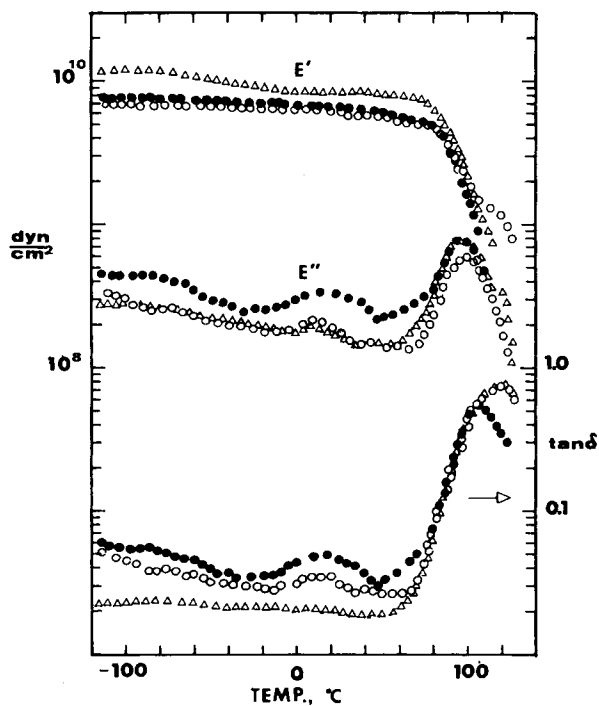


Fig. 2. Thermomechanical spectra of unmodified CPP and some of the phosphorylated products. (●) sample a; (○) sample b; (Δ) sample c.

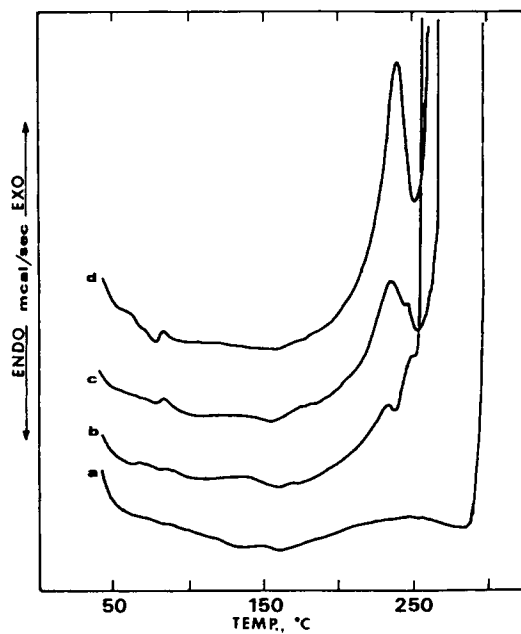


Fig. 3. DSC thermograms of unmodified CPP and the phosphorylated products obtained. For identification of curves see Table I.

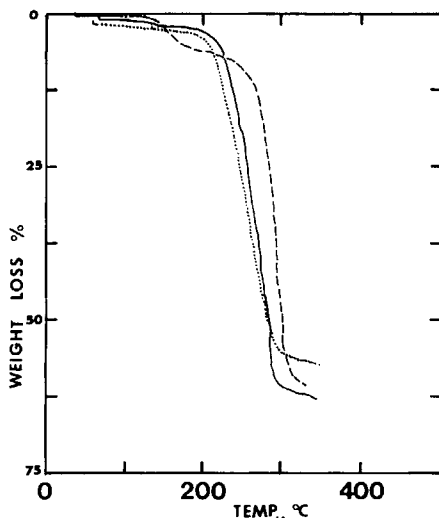


Fig. 4. Comparison of thermogravimetry curves of CPP and modified products. (---) CPP; (—) sample c; (· · · ·) sample d. For identification of curves see Table I.

mixture. This is attributed to double bond formation. Double bond formation was demonstrated by titration with a bromine iodide (BrI) solution.

The products obtained by the above phosphorylation reaction were examined by IR spectroscopy. In Figure 1 the P—O—C band at 9.6μ is observed. The P→O band at 8μ coincides with the absorption of CPP.

As is shown in Table I, the number-average molecular weight \bar{M}_n as well as the chlorine content is reduced with the reaction progress, but the phosphorus content increases progressively. Samples b, c, and d are soluble in toluene and

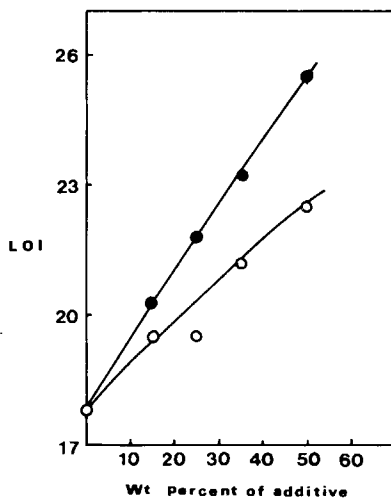


Fig. 5. Effect of additive on polyethylene. (○) CPP (sample a); (●) partly phosphorylated CPP (sample d).

chloroform, but sample e is insoluble in the above solvents. Also they are soluble in trimethylphosphite at 115°C; again sample e is insoluble.

To determine the characteristic transitions and the effect of substitution on the solid state mechanical behavior of CPP, the dynamic mechanical properties of unmodified and phosphorylated CPP were studied. This is useful not only to assess the degree of stiffness of the new materials and its temperature dependence, but also the degree of compatibility of the modified products with other polymeric materials. In this paper we report only on the thermomechanical spectra of the nonblended products.

The temperature dependence of the storage E' and loss modulus E'' calculated from the original experimental data is given in Figure 2.

The three main relaxations of the unmodified CPP can be identified on the basis of the reported thermomechanical spectra of solution¹⁹- and emulsion²⁰-chlorinated polyethylene and the PP homopolymer.²¹ At these high degrees of chlorination, crystallinity is destroyed, and the main T_g transition is located at 97°C. As the modulus variation shows, the polymer retains its glassy character up to approximately 90°C. Substituting the chlorine atoms with the $(\text{CH}_3\text{O})_2\text{P}(\text{O})$ — bulky moieties does not shift appreciably the main α relaxation. The β relaxation due to the movement of the branch points $-\text{C}(\text{CH}_3)-$, or $-\text{C}(\text{Cl})-$ in the amorphous regions is located at about 10°C. Substituting the Cl atoms with the phosphonate groups reduces the intensity of the peak. Apparently, the bulkiness of the substituent reduces the mobility of the branch points. The same remark applies to the reduction of the intensity of the weak γ relaxation at about -90°C , which has been attributed to the relaxation of a few chain segments in the amorphous regions of PP.²¹ Concluding, because of the polar character of both the Cl— and the $(\text{CH}_3\text{O})_2\text{P}(\text{O})$ — substituents, no drastic changes were observed between the CPP and the phosphorylated product. Similar behavior was reported by MacKnight and co-workers⁹ for the phosphorylated low density PE.

Thermal stability of phosphorylated CPP compared with the thermal stability of the starting material was studied by differential scanning calorimetry. Figure 3 shows DSC thermograms of samples a, b, c, d. The broad endotherm of the CPP can be attributed to moisture evaporation and limited dehydrochlorination. This also is observed to a lesser extent for the modified CPP products. The first exotherm starts in the case of CPP at about 165°C, and the same holds true for the phosphorylated products.

The flame retardancy of partly phosphorylated CPP was studied using the oxygen index test. All samples (b, c, d, e) have a reduced fire retardancy (Table I) compared with CPP (sample a).

These experimental results may be related with the thermal behavior as shown in the DSC thermograms (see Fig. 3). This figure shows that sample a (CPP) gives at 225°C the smallest exotherm decomposition peak compared with those of all phosphorylated CPP. From this it is concluded that the amount of pyrolysis products in the case of partly phosphorylated CPP is greater, a fact that leads to their increased flammability, compared with those of CPP.

The presence of exothermic peaks for some treated fabrics²² has been interpreted as the result of decomposition. Also fabrics treated with flame-resistant phosphorus containing formulations had lower decomposition temperatures. This is in agreement with the observation that both exothermic peaks (chain

scission followed by monomer oxidation²³) are shifted to lower temperatures for the modified CPP products; see Figure 3. This interpretation is corroborated by the results of thermogravimetric analysis (see Fig. 4). Comparison of the weight loss curves indicates that the main decomposition temperature of the phosphorylated products shifts to lower temperatures compared to CPP and the temperatures of the first DSC exotherm coincide with those where the rate of weight loss becomes significant; compare Figures 3 and 4.

Although the fire retardancy of the above polymeric products is less than that of the CPP, they give better results as flame-retardant additives compared with the CPP. This was observed from oxygen index testing using sample d as flame retardant additive in PE, PP, and PS.

More specifically, as is shown in Figure 5, in the case of polyethylene, the partly phosphorylated CPP is more effective than CPP in the range of additive content 15–50%. The flammability of polyethylene having the above additive content was in the range of 20.3–25.5 in terms of the oxygen index. At the same level of additive content of CPP, the flammability of polyethylene was between 19.5 and 22.5.

Likewise for polypropylene, we can observe in Figure 6 that the partly phosphorylated CPP is more effective than CPP in the same range of additive contents. Also, as is evident in Figure 6, when the additive content becomes more than 50%, CPP has a tendency to be more effective.

The effect of the same flame retardant additive on polystyrene is indicated in Figure 7. From this figure it is concluded that the partly phosphorylated CPP gives more flammability reduction than CPP, in the composition range of 15–40%. When the additive content is larger than 40%, CPP becomes more effective.

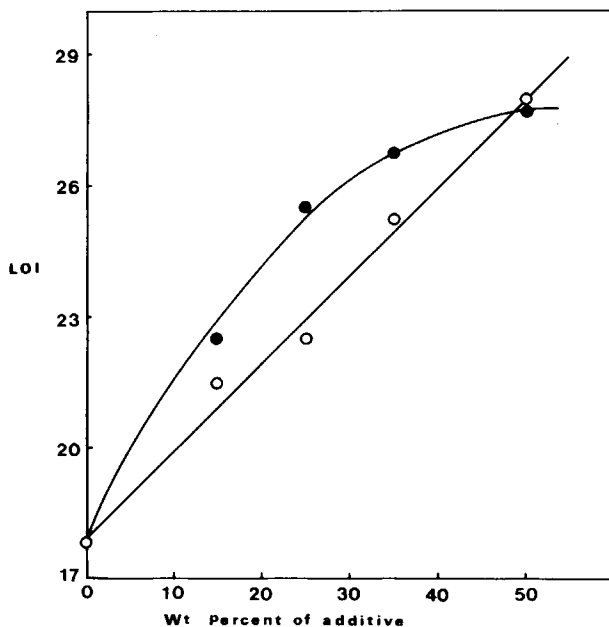


Fig. 6. Effect of additive on polypropylene. (O) CPP (sample a); (●) partly phosphorylated CPP (sample d).

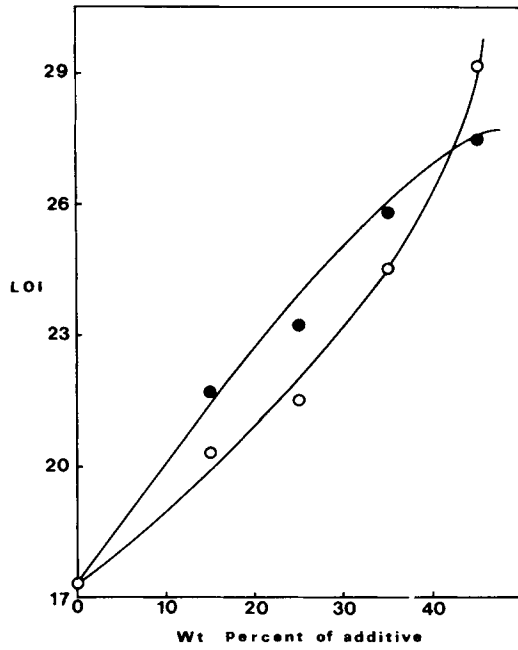


Fig. 7. Effect of additive on polystyrene. (O) CPP (sample a); (●) partly phosphorylated CPP (sample d).

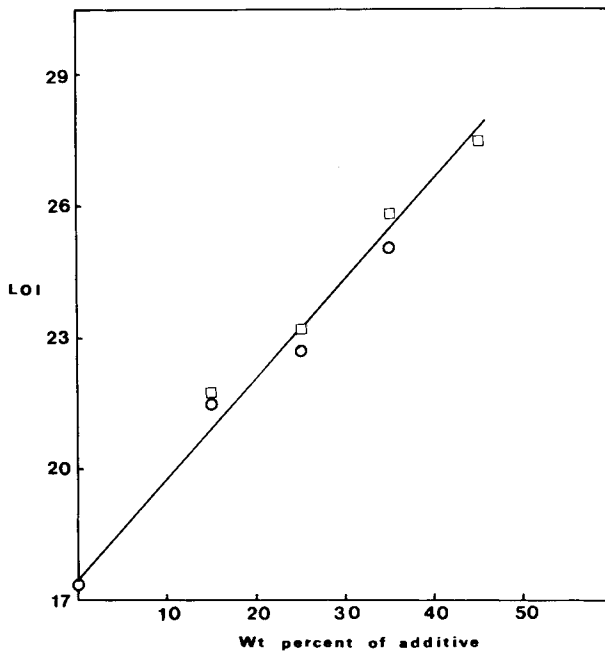


Fig. 8. Effect of additive (partly phosphorylated CPP) with different phosphorus content on polystyrene. (O) sample c; (□) sample d.

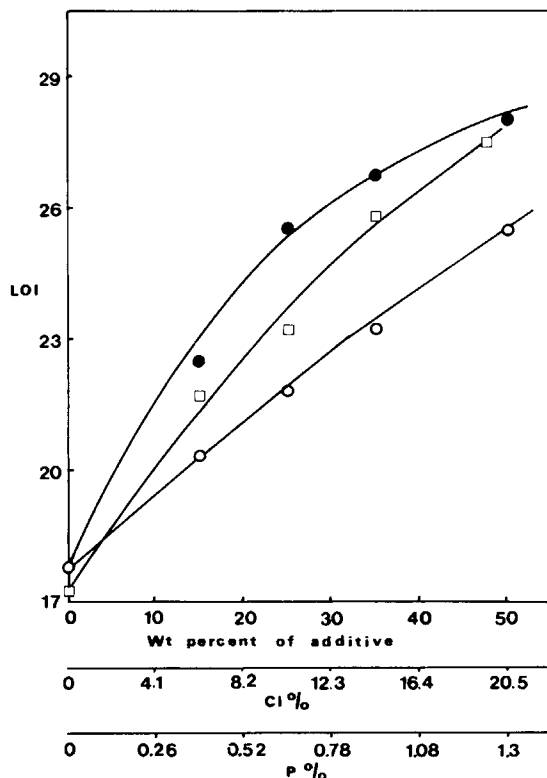


Fig. 9. Comparison of partly phosphorylated CPP (sample d) as a flame retardant additive on PE (○), PS (□), and PP (●).

In Figures 6 and 7 it is shown that at relatively high concentrations (ca. 40%), the phosphorylated CPP additive has lower fire-retardant effect than CPP. This is due to lower synergism and the fact that the CPP itself has a higher LOI than the modified products (see Table I). This explains the crossing of lines observed at high concentrations of additive.

The above results lead to the conclusion that the fire-resistant synergism of the elements phosphorus and chlorine gives better results than chlorine itself in such small chlorine percentage contents.

Sample c has also been used as flame retardant additive in PS, in order to compare the results with those of sample d. From Figure 8 one can see that samples c and d have about the same flame resistance effect.

From this it is concluded that in the case of PS the synergistic effect of phosphorus and chlorine is not significantly different in such percentage contents.

Finally, as is indicated in Figure 9 the partly phosphorylated CPP is less effective in PE, the results are better in PS and best results are obtained in the case of PP.

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