

Effect of Tetrabromobisphenol A Diallyl Ether on the Flame Retardancy of High Impact-Strength Polystyrene

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Synopsis

The effect of tetrabromobisphenol A diallyl ether (TBBA-DAE) on the flame retardancy of high impact-strength polystyrene (HIPS) was studied and compared with that of tetrabromobisphenol A (TBBA). Experimental results showed that the flame retardancy of TBBA-DAE was superior to that of TBA by thermomixing in the solid state. However, this phenomenon was not obvious by mixing in solution. This effect might result from the bromination of HIPS by the modified Claisen rearrangement of TBBA-DAE during thermomixing in the solid state. Simultaneous addition of the mixture of TBBA-DAE or TBBA with diphenyl isooctylphosphite (DPIOP) into HIPS caused a synergistic effect of flame retardancy and the effect of TBBA-DAE was better than that of TBBA.

INTRODUCTION

In an age of increasing usage of polymers, their flame retardancy has been receiving increasing attention as a serious problem related to product safety. There are two approaches that can be used to improve the flame resistance of polymer materials. One is to mix flame retardants physically with polymers and the other is to graft chemically the fire-resistant elements into the polymer backbone.

Tetrabromobisphenol A (TBBA) has been widely used as a flame retardant and its mechanism of flame retardancy has been described in many reports.¹⁻⁴ Several patents⁵⁻¹⁶ have reported that tetrabromobisphenol A diallyl ether (TBBA-DAE) could be used as a flame retardant added in many polymer materials; however, there is no report comparing the effects of TBBA and TBBA-DAE on the flame retardancy and mechanical properties of polymers. In this article, the flame retardancy of TBBA-DAE on high impact-strength polystyrene (HIPS) will be investigated and compared with that of TBBA. Comparison of their mechanical properties will be presented in another report.

Granzow and Savides¹⁷ showed that the flame retarding effect of adding both bromide and phosphide to plastics is higher than that of the sum of adding bromide or phosphate alone and it is referred as a "synergistic effect." Recently, we have synthesized a compound containing both bromine and phosphorus from phosphite and a bromo-compound and added it to HIPS. This material exhibited a higher synergistic effect of flame retardancy than simply adding the mixture of bromo-compound and phosphite.¹⁸ In this study,

the synergistic effects of TBBA and TBBA-DAE with phosphite, such as diphenyl isooctylphosphite (DPIOP), on the flame retardancy of HIPS will also be investigated.

EXPERIMENTAL

Materials

HIPS (Taita-581) was supplied from Taita Chemicals Ltd., Taiwan, and polyethylene (PE, NA289) was obtained from USI Far East Corp. DPIOP used as a stabilizer was supplied by Weston Chemical Co. Allyl chloride was purchased from Wako Pure Chemical Industries Ltd., Japan, and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPOE) and tetrabromobisphenol A (TBBA) were obtained from local suppliers.

Synthesis

TBBA-DAE. In a typical reaction,¹⁹ to a solution of TBBA (10 g) in methanol (50 mL), a solution of sodium carbonate (2 g in 6 mL of water) and 4.7 g of allyl chloride was added and stirred under reflux for 3 h (at about 50°C). After cooling, the precipitated product was filtered and washed several times with water. Yield: 85%; mp 118°C. IR (KBr): 1650 (m, allyl C = C), 1280 (s, C — O), 870 cm⁻¹ (s, C — Br), with no hydroxyl absorption.

Allyl Tetrabromo-*p*-Cresol Ether (TBPC-AE). ²⁰Tetrabromo-*p*-cresol (TBPC, mp 203°C) was prepared by the reaction of *p*-cresol and bromine with aluminum trichloride as a catalyst as described in our previous report.¹⁸ TBPC-AE was prepared in 80% yield from TBPC and allyl chloride in a sodium carbonate aqueous solution by a procedure described for TBBA-DAE; mp 117°C. IR (KBr): 1640–1650 (m, allyl C = C), 1300 (s, C — O), 820 cm⁻¹ (m, C — Br), without hydroxyl absorption.

Allyl (4-Hydroxy-2,3,5,6-Tetrabromobenzyl) Ether (HTBB-AE). We have described a synthetic procedure for 4-hydroxyl-2,3,5,6-tetrabromobenzyl bromide (HTBBB, mp 185°C) from TBPC and bromine in benzene under radiation of a 250 W reflector lamp in our previous report.¹⁸ Equimolar HTBBB and allyl alcohol were mixed in the sodium carbonate solution at room temperature to produce HTBB-AE with almost 100% yield and mp 93°C. IR (KBr): 3150–3250 (broad, O — H), 1650 (m, allyl C = C), 840 cm⁻¹ (m, C — Br).

Bromination of HIPS. HIPS (10 g) was dissolved in 300 mL of dichloromethane; to this solution a solution of AlCl₃ (0.2 g) and a calculated amount of bromine (0.2–1.0 g) in dichloromethane (50 mL) was added gradually, and the mixture was stirred at room temperature for 3 h. The resulting polymer was precipitated in methanol, washed well with methanol, and dried at 30°C under vacuum for 6 h. Yield: 10.6 g. Besides the characteristic absorptions of HIPS, the IR spectrum showed some additional bands due to the presence of C — Br.

Instruments

The instruments used included Brabender plasticcorder torque rheometer PLE-330, hydraulic (oil) presses (Shung Long Iron Company), oxygen index

determination apparatus (Suga ON-1 meter, Japan), mp determination apparatus (Yamato Model MP-21), and JASCO-IRA-2 IR spectrometer.

Oxygen Index Measurement

The flame retardancy of the polymer sample was determined in terms of the oxygen index according to ASTM D2863-77. The oxygen index (OI) is defined as the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that is necessary to ignite and to support a flame.

Preparation of Specimens

Thermomixing in Solid State

HIPS and PE were individually mixed with different amounts of bromo-compounds such as TBBA, TBBA-DAE, BTBPOE, TBPC-AE, and HTBB-AE, or comixed with phosphorus compound such as DPIOP by Brabendar. Then, the mixtures were molded into sheets by a hot press according to the conditions listed in Table I. The compressed sheets were cut into test specimens with 7 mm width, 3 mm thickness, and 100 mm length used for oxygen index measurement.

Mixing in Solution

About 5 g of HIPS and different amounts (1–10 wt %) of bromo-compounds, such as TBBA-DAE and TBBA, were dissolved in 100 mL of tetrahydrofuran (THF) to form a clear solution. The viscous HIPS solution was spread on a glass plate and dried at 35°C under vacuum to yield films with about 3 mm thickness. These polymer films were then cast into 15 × 5 cm specimens used for flammability testing.

RESULTS AND DISCUSSION

Effects of Thermomixing in Solid State and Solution Mixing on the Flame Retardancy of HIPS

Some bromine-containing flame retardants such as TBBA, BTBPOE, and TBBA-DAE were thermomixed in solid state with HIPS at 170°C and the

TABLE I
Mixing the Molding Conditions for HIPS and PE

	Mixing			Molding		
	Temperature (°C)	Time (min)	Rotating speed (rpm)	Temperature (°C)	Time (min)	Pressure (kg/cm ²)
HIPS	170	5	50	175	3	150
HIPS	170	8	50	175	3	150
HIPS	170	12	50	175	3	150
PE	150	5	50	150	3	150
PE	180	5	50	150	3	150

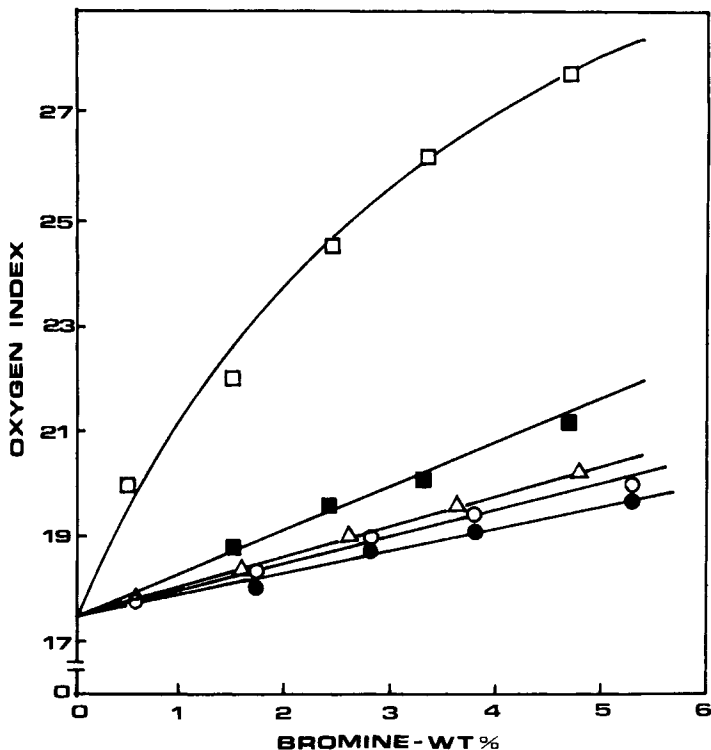


Fig. 1. Plots of OI vs. bromine concentration in HIPS mixed with TBBA [(○) in solid state; (●) in solution], BTBPOE (Δ), and TBBA-DAE [(□) in solid state; (■) in solution].

admixtures were molded into sheets for flammability test. Their effects on the flame retardancy of HIPS are shown in Figure 1. It was found that TBBA-DAE showed a much better fire resistance than BTBPOE and TBBA for the same bromine concentration, and the latter two additives showed a similar flame-retarding effect. The OI of HIPS is linearly proportional to the bromine content within 5 wt % when mixed with TBBA or BTBPOE, while it increases nonlinearly with the bromine concentration when mixed with TBBA-DAE. At the same bromine concentration such as at 3 wt %, the OI of HIPS is about 19 when mixed with the former, while it can be enhanced to 25.5 if the bromide is replaced by TBBA-DAE. This result revealed that TBBA-DAE had better flame retardancy than commercial bromine-containing flame retardants such as TBBA and BTBPOE when they were thermomixed with HIPS.

While TBBA or TBBA-DAE was mixed with HIPS by solution mixing, the flame retardancy of TBBA-DAE was still higher than that of TBBA, but the difference was not so much as in the case of thermomixing. The OI of HIPS is only 20 at 3 wt % of bromine concentration by mixing with TBBA-DAE in solution and it shows a linear relationship between OI and bromine concentration. This indicates that the flame retardancy of TBBA-DAE seems to be related to the temperature of mixing. At higher temperature, such as 170°C, the *o*-allylatic compound of brominated phenol could produce the modified

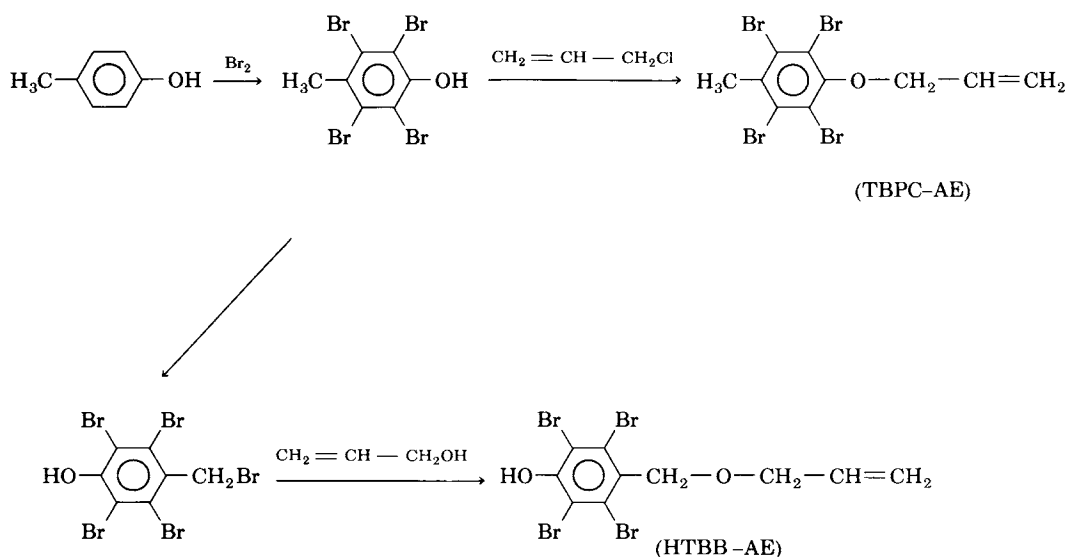
Claisen rearrangement²¹ to release the bromine radical, which might be grafted into the polymer backbone of HIPS. In our initial study, the HIPS whose matrix was bonded with bromine showed a better flame retardancy than that mixed physically with a brominated compound.

Effects of Isomers of Allyl Derivative on HIPS

For further understanding the effect of allyl derivative, two allyl derivatives of TBPC-AE and HTBB-AE were synthesized starting from the bromination of *p*-cresol as shown in Scheme 1. They were thermomixed with HIPS at 170°C, and the mixtures were molded into sheets used for flammability test. As shown in Figure 2, the oxygen index of HIPS for the addition of TBPC-AE was higher than that for HTBB-AE on the same additive concentration. It implied that the flame retardancy is related to the structures of allyl ether compounds. It has been reported²¹ that the *o*-allylatic product of phenolic brominated compounds may produce the modified Claisen rearrangement to release the bromine radical during thermomixing. The better flame retardancy of the specimens of HIPS containing TBPC-AE may be attributed to this modified Claisen rearrangement. Further study of direct evidence such as spectral data is required to account for this phenomenon.

Flame Retardancy of Brominated HIPS

To investigate whether the polymer matrix bonded with bromine had higher flame retardancy than that physically mixed with the brominated



Scheme 1

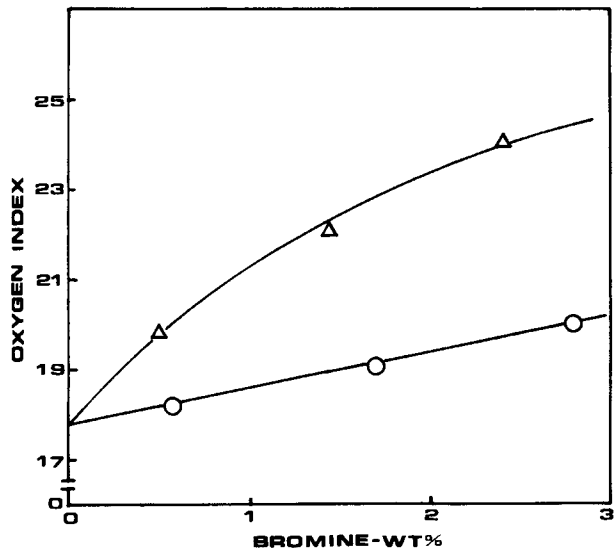


Fig. 2. Plots of OI vs. bromine concentration in HIPS mixed with HTBB-AE (○) and TBPC-AE (△).

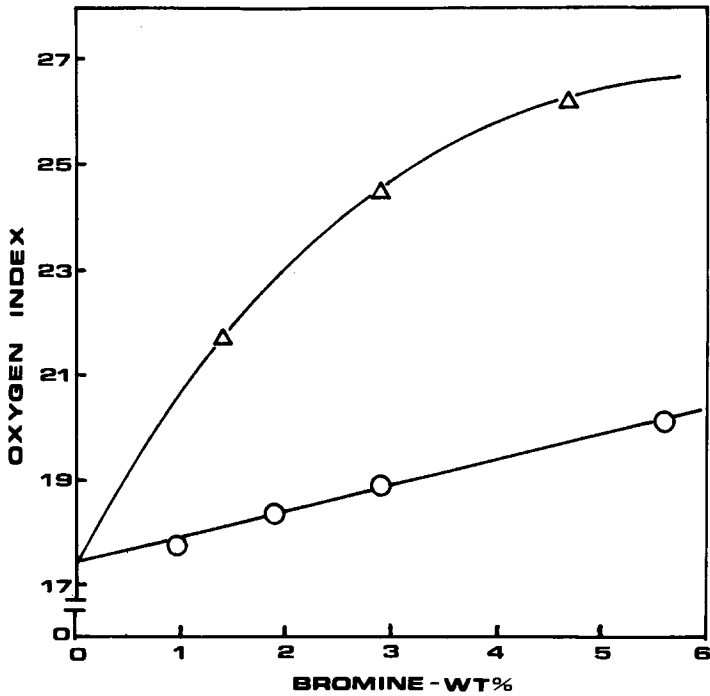


Fig. 3. Plots of OI vs. bromine concentration of brominated HIPS (△) and HIPS mixed with TBBA (○).

compound, brominated HIPS was prepared from the solution of HIPS and a calculated amount of bromine in the presence of aluminum trichloride in dichloromethane. The flame retardancy of the specimens of brominated HIPS was compared with that of the specimens of HIPS physically mixed with brominated compound. As shown in Figure 3, the testing specimens of brominated HIPS had a higher oxygen index than that of HIPS thermomixed with brominated compound in the same bromine concentration. Thus, it is reasonable that the matrix of HIPS is bonded with the bromine by the bromine radical produced from the allylatic compound of brominated phenol during thermomixing, leading to better fire resistance.

Effect of Thermomixing Time on the Flame Retardancy of HIPS

HIPS was thermomixed with TBBA and TBBA-DAE at 170°C for 8 and 12 min, and the oxygen index measurements of the specimens were taken. As shown in Figure 4, the oxygen index of HIPS sample mixed with TBBA did not vary with the thermomixing time, whereas, if the additive amount of TBBA-DAE is above 1 wt % of bromine concentration, a longer mixing time leads to a higher oxygen index. This may be explained by the fact that more bromine was grafted into the matrix of the polymer.

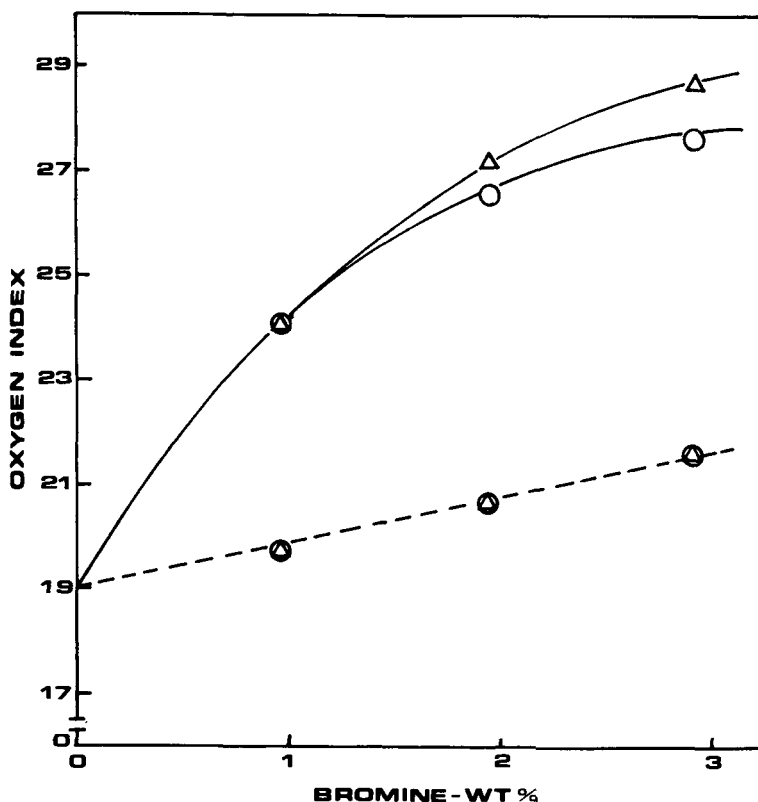


Fig. 4. Plots of OI vs. bromine concentration in HIPS thermomixed with TBBA (---) and TBBA-DAE (—) at 170°C for 8 min (○) and 12 min (△).

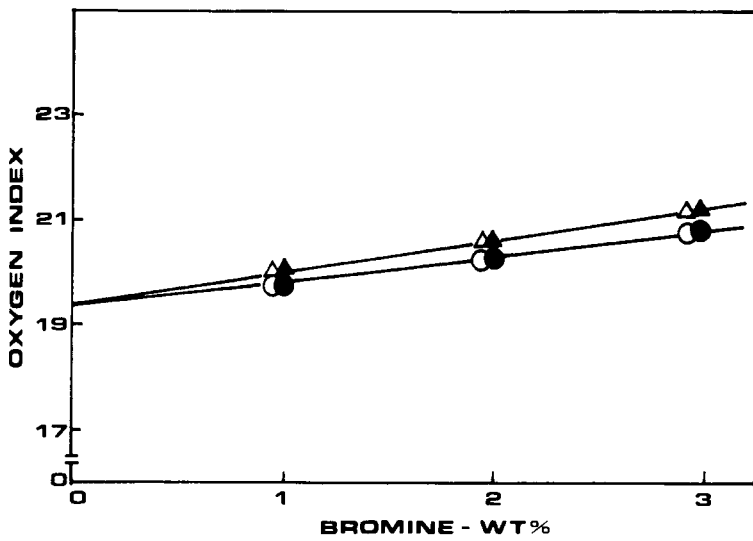


Fig. 5. Plots of OI vs. bromine concentration in PE mixed with TBBA [(○) at 150°C; (●) at 180°C] and TBBA-DAE [(△) 150°C; (▲) 180°C].

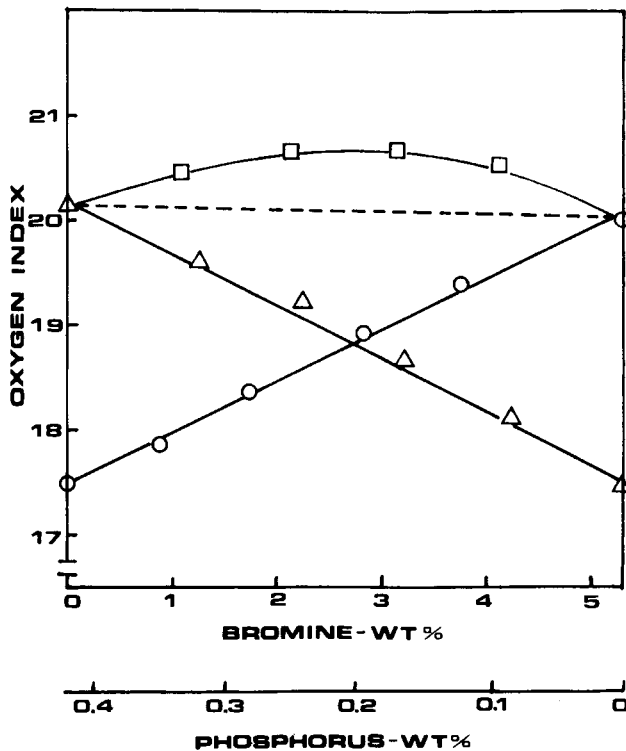


Fig. 6. Synergistic effects of bromine plus phosphorus concentration in HIPS: (○) TBBA; (△) DPIOP; (□) mixture of TBBA and DPIOP; (---) theoretical OI of TBBA plus DPIOP.

Effects of TBBA and TBBA-DAE on the Flame Retardancy of PE

The mixture of TBBA or TBBA-DAE with PE was thermomixed in the solid state at 150 and 180°C, respectively. The results of oxygen index measurements of their specimens are shown in Figure 5. TBBA-DAE just showed a slightly higher flame retardancy than TBBA in the same bromine concentration even at 180°C of mixed temperature. This probably indicates that the bromine radical produced by the modified Claisen rearrangement of TBBA-DAE could not be grafted into the $-C-C-$ chain of PE so an obvious improvement of flame retardancy was not obtained.

Effect of Simultaneous Mix of Bromo-Compound and Phosphorus Compound in HIPS

Because TBBA-DAE is unstable when thermomixed with HIPS, a small quantity of DPIOP may be added as stabilizer to prevent the specimens from discoloration. Granzow and Savides¹⁷ have reported that there exists a synergistic effect of flame retardancy when the polymer is mixed with both bromo-compounds and phosphorus compounds simultaneously. In our studies, the synergistic effect is also found when HIPS was mixed with both DPIOP

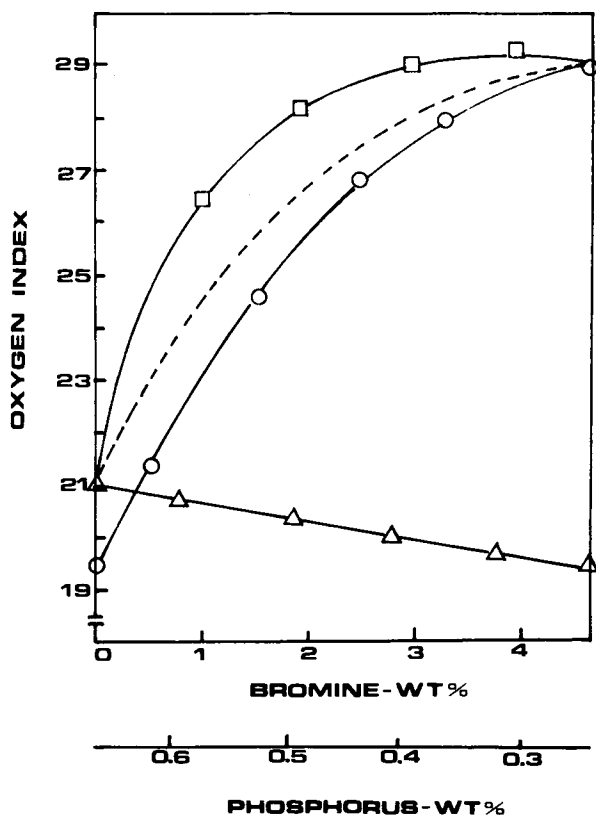


Fig. 7. Synergistic effects of bromine plus phosphorus concentration in HIPS: (○) TBBA-DAE; (Δ) DPIOP; (□) mixture of TBBA-DAE and DPIOP; (---) theoretical OI of TBBA-DAE plus DPIOP.

and TBBA or TBBA-DAE. As shown in Figures 6 and 7, the mixture of TBBA or TBBA-DAE with DPIOP revealed a synergistic effect on the flame retardancy of HIPS. TBBA-DAE also showed a higher effect than TBBA and this also can be owing to the possible Claisen rearrangement produced from the former, although in the presence of DPIOP.

CONCLUSIONS

When TBBA-DAE was used as a flame retardant to mix with HIPS at higher temperature, such as 170°C, the flame retardancy of their specimens was higher than the one containing common flame retardants such as TBBA and BTBPOE. However, the flame retarding effect of TBBA-DAE was just slightly better than that of TBBA when mixed with HIPS at a lower temperature or in solution. This may be explained by the fact that TBBA-DAE produced the modified Claisen rearrangement reaction at higher temperature to release the bromine radical, which may be grafted into the matrix of HIPS, resulting in a higher flame retardancy. Moreover, HIPS grafted chemically with bromine showed better flame retardancy than that mixed physically with bromo-compound such as TBBA.

Simultaneous addition of bromo-compound of TBBA or TBBA-DAE and phosphorus compound of diphenyl isooctylphosphite in HIPS produced a synergistic effect on the flame retardancy, and the effect of TBBA-DAE was higher than that of TBBA.

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