Polymer Bulletin 11, 275–280 (1984)

Polymer Bulletin

Effect of Free Radicals Generating Compounds Towards the Flammability of *w*-Phosphonated Polystyrenes – V

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SUMMARY

Effect of some free-radicals generating compounds, such as organic peroxides, hydroperoxides and polysulfides, on the Oxygen Index of end phosphonated polystyrenes is investigated. It is shown that some combinations of end phosphonated polystyrene with free-radicals initiators, may be said to have a synergestic effect on flame-retardant properties of standard polystyrene.

INTRODUCTION

The synergism in flame retardancy of thermoplastic materials remains in many cases without a meaningful sense, especially when both ingredients of the mixture under consideration are active flame-retardants. This is due to the fact that, frequently, authors are based on the stated or implicit assumption that the flame-retardant response is linearly related to additive concentration. This hypothesis can lead, in many instances, to an artifactual synergism (KURYLA, 1975). On the other hand, the synergism of halogen or phosphorus additives by free-radical generating compounds appears to be an artifact of melt-viscosity depression and dripping of the polymer (EICHHOEN, 1964, GOUNLOCH et al. 1971, FENIMORE, 1968). The aim of this study is to elucidate the nature of interactions between end phosphonated polystyrenes and some free-radicals initiators. First, it is demonstrated that free-radicals generating compounds, such as organic peroxides, hydroperoxides and polysulfures, are not active flame-retardants. In this case a synergism can be easily identified without reference to any mathematical model (KURYLA, 1975). On the other hand, the flammability of mixtures of end phosphonated polystyrenes with free-radicals initiators is evaluated by using a modified Oxygen Index method (CHIOTIS et al. 1982). This method prevent any dripping of the polymer mixture during burning, thus melt-viscosity depression effect is eliminated.

EXPERIMENTAL

Synthesis of end phosphonated polystyrenes

End phosphonated polystyrenes were synthesized according to the experimental method described (CLOUET et al. 1981).

Synthesis of polysulfides

Polystyrene-polysulfide samples were prepared as described (BOSCATO et al. 1979).

Determination of modified Oxygen Index (OI)m

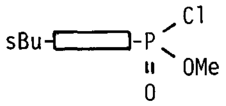
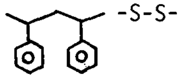
The (OI)m of mixtures was determined upon the method of (CHIOTIS et al. 1982).

RESULTS AND DISCUSSION

1)Effect of polystyrene-polysulfide

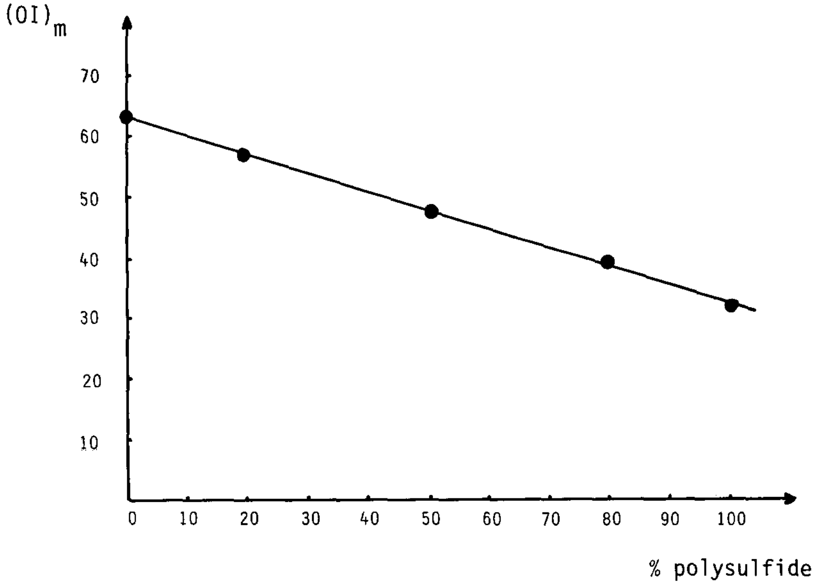
Various blends of the two polymers of table 1 were prepared and tested using the modified Oxygen Index method.

Table 1 - Data about polymers used to prepared blends

Ref.	Structure of polymer	$\bar{M}_n$	% P(w/w)	% Cl(w/w)	% S(w/w)
PPS	 sBu-P(O)(Cl)OMe	7 000	0.27	0.45	0
SPS	 -S-S-	20 000	0	0	22.5

The fig.1 shows the flame-retardancy response observed in this case.

Figure 1 - Modified Oxygen Index for PPS and SPS polymers versus polysulfide concentration



In this case, we have a simple additivity response, expressed by the following relationship:

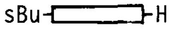
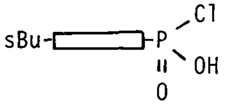
$$(\mathrm{OI})_{\mathrm{blend}} = \alpha\,(\mathrm{OI})_{\mathrm{PPS}} + \beta\,(\mathrm{OI})_{\mathrm{SPS}}$$

$$\beta = \alpha - 1$$

2) Effect of hydroperoxides

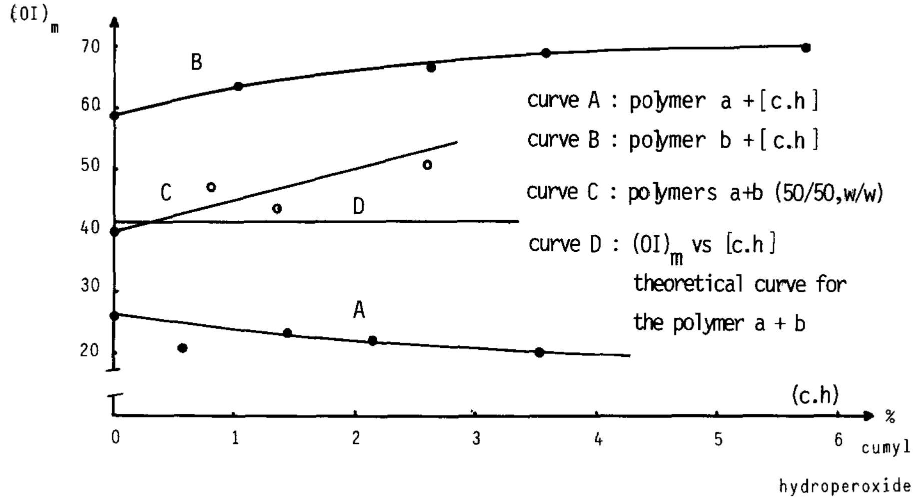
A series of blends of polymers of table 2, with cumyl hydroperoxide (c.h) are prepared, and tested following the modified Oxygen Index method.

Table 2 - Data about polymers used to prepared blends with cumyl hydroperoxide (c.h)

Ref.	Structure of polymer	$\bar{M}_n$	% P(w/w)	% Cl(w/w)	(OI)m
a		10 200	0	0	26
b		8 000	0.2	0.3	59

The curves of the flame-retardancy responses of blends versus concentration of cumyl hydroperoxide are shown in Fig.2:

Figure 2 - Modified Oxygen Index for polymers a and b versus cumyl hydroperoxide concentration



Curve A shows that addition of cumyl hydroperoxide to anionic polystyrene lead to a drecreasing of (OI)m. This may be due to the fact that cumyl hydroperoxide, when decomposed by the heat from the flame, accelerates the breakdown of the polymer, causing a higher evolution of flammable polymer fragments. However, curve B, concerning blends of an end phosphonated polystyrene and cumyl hydroperoxide, indicates that, in this case, cumyl hydroperoxide exhibits an increase of the initial (OI)m of the phosphonated polystyrene. Thus, one can deduce that there is a synergistic effect between the cumyl hydroperoxide and the phosphonated group bounded to the end of a polystyrene chain. Curve C, shows that the evolution of (OI)m of a 50/50 (w/w) blend of the two polymers of table 2 versus the concentration of cumyl hydroperoxide. The calculated curve D represents the case of a simple additivity response of the two compounds (anionic polystyrene (a) and end phosphonated polystyrene (b)) against the cumyl hydroperoxide concentration:

$$\underset{(\text{calc.})}{\text{Curve D}} \; : \; (\text{OI})_{\text{theor.}} = \alpha(\text{OI})_a + \beta(\text{OI})_b$$

$$\alpha = \beta = 0.5$$

It must be pointed out that, for a concentration of cumyl hydroperoxide higher than 0.5% we observe the following relationship:

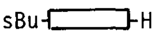
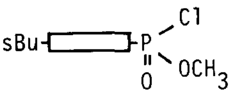
$$\text{Curve C}_{\text{exp.}} : \; (\text{OI})_{\text{exp.}} > (\text{OI})_{\text{theor.}}$$

For these concentrations there is a synergistic effect between end phosphonated polystyrene and cumyl hydroperoxide.

3) Effect of benzoyl peroxide (b.p)

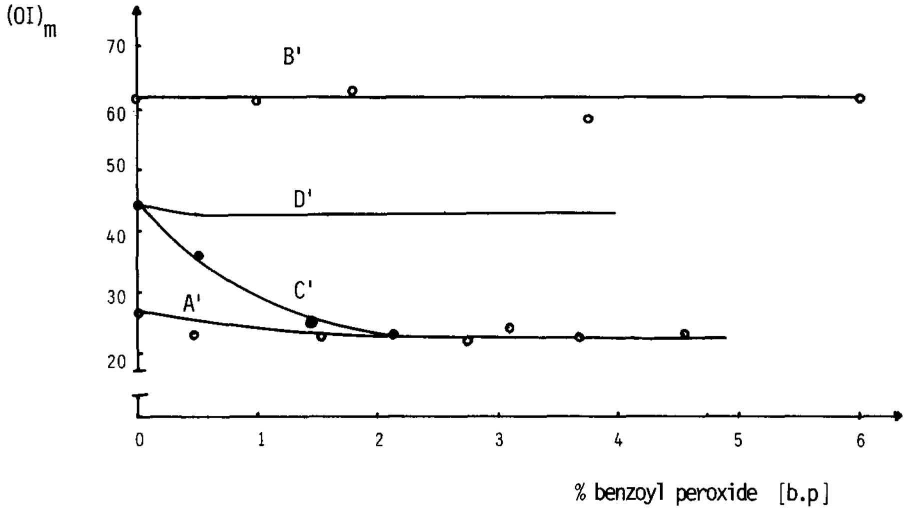
In a similar way, as above, blends of polymers of table 3 were prepared and tested using the modified Oxygen Index method.

Table 3 - Data about polymers used to prepare blends with benzoyl peroxide

Ref.	Structure of polymer	$\bar{M}_n$	% P(w/w)	% Cl(w/w)	(OI)m
a'		10 200	0	0	27
b'		7 000	0.27	0.45	62

The Fig.3 illustrates the (OI)m evolution versus concentration of benzoyl peroxide, for various blends.

Fig.3 - Modified Oxygen Index for polymers a' + b' versus benzoyl peroxide concentration



Curve A' : polymer a' + [b.p]

Curve B' : polymer b' + [b.p]

Curve C' : polymers a' +[b.p] (50/50, w/w)

Curve D' : theoretical curve for polymers a' + b'

Curve A' shows that addition of benzoyle peroxide to anionic polystyrene lead to a decreasing of the (OI)m value. This is similar to the case observed with cumyl hydroperoxide (curve A, fig.2). Curve B' express the fact that benzoyl peroxide does not have any effect of the (OI)m value of an end phosphonated polystyrene. The slight decrease of (OI)m value found in the case of a pure anionic polystyrene (curve A'), is not observed, the meaning of it is that there is a small synergistic effect between the end phosphonated group and benzoyl peroxide. Curve C' concerning a 50/50, (w/w)blend of the two polymers of table 3, shows that there is a drastic effect of benzoyl peroxide on the (OI)m value of such a blend.

Curve $D_{calc.}$ simple additivity response $(OI)_{blend} = \alpha\, (OI)_{a'} + \beta\, (OI)_{b'}$

Curve $C'_{obs.}$: $(OI)_{blend} < \alpha (OI)_{a'} + \beta (OI)_{b'}$

Comparison of curves C' and D' indicates that there is an important antagonistic effect between an end phosphonated polystyrene and benzoyl peroxide, if they are used together as flame-retardant fitters for standard polystyrene.

CONCLUSION

About the above investigations, it appears that, a generalization concerning flame-retardant interactions between free-radicals generating compounds and end phosphonated polystyrene is not valid. A synergistic effect is observed between end phosphonated polystyrene and cumyl hydroperoxide only. Any effect is found between end phosphonated polystyrene and benzoyl peroxide. A simple additivity effect seems to be the case of blends of end phosphonated polystyrene and polystyrene-polysulfide.

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Accepted December 28, 1983