

Effects of Brominated Flame Retardants and Crosslinking Agents on the Flame Retardancy of Rubbers

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Synopsis

Tetrabromo-*p*-cresol (TBPC), pentabromophenol (PBP), and their allyl ether derivatives—tetrabromo-*p*-cresol allyl ether (TBPC-AE) and pentabromophenol allyl ether (PBP-AE)—were used in the study of flame retardancy of ethylene-vinyl acetate (EVA) copolymer and styrene-butadiene rubber (SBR), which were cured by dicumyl peroxide (DCP) and sulfur, respectively. The dependence of the flammability of crosslinking polymers on the polymer matrix, its additives, and the degree of crosslinking was investigated. The empirical equations of flame retardancy were established for these rubbers and compared with the measured values. It was found that the oxygen index of SBR-S system was in accordance with the empirical equations, while the EVA-DCP system, affected by the decomposed residue of DCP, showed a slight deviation. The brominated phenolic compounds of allyl ether (BPs-AE) showed a greater deviation than their precursors. This may be due to the fact that allyl group could react with DCP and lose its excellent flame resistance characteristic, which may be caused by the modified Claisen rearrangement produced in the thermal processing or burning. The phenolic brominated compounds containing the allyl group and a higher bromine content showed better flammability.

INTRODUCTION

The consumption of synthetic rubbers has increased sharply in the last decade. For example, ethylene vinylacetate (EVA) copolymers are widely used as a modifier in hot melt adhesives, wires and cables, and film laminates for packing.¹⁻⁴ Also, styrene butadiene rubber (SBR) is employed in underground coal mining. Although synthetic rubbers have made a great contribution to many industries, almost all are combustible in air. To reduce the combustibility, there are several approaches that can be used to improve the flame resistance of these materials.⁵⁻⁷ One of these is to add fire retardants to the polymeric materials. Organic bromides have long been recognized as effective flame retardants for polymeric materials.^{8,9} Drake and Hastie¹⁰ assumes that bromides release volatile species, mainly hydrogen bromide, into the gas phase combustion zone where these species interfere with the free radical chain branching reactions to remove the high energy OH and H radicals and inhibit the combustion process. The alternate physical mechanism proposed by Larsen^{11,12} postulates that changes in mass and heat transfer are responsible for reduction in flame propagation.

The flammability of rubbers had been studied by blending with a large amount (minimum 30 phr) of flame retardants and achieved by modifying the cure system using curing accelerators and organic peroxide.¹³ In this study, a

small amount (maximum 10 phr) of phenolic brominated compounds was mixed with the rubber systems of EVA-DCP and SBR-S, and an attempt was made to find the factors influencing the flammability and to establish the relationships between the oxygen index and these factors. Finally, the empirical equations of the oxygen index for these two rubber systems to calculate the flame retardancy of rubbers are proposed.

EXPERIMENTAL

Materials

The following materials were used in the study: EVA copolymer (UE631, VA20%) and SBR 1745 were supplied by USI Far East Corp. and Taiwan Synthesis Rubber Corp., respectively; carbon black (VULCAN XC-72) was purchased from Cabot. Dicumyl peroxide (DCP) was provided by Nippon Oil and Fats Co., Ltd.; 2-benzothiazole disulfide (MBTS) was obtained from Premier Chemical. Phenol, *p*-cresol, allyl chloride, bromine, aluminum chloride, and sodium sulfite were all pure grade and purchased from WAKO Pure Chemical, Ltd., Japan. 2-Phenyl-2-propanol was obtained from T.C.I., Japan.

Tetrabromo-*p*-cresol (TBPC) was synthesized by the reaction of *p*-cresol and bromine with AlCl_3 as a catalyst.¹⁴ Tetrabromo-*p*-cresol allyl ether (TBPC-AE) was obtained from the reaction of allyl chloride and TBPC.¹⁵ Pentabromophenol (PBP) was prepared by phenol and bromine by using AlCl_3 as a catalyst.¹⁶ PBP-AE was synthesized from PBP as TBPC-AE from TBPC.

Instrument

The base formation was mixed by roller mixer and molded into sheets by hydraulic oil press. Optimum cure time and maximum torque were determined by a rheometer (Monsanto 100). Oxygen index determinations were made with a Suga ON-1 meter.

Flammability Test

The flammability test was conducted in accordance with ASTM D2863-77. Five to 10 specimens of $3 \times 6 \times 100$ mm were cut from the molded sheets of EVA or SBR vulcanizates. The oxygen index (OI) is used to measure the flame-retardancy effect of various additives and is defined as the minimum oxygen concentration, expressed as volume percent, in a mixture of oxygen and nitrogen at which steady combustion will take place. The OI value was reported as the average of the measure values reproducible within ± 0.25 .

Experimental Method

The Flame-Retardancy Effects of Additives on EVA

Preparation of EVA Sheets. The base formulation containing EVA (100 phr), carbon black (40 phr), and stearic acid (1 phr) were mixed in a two-roll mill at 100°C for 15 min. Individual rubber stocks were prepared by incorporating variable amounts of DCP and brominated compounds in the roller for 5

min. Part of the rubber stock was then molded into sheets 1 or 3 mm thick at 170°C and 150 kg/cm² for different optimum cure times, as determined by a Monsanto rheometer.

Effect of DCP on EVA. Various amounts of DCP (0–5 phr) were added into the base formulation of EVA and molded into sheet at 170°C to make the oxygen index measurement. The maximum torque, obtained from a rheometer, acted as the relative value of the degree of crosslinking.

Effects of Phenolic Brominated Compounds on EVA. The base formulation was blended with various kinds of brominated compounds, including PBP, TBPC, PBP–AE, and TBPC–AE in various additive amounts and molded into sheets for 5 min to make the oxygen index measurement.

Effects of DCP and Its Thermo-Decomposed Residual on EVA. Various amounts of 2-phenyl-2-propanol were added into the base formulation of EVA and molded into sheets for 5 min to make the oxygen index measurement. Also, the EVA formulations were molded into sheets at 100°C to make the oxygen index measurement.

Effect of the Simultaneous Addition of Brominated Compounds and DCP. The base formulation was blended with 3 phr of DCP and various kinds of brominated compounds to make the oxygen index measurement in various additive amounts.

The Flame-Retardancy Effects of Additives on SBR

Preparation of SBR Sheet. The masterbatch containing SBR (100 phr), carbon black (40 phr), and stearic acid (1 phr) was mixed in a roller mixer at 90°C for 15 min, and then a crosslinking agent made up of 1 phr sulfur and 3 phr MBTS, or brominated compounds were added and blended for 5 min. Part of the rubber stock was molded into sheets 3 mm thick at 170°C and 150 kg/cm² for optimum cure time, determined by a Monsanto rheometer.

Effect of the Degree of Crosslinking on SBR. The base formulation of SBR was blended with 3 phr sulfur and 1 phr MBTS. The molded sheets making the oxygen index measurement were prepared according to the different cure time containing maximum torque 10, 20, 30, 40, and 50 (lb-in.) separately.

Effects of Brominated Compounds on Unvulcanized SBR. The molded sheets making oxygen index measurement were prepared by blending the masterbatch with PBP or PBP–AE in various amount and molded for 5 min.

Effects of Brominated Compounds on Vulcanized SBR. The masterbatch was blended with crosslinking agent made up of 3 phr sulfur, 1 phr MBTS, and PBP or PBP–AE to make the oxygen index measurement in various additive amounts.

RESULTS AND DISCUSSION

Flame-Retardancy Effects of Additives on EVA

EVA copolymers, containing no double bonds, is a rubber material with good aging resistance. In this study, EVA containing 20% VA was mixed with carbon black and stearic acid to act as the base formulation. The effects of

DCP and phenolic brominated compounds and their allyl ether derivatives on the flame retardancy of EVA were studied.

The flame retardancy should be a function of the degree of crosslinking because the flame resistance of rubber is related to the degree of crosslinking.¹³ The maximum torque, as determined by a Monsanto rheometer, can be used as a relative value for the degree of crosslinking. The relationships between individual variables and the oxygen index were established by experiment in this study, and then the empirical equations of the oxygen index to cured EVA were obtained by using the additive method and compared with the measured value.

Effect of the Degree of Crosslinking on EVA

To elucidate the effect of DCP on the degree of crosslinking and flammability, we cured the base formulation with various amounts of DCP. The result is given in Figure 1. The optimum cure time at 170°C was in the range of 8–9 min, indicating that an increase in DCP gave better maximum torque at optimum cure time. The oxygen index measurement of the vulcanizates cured with DCP is shown in Figure 2. The limited oxygen index is obtained with the increase in the amount of DCP. If the additive amounts of DCP in Figure 2 is replaced with the maximum torque of EVA vulcanizates, there is a linearship between the oxygen index and maximum torque below 3 phr of DCP additive amount, as indicated in Figure 3 and Eq. (1):

$$OI(EVA) = 21 + 0.0125K \quad (1)$$

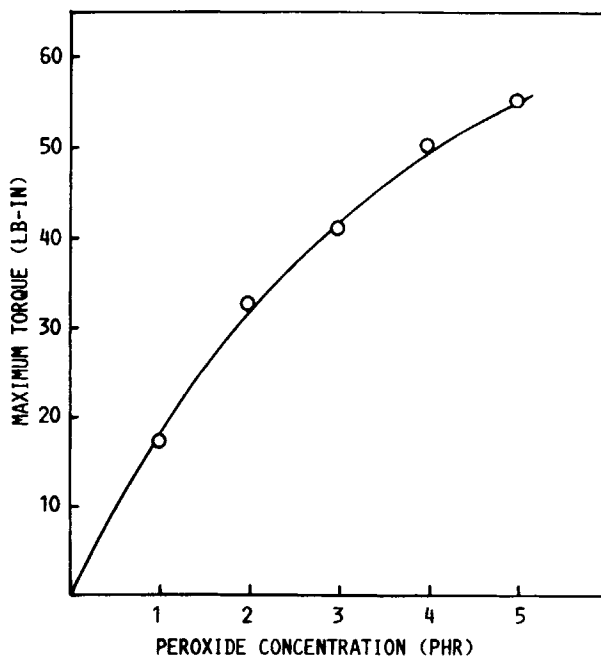


Fig. 1. Plot of maximum torque vs. additive concentration of DCP in EVA.

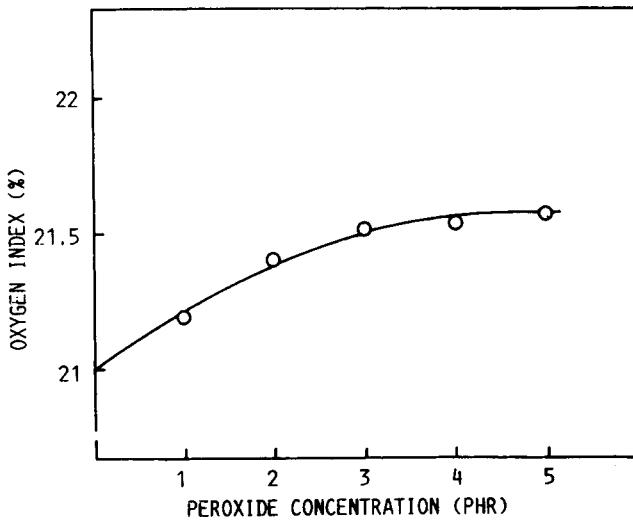


Fig. 2. Plot of oxygen index vs. additive concentration of DCP in EVA, molded at 170°C.

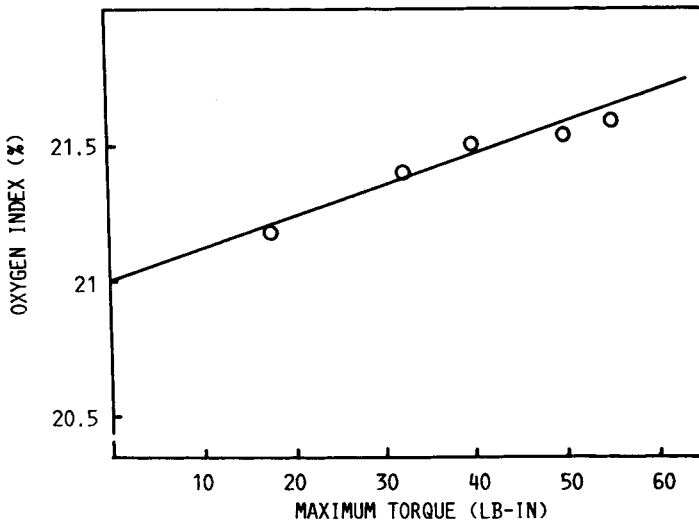


Fig. 3. Plot of oxygen index vs. maximum torque of EVA, without flame retardant.

where K represents maximum torque (lb-in.), measured from the rheographs of the corresponding stocks.

Effects of Phenolic Brominated Compounds on EVA

Pentabromophenol (PBP), tetrabromo-*p*-cresol (TBPC), and their allyl ether derivatives, pentabromophenol allyl ether (PBP-AE) and tetrabromo-*p*-cresol allyl ether (TBPC-AE), are used as phenolic brominated compounds to add to the EVA base formulation. Their flame-retardancy effects on the oxygen index of EVA are shown in Figure 4. This figure shows that allyl derivatives give a slight enhancement in the oxygen index than their precursors. The flame-

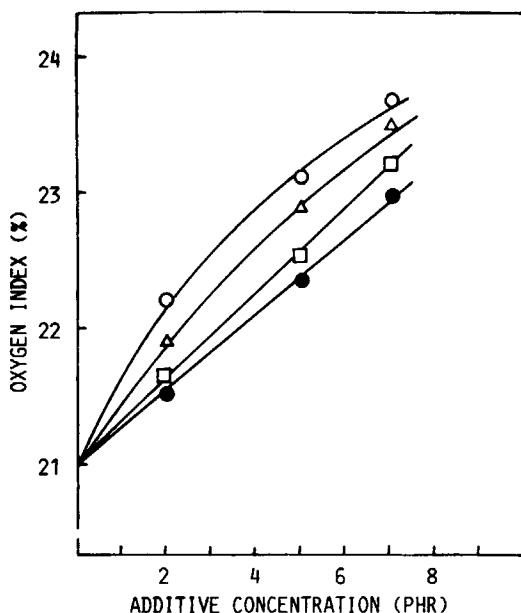


Fig. 4. Plots of oxygen index vs. additive concentration of phenolic brominated compounds in uncure EVA: (○) TBPC-AE; (△) PBP-AE; (□) PBP; (●) TBPC.

retardancy effect of PBP is higher than TBPC in the same additive amount because the former contains a higher bromine concentration. However, TBPC-AE shows better flammability than PBP in the same additive amount due to the presence of allyl group of the former. The phenolic brominated compounds containing *o*-allyl structure are apt to rearrange to form the thermally stable structure of *c*-allyl according to the modified Claisen rearrangement.¹⁷ As a result, the brominated phenolic compounds containing *o*-allyl structure produce the bromine free radical in rearrangement, which gives a better flame-resistance effect. Therefore, the greater the weight percentage of *o*-allyl group, the better the flammability.

According to the oxygen index data in Figure 4, the empirical equations of the oxygen index are established as a function of brominated compounds and shown in Eqs. (2)–(5):

$$\text{For PBP: OI (EVA)} = 21 + 0.29X \quad (2)$$

$$\begin{aligned} \text{For PBP-AE: OI (EVA)} &= 21 + 0.48X - 0.029X^2 \\ &+ 7.2 \times 10^{-4}X^3 \end{aligned} \quad (3)$$

$$\text{For TBPC: OI (EVA)} = 21 + 0.27X \quad (4)$$

$$\begin{aligned} \text{For TBPC-AE: OI (EVA)} &= 21 + 0.73X - 0.082X^2 \\ &+ 4.3 \times 10^{-3}X^3 \end{aligned} \quad (5)$$

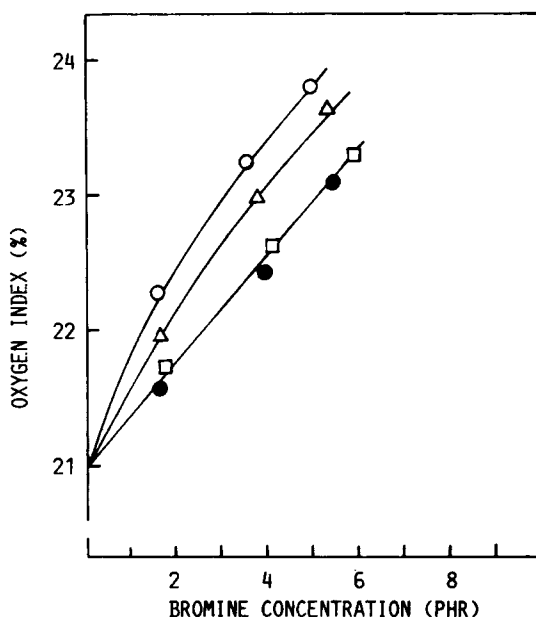


Fig. 5. Plots of oxygen index vs. bromine concentration of phenolic brominated compounds in uncure EVA: (○) TBPC-AE; (△) PBP-AE; (□) PBP; (●) TBPC.

where X represents the additive concentration (phr) of phenolic brominated compounds in EVA.

The dependence of oxygen index on bromine concentration is shown in Figure 5. The oxygen index increases with bromine concentration. The efficiency curves for PBP and TBPC containing no *o*-allyl group are linear and have the same slope among additive amount. The PBP-AE and TBPC-AE containing the *o*-allyl group give better flammability and show different nonlinear curves. The former shows higher oxygen index due to higher weight percent of the *o*-allyl group.

The crosslinking of EVA rubbers may be influenced by the coexistence of EVA and brominated compounds described above. To predict the flammability of EVA rubbers, one needs to know not only the flame-resistance constant of brominated compounds but also the degree of crosslinking, which can be replaced with the maximum torque.

Effect of DCP and Its Decomposed Residue on EVA

As indicated in Figure 3, there is a linear relationship between the oxygen index and maximum torque, while the ratio of OI/DCP illustrated by Figure 2 shows the limited value. The flame-resistance effects of EVA formulation containing various amounts of DCP and molded at 100°C are shown in Figure 6. The oxygen index decreases with the increase in the additive amount of DCP. When EVA formulation is mixed with the residue of DCP thermal decomposition, 2-phenyl-2-propanol, the oxygen index also exhibits depression as shown in Figure 7. The efficiency curve is linear in EVA, and is described by

$$\text{OI(EVA)} = 21 - 0.168Z \quad (6)$$

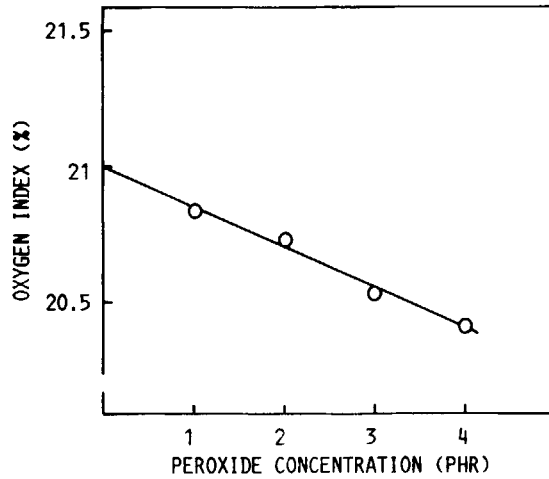


Fig. 6. Plot of oxygen index vs. additive concentration of DCP in EVA, molded at 100°C.

where Z represents the additive amount of 2-phenyl-2-propanol (phr). Experimental results shown in Figure 3 indicate the relationship between the oxygen index and maximum torque using DCP as a crosslinking agent, containing the combustible compounds. The ideal relationship between the degree of crosslinking and the oxygen index corrected by Eq. (6) is established and shown in Figure 8 and Eq. (7):

$$OI(EVA) = 21 + 0.025Y \quad (7)$$

where Y represents the maximum torque of EVA (lb in.).

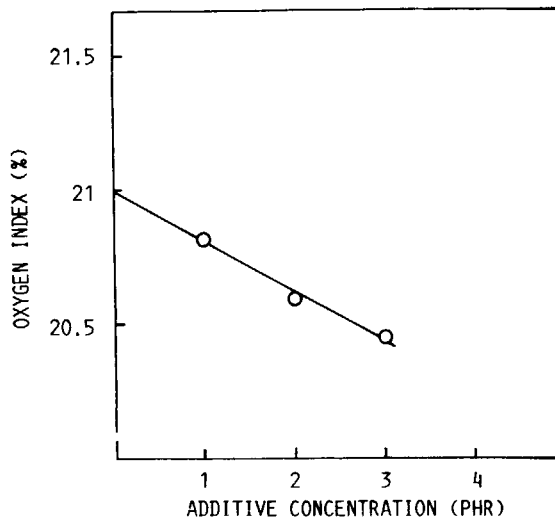


Fig. 7. Plot of oxygen index vs. additive concentration of 2-phenyl-2-propanol in EVA, without flame retardant.

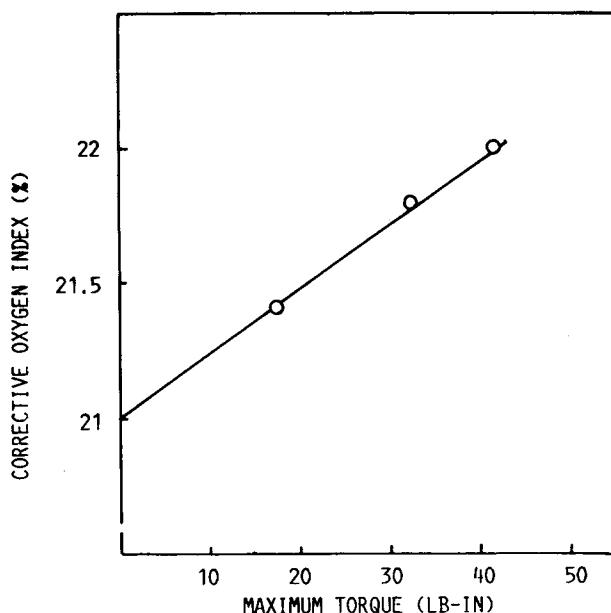


Fig. 8. Plot of corrective oxygen index vs. maximum torque in EVA.

Empirical Equations of Oxygen Index on EVA Rubber

The oxygen index of an uncured EVA base formulation is 21 obtained from the above figures. The flame-retardancy coefficient of the degree of crosslinking is 0.025 from Eq. (7). The constant affected by the decomposed residue of DCP is -0.168 from Eq. (6). The estimated empirical equations are obtained by combining the flame-retardancy constants described above:

$$\text{For PBP: OI (EVA)} = 21 + 0.29X + 0.025Y - 0.168Z \quad (8)$$

$$\begin{aligned} \text{For PBP-AE: OI (EVA)} &= 21 + 0.48X - 0.029X^2 + 7.2 \\ &\times 10^{-4}X^3 + 0.025Y - 0.168Z \quad (9) \end{aligned}$$

$$\text{For TBPC: OI (EVA)} = 21 + 0.27X + 0.025Y - 0.168Z \quad (10)$$

$$\begin{aligned} \text{For TBPC-AE: OI (EVA)} &= 21 + 0.73X - 0.082X^2 + 4.3 \\ &\times 10^{-3}X^3 + 0.025Y - 0.168Z \quad (11) \end{aligned}$$

Flame-Resistance Comparisons of Phenolic Brominated Compounds between Measured and Estimated Values

The maximum torque in optimum cure time is measured by adding various flame retardants to EVA at 170°C , as shown in Figure 9. The estimated values of the oxygen index were obtained by substituting the maximum torque in Figure 9 into Eqs. (8)–(11), and comparing them with the measured values. The results are indicated in Figures 10–13. The measured values are slightly

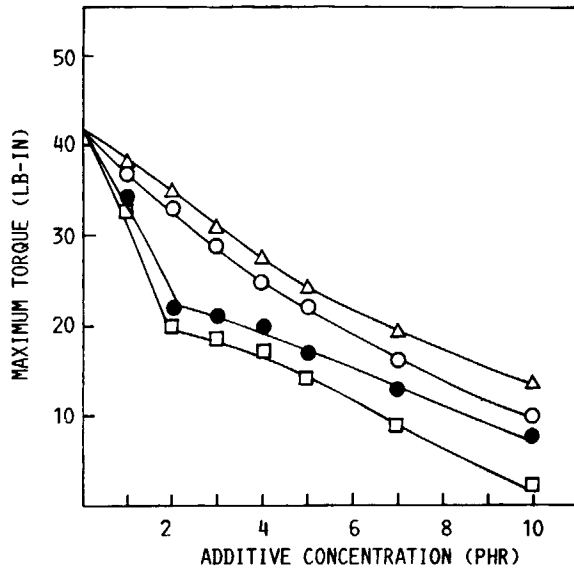


Fig. 9. Plots of maximum torque vs. additive concentration of bromides in EVA vulcanized with 3 phr DCP: (□) PBP; (△) PBP-AE; (●) TBPC; (○) TBPC-AE.

lower than the estimated ones. This may be caused by the rapid depression of the maximum torque and the decomposed residue of DCP. When the additive amounts of TBPC or PBP exceeds 3 phr, the positive effect on flame-retardancy caused by the increase of bromine content can compensate the negative effect caused by the above two factors and so the measured values show a slighter deviation from the estimated ones (see Figs. 10 and 12). While, in the cases of TBPC-AE and PBP-AE, parts of their allyl groups will react

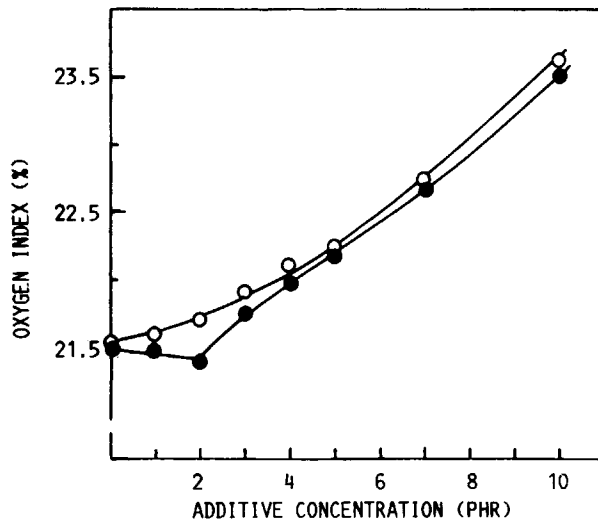


Fig. 10. Plots of oxygen index vs. additive concentration of PBP in cure EVA: (○) empirical value; (●) measured value.

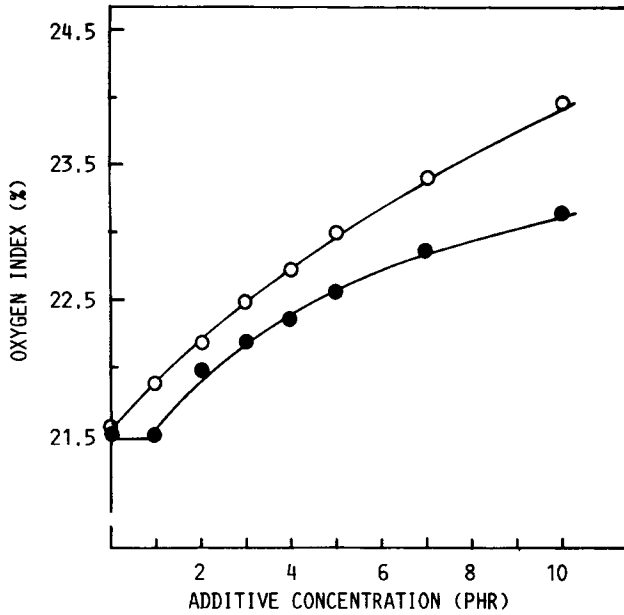


Fig. 11. Plots of oxygen index vs. additive concentration of PBP-AE in cure EVA: (○) empirical value; (●) measured value.

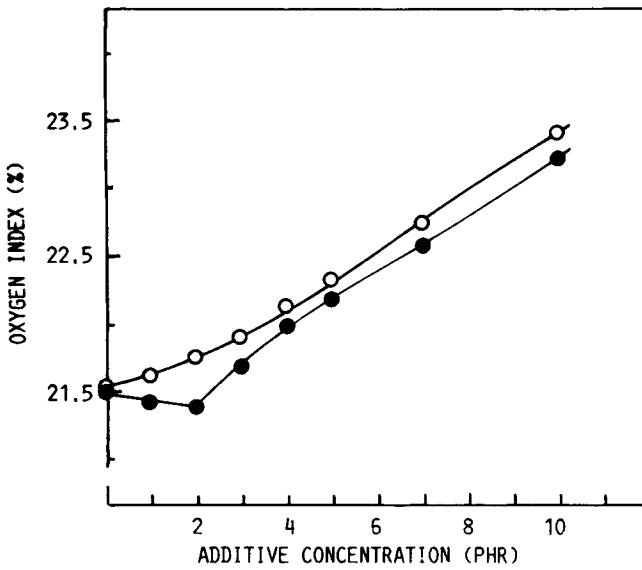


Fig. 12. Plots of oxygen index vs. additive concentration of TBPC in cure EVA: (○) empirical value; (●) measured value.

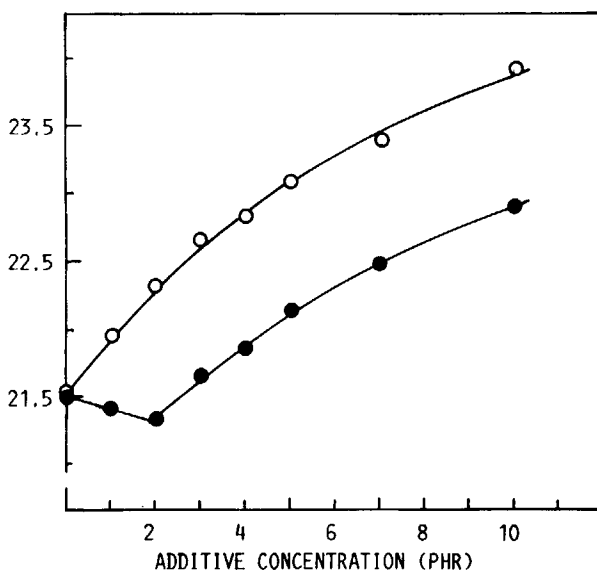


Fig. 13. Plots of oxygen index vs. additive concentration of TBPC-AE in cure EVA: (○) empirical value; (●) measured value.

with the cumyloxy free radical to interfere with the modified Claisen rearrangement, which may occur during thermal processing. As a result, the measured OI values of EVA show a greater deviation from the estimated ones by adding TBPC-AE and PBP-AE (see Figs. 11 and Figs. 13).

The Flame-Retardancy Effects of Additives on SBR

SBR copolymers, containing double bonds, show abrasion and aging resistance. Sulfur and accelerators are always used to produce a crosslinking structure. The base recipe used in this study contains 40 phr of carbon black and 1 phr of stearic acid. The masterbatch was mixed with a crosslinking agent or flame retardants, depending on what is needed. The empirical equations are established as functions of the degree of crosslinking and the additive amounts of flame retardants and compared with the measured values.

Relationships between Oxygen Index and the Degree of Crosslinking

It has been known that the flame resistance is affected by the decomposed residue of DCP described above. For further study of the effect of crosslinking agent on flame retardancy, the SBR masterbatch is mixed with MBTS and sulfur, which will not produce any residue during thermal processing. The dependence of the oxygen index on the degree of crosslinking is shown in Figure 14. It was found that the oxygen index of vulcanized SBR increases with its maximum torque. In addition, there exists a linear relationship, as described by

$$\text{OI(SBR)} = 18.8 + 0.012B \quad (12)$$

where B represents the maximum torque of SBR (lb-in.).

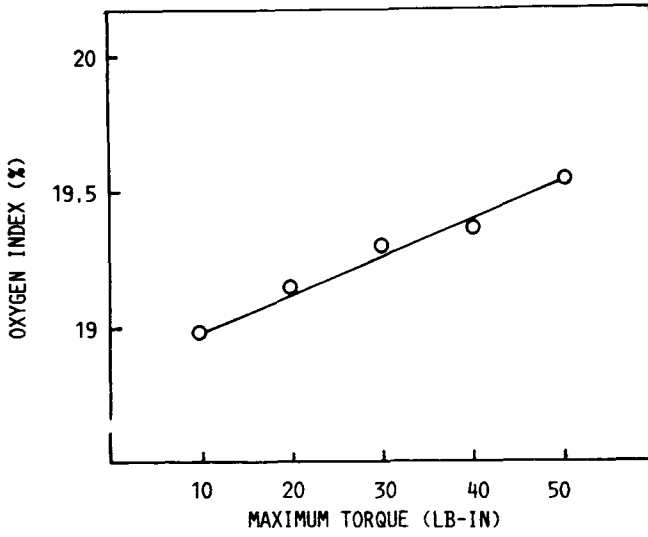


Fig. 14. Plot of oxygen index vs. maximum torque of SBR, without flame retardant.

Effects of Phenolic Brominated Compounds on Unvulcanized SBR

The flame-resistance effects of SBR recipe blended with various amounts of PBP or PBP-AE are shown in Figure 15. The oxygen index increases with an increase in the amount of brominated compounds. There is a linear relation-

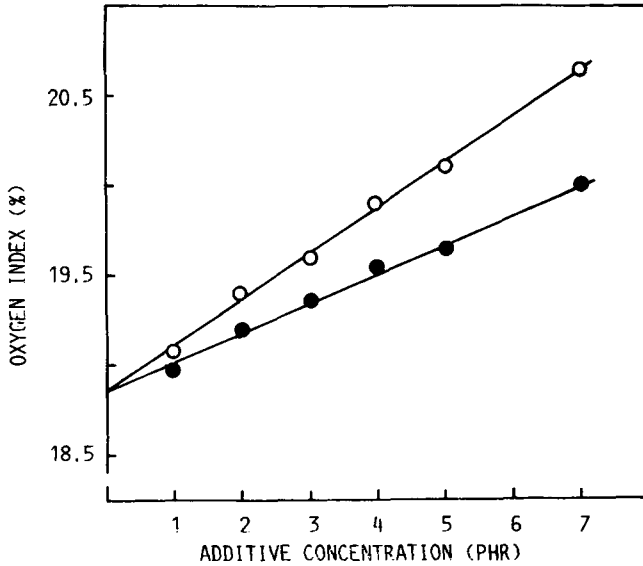


Fig. 15. Plots of oxygen index vs. phenolic brominated compounds in unvulcanized SBR: (○) PBP-AE; (●) PBP.

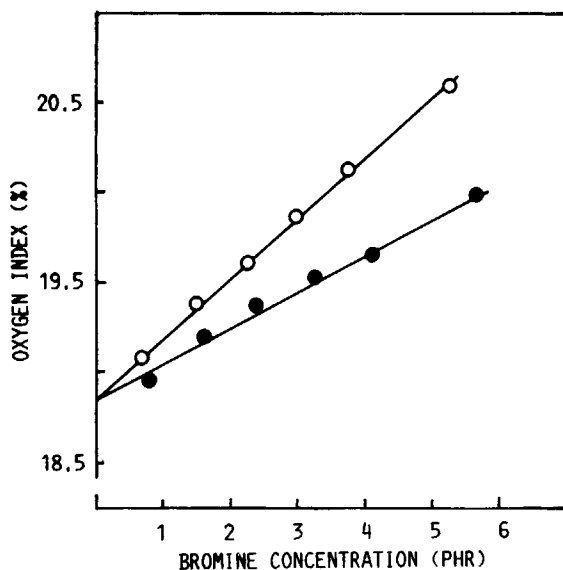


Fig. 16. Plots of oxygen index vs. bromine concentration of phenolic brominated compounds in unvulcanized SBR: (○) PBP-AE; (●) PBP.

ship between the oxygen index and the additive amounts up to 7 phr. The efficiency curves are described by

$$\text{For PBP: } \text{OI}(\text{SBR}) = 18.8 + 0.17A \quad (13)$$

$$\text{For PBP-AE: } \text{OI}(\text{SBR}) = 18.8 + 0.26A \quad (14)$$

where A represents the additive concentration of brominated compounds in SBR (phr). The intercepts correspond to the oxygen index values of the SBR base recipe, while the slope gives an increase of the oxygen index per phr brominated compounds in SBR stocks. The PBP-AE shows better flammability than PBP because the former will bring about a modified Claisen rearrangement in the thermal state. The dependence of the oxygen index on the bromine concentration is shown in Figure 16. The oxygen index increases with bromine concentration.

Empirical Equation of Oxygen Index on SBR

As described above, the flammability of SBR is affected by the degree of crosslinking and the additive amounts of brominated compounds. By combining Eqs. (12)–(14), the empirical equations of oxygen index can be expressed:

$$\text{For PBP: } \text{OI}(\text{SBR}) = 18.8 + 0.17A + 0.012B \quad (15)$$

$$\text{For PBP-AE: } \text{OI}(\text{SBR}) = 18.8 + 0.26A + 0.012B \quad (16)$$

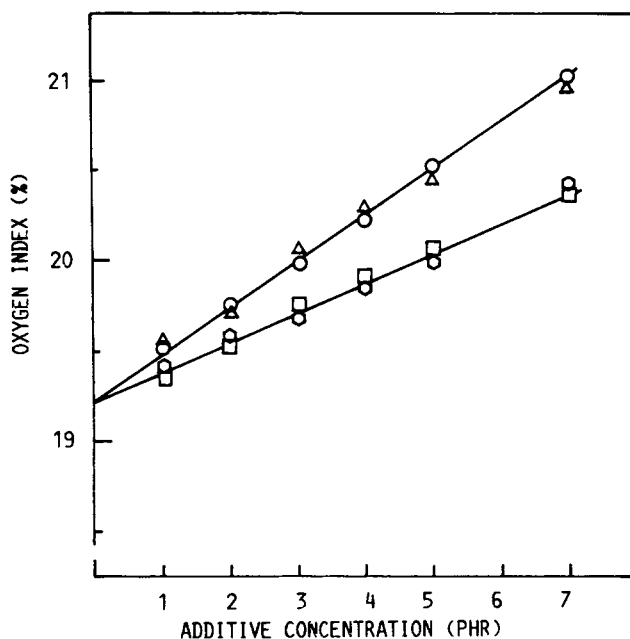


Fig. 17. Plots of oxygen index vs. additive concentration of phenolic brominated compounds in vulcanized SBR: (○) empirical value and (Δ) measured value for PBP-AE; (□) empirical value and (○) measured value for PBP.

Flame-Resistance Comparison of Phenolic Brominated Compounds between Measured and Estimated Values in SBR

To compare the oxygen index of SBR between measured and estimated values, the SBR recipe is mixed with 3 phr sulfur, 1 phr MBTS, and various additive amounts of flame retardants. The results are shown in Figure 17. The maximum torque is 50 lb in. by mixing with various kinds of brominated compounds in various additive amounts, and it shows that the crosslinking of SBR will not be affected by brominated compounds up to 7 phr. The efficiency curves are linear and have the same slope because sulfur does not produce the combustible compounds in the thermal state and will not bring about a free radical reaction with PBP-AE. The intercepts increase from 18.8, as shown in Figure 17, to 19.2, indicating that the degree of crosslinking increases the flame resistance by 0.4 unit. Hence, the allyl group does not react with sulfur or MBTS in SBR-S system during thermal processing. The measured values are the same as the values calculated from empirical equations. Thus, the flammability of SBR can be predicted by the above empirical equations.

CONCLUSION

1. The flammability of polymeric materials is dependent on the characteristic of matrix and flame retardants, their amounts, and the degree of crosslinking. The flame resistance of polymers can be predicted by the empirical

equations containing the degree of crosslinking and amounts of brominated compounds.

2. The measured values are consistent with the estimated ones in SBR rubbers cured by sulfur and an accelerator.

3. The flame-retardancy effect of EVA, cured by DCP, is affected by the amounts of DCP and its decomposition residue in the thermal state, which gives a negative flame resistance. Hence, the predicted model must consider this factor.

4. The brominated compounds containing *o*-allyl structure show better flammability than its precursors. It may be caused by the modified Claisen rearrangement of the *o*-allyl structure in the thermal blending, which will release the bromine radical and produce the brominated reaction for polymeric materials.

5. The greater difference between the measured and estimated values for brominated allyl ether compounds is due to the reaction of DCP and the allyl group during thermal processing, which may destroy parts of the allyl structure and lead to poor flammability owing to the hindrance of the modified Claisen rearrangement of *o*-allyl group.

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