Decabromobiphenyl Oxide–Aluminum Hydroxide System as a Flame Retardant for Styrene–Butadiene Rubber

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ABSTRACT: Styrene–butadiene rubber (SBR) was treated with decabromobiphenyl oxide (DBBO) and/or aluminum hydroxide [$Al(OH)_3$] as a flame retardant. The flammability of the resulting system was determined by the limiting oxygen index method. The effect of the added flame retardants on the maximum torque (MH), curing rate, and tensile properties was also evaluated. The results showed, particularly, that DBBO was a more effective flame retardant than was $Al(OH)_3$. On the other hand, this brominated compound reduced the modulus of elasticity while its effect on the maximum torque was insignificant. Moreover, the addition of DBBO was found to decrease the curing rate of SBR. In contrast, $Al(OH)_3$ significantly increased the maximum torque and also markedly reduced the modulus of elasticity. Moreover, the effect of the treatment with $Al(OH)_3$ on the curing rate was found to be insignificant. The flammability measurement of the SBR treated with different mixtures of the two flame retardants indicated that the two compounds reacted slightly antagonistically. The addition of $Al(OH)_3$ to DBBO in a mixture that was applied to SBR remedied some negative impacts on the mechanical properties when DBBO was added separately to the rubber. The value of the maximum torque of SBR increased and the curing rate slightly increased as well. Meanwhile, the values of the modulus of elasticity were not affected. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2134–2139, 2000

Key words: styrene–butadiene–rubber; flame retardant; decabromobiphenyl oxide; mechanical properties

INTRODUCTION

The use of synthetic polymeric materials has increased sharply over the past few decades. A great concern regarding their flammability was noted and methods reducing their potential hazard were investigated. Much of that concern was directed to the combustion of synthetic polymers and little was directed to the elastomeric products.[1,2] Although synthetic rubbers have made a great contribution to many industries, almost all are combustible in air. Styrene–butadiene rubber (SBR) is one of the elastomers which is widely employed in the tire industry and in underground coal mining, rugs, carpet underlay, and car floor mats, among other uses. Great attention has been paid to modifying SBR's combustion characteristics. Several approaches were made to decrease the tendency of elastomeric materials to burn.[3–9] One of these is the compounding of the rubber with flame-retardant additives, for example, metal hydroxide, phosphorus-containing additives, and chlorinated compounds. Another approach has involved the treatment of the elastomer with specific reagents. A third approach is to incorporate a small percentage of special monomers that contain in their structures one or two elements which are known to impart a degree of flame retardation. However, the first approach, using flame-retardant additives, is the most widely used in practice due to its ease of applica-

Table I Average Composition of SBR Compound and Source of Additives

Material	phr	Source[a]
SBR	100.00	Petroflex
Carbon black N-326	72.00	Alexandria carbon black
Carbon black N-660	24.00	
Zinc oxide	2.70	Element and Carla Schenectady
Stearic acid	0.85	
Formaldelyde resin	2.00	
Aromatic oil	2.20	Misr petroleum oil
Insoluble sulfur	3.80	Flexsys
MBTS	1.10	General Qimica
CTP	0.11	Flexsys

[a] Petroflex (Brazil: Duque-De-Caxias); Element & Carla (England: Birtley-Chester); Schenectady (England: Wolver-Hampton); Flexeyes (Germany: Nien-Burg); General Qimica [Spain: Zubillaga-Lantron (Alava)]; Alexandria carbon black (Alexandria-Egypt); Misr petroleum oil (Alexandria-Egypt).

tion. One factor of great importance to be taken into consideration when formulating a flame-retardant rubber is to compromise between the original physical and mechanical properties of the rubber and the modified combustion characteristics. However, the degree of acceptance of the change which might occur in the physical or mechanical properties of rubber is determined by the type of the application for which the modified rubber will be used. For example, in the tire industry, where the mechanical properties of the rubber is the main concern, a change of about 10–20% in the modulus of elasticity is considered a significant change, which may not be as significant in other applications. This could counteract the advantage of imparting a degree of flame retardance to the product.

In this work, attention was paid to evaluating the flammability characteristics of SBR which is compounded with different mixtures of decabromobiphenyl oxide (DBBO) and aluminum hydroxide [$Al(OH)_3$] as flame retardants. The effect of the added compounds on some of the physical and mechanical properties, including maximum torque, curing rate, and the modulus of elasticity, was also evaluated.

EXPERIMENTAL

Materials and Samples Preparation

Table I shows the composition and the source of the chemical additives used in the compounding of SBR. DBBO (saytex 102 E, City University of London, UK) and $Al(OH)_3$, produced by BDH (Poole, UK), respectively, were used as flame retardants. All the chemicals used were of a good-quality commercial grade and were applied without further purification.

Flammability Measurements

These were made by the limiting oxygen index (LOI) technique, using a Stanton–Redcroft apparatus designed to meet ASTM D2843 specifications.

Mechanical Measurements

Maximum Torque (Mh) and Curing Rates

The maximum torque and the curing rate were measured using a Monsanto MDR 2000 rheometer and according to the ISO 3417 specification. The test was carried out at 180°C for 4 min. Figure 1 shows a typical rheograph from which the time required to reach a torque of 50 or 90% of the maximum torque (t_{50} or t_{90}) was derived.

Tensile Test

The samples were prepared according to ASTM D15-60T and the dumbbell-shaped samples were cut and tested according to ASTM D412 Method A.

RESULTS AND DISCUSSION

Effect of Addition of DBBO and $Al(OH)_3$

Flammability Measurements

Figure 2 shows the effect of various concentrations of DBBO and $Al(OH)_3$ on the flammability of SBR. The results show that DBBO is a very effective flame retardant for rubber and the LOI value significantly increases as the concentration of DBBO was increased. The value for the untreated SBR sample is 20.6 and reaches 37.7 when 10 phr of DBBO was used. The results also show that the addition of 10 phr of $Al(OH)_3$ increases the LOI value to 21.8, a value which is not as high as is the increase that occurred when the rubber was treated with DBBO. During the decomposition of DBBO, volatile species, composed mainly of hydrogen bromide, are released into the gas phase. These species interfere with the radical chain branching reactions to replace the high-energy OH$\surd$ and H$\surd$ radicals which are responsible for

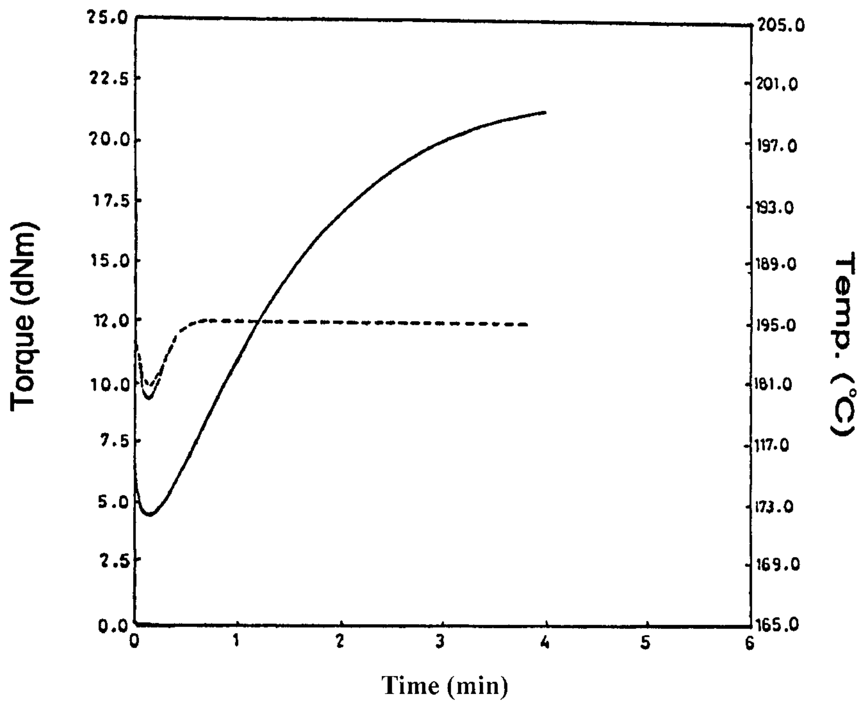

Figure 1 Typical rheometer curve.

the propagation of the flame and thus inhibit the combustion process. This is probably the reason for the observed reduction in the flammability of the rubber after the addition of DBBO. On the other hand, during the endothermic decomposition of $Al(OH)_3$, energy amounting to 1211 kJ/kg is absorbed from the combustion energy of the rubber and, hence, cooling the rubber down below the ignition temperature. This process continues until all the flame retardant has decomposed. In addition, during the decomposition of the inorganic compound, its water of hydration is released into the gas phase. This dilutes the flammable gases above the burning polymers and also hinders it from further access to atmospheric oxygen. Hence, $Al(OH)_3$ interacts with the rubber by acting as a heat sink and producing water vapor and thus reduces its flammability.

Mechanical Measurements

Rheometric Parameters. Figure (3) shows the effect of various concentrations of DBBO and $Al(OH)_3$ on the values of the maximum torque (MH) of SBR. The values obtained were the average of several measurements with a maximum

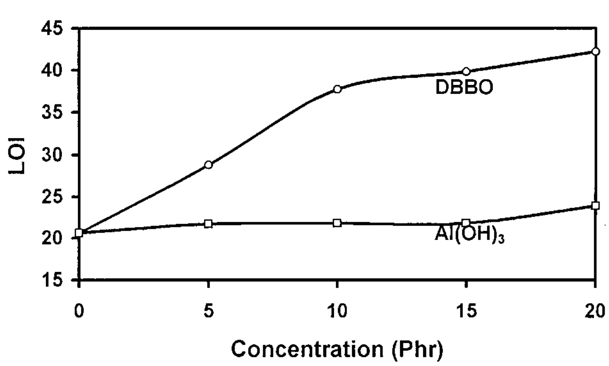

Figure 2 Effect of various concentrations of DBBO and $Al(OH)_3$ on the LOI of SBR.

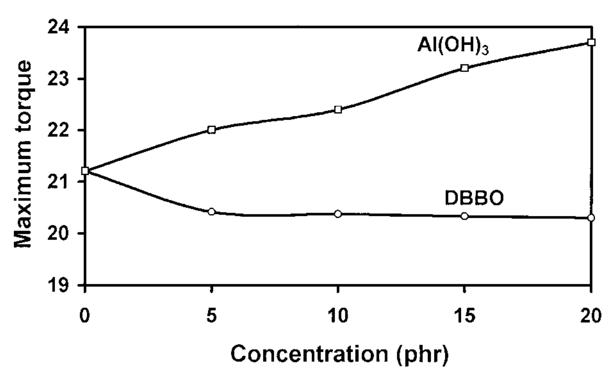

Figure 3 Effect of various concentrations of $Al(OH)_3$ and DBBO on the maximum torque of SBR.

Table II Effect of Various Concentrations of DBBO on the Time to Reach 50% and 90% of Maximum Torque

DBBO (phr)	t_{50} (mm)	t_{90} (mm)
0	1.27	2.77
5	1.34	2.88
10	1.36	2.90
15	1.36	2.89
20	1.37	2.90

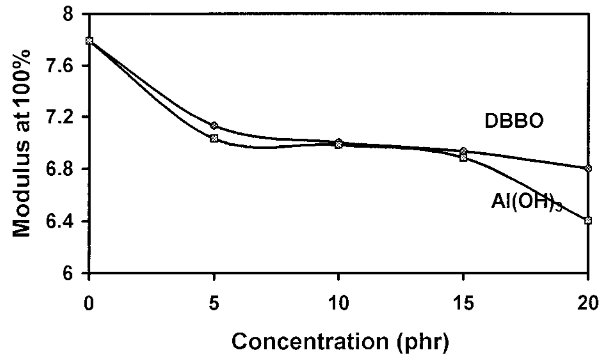

Figure 4 Effect of various concentrations of DBBO and $Al(OH)_3$ on the modulus at 100% of SBR.

standard deviation of ±0.2. The results show that the treatment with DBBO did not significantly affect the values of the maximum torque. The value for the untreated sample was 21.2 dNm and decreased to 20.3 dNm when 20 phr of DBBO was used. On the other hand, the values of the maximum torque (MH) significantly increased as the concentrations of $Al(OH)_3$ increased. The value obtained for the sample treated with 20 phr is 23.7 dNm.

Tables II and III indicate the values of the time needed to reach 50 or 90% of the maximum torque (t_{50}, t_{90}) for samples treated with different concentrations of DBBO and $Al(OH)_3$. The results, which have a maximum standard deviation of ±0.045, show that the addition of DBBO increases t_{50} and t_{90}. The value of t_{50} for the untreated SBR sample is 1.27 mm, and this increases to 1.36 mm when 10 phr of DBBO was added. This indicates that the treatment with DBBO decreased the curing rate. In contrast, the addition of $Al(OH)_3$ was found to produce little change in the values of t_{50} and t_{90} of the SBR.

Tensile Properties. Figure (4) shows the effect of various concentrations of DBBO and $Al(OH)_3$ on the tensile properties of SBR. The estimated maximum standard deviation of the modulus of elasticity at 100% is ±0.1. The results indicate that the addition of DBBO or $Al(OH)_3$ to the rubber decreases the modulus of elasticity when compared with the untreated rubber (Tables IV and V). However, the reduction of the modulus of elasticity which occurred after the SBR treatment with $Al(OH)_3$, particularly at high load, was higher than that observed after the addition of the brominated flame retardant. For example, the value of the modulus of elasticity at 100% obtained for untreated rubber was 7.79. This decreased to 6.8 and 6.40 after the addition of 20 phr of DBBO and 20 phr of $Al(OH)_3$, respectively. The DBBO molecule is very bulky stereochemically due to the presence of 10 bulky bromine atoms in addition to the presence of the backbone of biphenyl oxide which hinders the interaction between the sulfur and the polymer to form vulcanized polymer. This could be the reason for the observed change in the physical and mechanical properties of SBR when DBBO is used.

Table III Effect of Various Concentrations of $Al(OH)_3$ on the Time to Reach 50% and 90% of Maximum Torque

Al (OH_3) (phr)	t_{50} (mm)	t_{90} (mm)
0	1.27	2.77
5	1.29	2.80
10	1.26	2.77
15	1.25	2.74
20	1.26	2.76

Effect of Addition of Different Mixtures of DBBO and $Al(OH)_3$

Flammability Measurements

Figure (5) illustrates the effect of the addition of various mixtures of DBBO and $Al(OH)_3$, with a

Table IV Effect of Various Concentration of DBBO on the Tensile Properties of SBR

DBBO (phr)	Peak Stress (MPA)	Modulus At 100%	Modulus At 200%
0	18.90	7.79	17.11
5	18.90	7.15	15.77
10	18.10	7.00	15.27
15	17.70	6.93	14.93
20	17.40	6.80	14.81

Table V Effect of Various Concentrations of $Al(OH)_3$ on the Tensile Properties of SBR

Al $(OH)_3$ (phr)	Peak Stress (MPA)	Modulus At 100%	Modulus At 200%
0	18.90	7.79	17.11
5	17.50	7.03	15.85
10	16.35	6.98	15.15
15	16.15	6.88	15.00
20	15.62	6.40	14.35

total load of 20 phr. The results indicate that the two compounds react slightly antagonistically. For example, the LOI for the rubber containing a mixture of 10 phr of DBBO and 10 phr of $Al(OH)_3$ is 38.8. However, the LOI of the sample treated separately with 10 phr of DBBO is 37.7, and that for a sample containing 10 phr of $Al(OH)_3$, 21.8. It is of interest to note that in previous work, including ours, where cellulosic and thermoplastic materials were treated with the same brominated compound in conjunction with an aluminum-containing compound, the flame retardant was found to be synergistically enhanced.[10–12] This indicates that the two additives interact differently when they were used to treat rubber.

Mechanical Measurements

Rheometer Parameters. Figure 6 shows the effect of the addition of mixtures of DBBO and $Al(OH)_3$ at constant total load of 20 phr of the mixture on the maximum torque of the SBR compound. The results indicate that the addition of $Al(OH)_3$ to

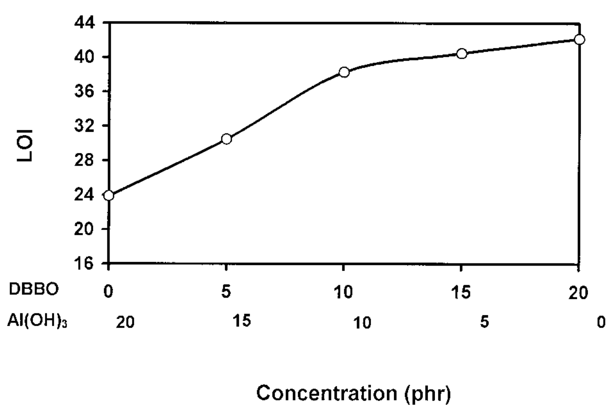

Figure 5 Effect of various mixtures of DBBO and $Al(OH)_3$ on the LOI of SBR at constant total load of 20 phr.

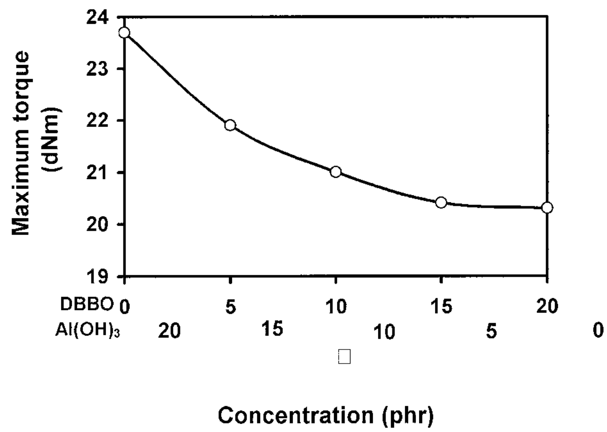

Figure 6 Effect of various mixtures of DBBO and $Al(OH)_3$ on the maximum torque of SBR at constant total load of 20 phr.

DBBO improves the values of the maximum torque. The value of the maximum torque obtained for untreated rubber was 21.18 dNm and that observed after the separate addition of 10 phr of DBBO was 20.37 dNm. This increased to 21.0 after the addition of 10 phr of $Al(OH)_3$ to DBBO. Table VI represents the effect of the addition of the mixture on the time required to reach 50 or 90% of MH. The results, which have a maximum standard deviation of ±0.01, indicate that the curing rate slightly improved after the addition of $Al(OH)_3$ compared with the sample treated with the DBBO separately. For example, t_{50} for untreated rubber was 1.27 mm and that observed after the treatment with 10 phr of DBBO was 1.36 mm. The addition of 10 phr of $Al(OH)_3$ to 10 phr of DBBO decreased the value of t_{50} to 1.32 mm.

Tensile Properties. Figure (7) shows the effect of the addition of various mixtures of $Al(OH)_3$ and

Table VI Effect of Various Mixtures of DBBO and $Al(OH)_3$ on the Time to Reach 50 and 90% of Maximum Torque

DBBO (phr)	$Al(OH)_3$ (phr)	t_{50} (mm)	t_{90} (mm)
0	0	1.27	2.77
10	0	1.36	2.90
0	10	1.26	2.77
0	20	1.26	2.76
5	15	1.32	2.24
10	10	1.32	2.90
15	5	1.33	2.90
20	0	1.37	2.90

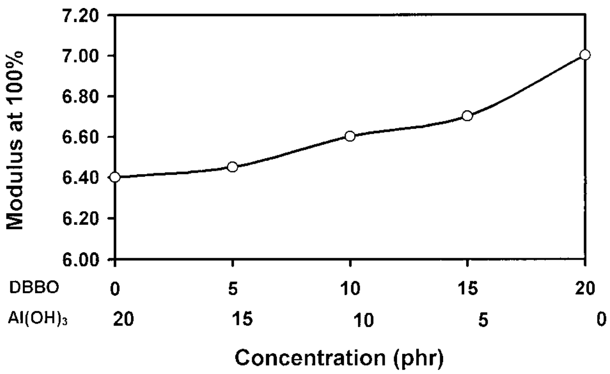

Figure 7 Effect of various mixtures of DBBO and $Al(OH)_3$ on the modulus at 100% at a constant total load of 20 phr.

DBBO on the modulus of the SBR compound. The results indicate that the treatment of the rubber with different mixtures of DBBO and $Al(OH)_3$ reduced the values of the modulus compared with that observed for untreated rubber or for that treated with DBBO and $Al(OH)_3$ on their own. For example, the value obtained for untreated rubber was 7.79 and for that treated with 10 phr of DBBO and 10 phr of $Al(OH)_3$ separately were 7.00 and 6.98, respectively. The value obtained for the mixture of 10 phr DBBO and 10 phr $Al(OH)_3$ was 6.60. This indicates that the mixture of the two compounds antagonistically affects the modulus of the SBR.

CONCLUSIONS

DBBO proved to be a very efficient flame retardant for SBR compared with $Al(OH)_3$. The addition of $Al(OH)_3$ to DBBO does not much increase the efficiency of DBBO as a flame retardant. However, it slightly improves some of the rubber mechanical properties compared to the rubber which was mixed with DBBO separately.

REFERENCES

1. Fabris, H. J.; Sommer, J. G. Rubb Chem Technol 1983, 50, 524.
2. Lyon, J. The Chemistry and Uses of Fire Retardant; Wiley-Interscience: New York, 1970.
3. Lawson, D. F.; Kay, E. L.; Roberts, D. T. Rubb Chem Technol 1975, 48, 124.
4. Kato, H.; Adech, H.; Fukita, H. Rubb Chem Technol 1983, 56, 287.
5. Yang, C.; Chen, W. J Appl Polym Sci 1988, 36, 963.
6. B. F. Goodrich Co. Belg Patent 720 954, March 3, 1969.
7. Polymer Corp.; Austral. Patent 32 843/68, August 7, 1969.
8. Schultz, D. R. Gummo Fasern Kunstst 1995, 49, 489.
9. Janowska, G.; Slusarski, L. J Thermal Anal 1995, 45, 1579.
10. Cullis, C. F.; Hirschler, M.; Khattab, M. A. Eur Polym J 1984, 20, 559.
11. Antia, F. K.; Cullis, C. F.; Hirschler, M. Eur Polym J 1981, 17, 451.
12. Hirschler, M.; Tsika, O. Eur Polym J 1983, 19, 375.