

The Comparison Between Synergistic Effect of Sb_2O_3 and $\text{Al}(\text{OH})_3$ on the Flame-retardancy of HIPS in the Presence of Tetrabromobisphenol-A

Ali-Reza Mahdavian^{*1}, Jalil Morshedian², and Mahdiah Rezaie²

(1) Department of Polymer Science; (2) Department of Plastics
Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115
Tehran, I.R. Iran

Received 23 May 2003; accepted 13 January 2004

ABSTRACT

Brominated flame-retardants are one of the common and efficient groups in producing flame retardant plastics, such as high impact polystyrene. Antimony trioxide is often used as a synergistic agent for halogenated flame-retardants. Aluminium trihydrate (ATH), also is a primitive additive for making flame retardant plastics but no report exists on synergistic effect of this compound in presence of brominated flame-retardant. In this research, the synergistic effect of Sb_2O_3 and ATH, in presence of tetrabromobisphenol-A as a flame-retardant agent has been compared. Limited oxygen indexes (LOI) of the compounded samples were measured by flammability tests. Also thermal gravimetry analysis (TGA) and scanning electron microscopy (SEM) were applied in order to study the thermal behaviour and morphology of the samples, respectively.

Key Words:

flame-retardancy; HIPS;
tetrabromobisphenol-A;
limiting oxygen index;
synergistic effect.

INTRODUCTION

Fire is an important part of combustion. The combustion of polymers is a multi-stage process involving of many mutually associated chemical and physical processes. From chemical aspects, combustion is an exothermic reaction that requires a

fuel, an oxidant and energy (the fire triangle). The mechanism of physical and chemical processes during combustion of polymers has been described in several reports [1-5].

In recent years, polymers-clay nanocomposites have attracted spe-

(*) To whom correspondence should be addressed.
E-mail: a.mahdavian@ippi.ac.ir

cial attention in the scope of flame retardancy. The main advantage of these composites is improvement of thermal resistance and flammability behaviours of corresponding polymers, nevertheless physical and mechanical properties of the polymer must not be changed markedly [6-9].

Brominated flame-retardants continue to offer high performance and cost efficiency for plastic compounds. From this group of flame-retardants, tetrabromobisphenol-A (TBBA) has been widely used and its application in polystyrene and other plastic compounds has been investigated before [10-12].

In order to consider resistance standards of polymeric materials against combustion, one should add large amounts of halogen inhibitors. Their content in the polymeric materials may be as high as 40% by weight. Such a large proportion of non-polymer component normally has bad effects on physical and processing properties of polymers like reducing or elimination of its transparency, changing its colour, accelerating degradation under conditions of use and often raising the cost of end-product [13]. It is, therefore, necessary to reduce the content of flame-retardants and ensure optimum physical and mechanical properties and processing of the obtained plastics.

Antimony trioxide (Sb_2O_3) shows no particular flame-retardant effect on its own. However, it produces a marked synergistic effect with halogen-containing compounds. The most important reaction takes place in the gas phase and as a result it has effects on the radical chain mechanism. Antimony trioxide reacts with the halogen chloride produced during degradation of the halogenated flame-retardant and forms antimony trichloride and various antimony oxychlorides, which act as radical interceptors like HCl or HBr in the polymeric base [12].

Inorganic metal hydroxides make up more than 50% of the mass of all flame-retardants sold worldwide. Depending on the type of polymeric material and its end-use, a flame retardant filler is added in amount of 5-65% by weight specifically in the case of aluminium trihydrate (ATH) [$\text{Al}(\text{OH})_3$]. ATH starts to breakdown in the temperature range from 180°C to 200°C, converting to aluminium oxide taking place in an endothermic reaction with release of water vapor. The advantages and disadvantages of Sb_2O_3 and ATH have been reported exceedingly before [12].

High impact modified polystyrene (HIPS) is wide-

ly used for numerous applications such as in particular buildings, transportation and electrical applications. In many of these, fire safety regulation rules must be considered and so flame-retardants have to be used to improve the ignition resistance of polymers [13] due to some disadvantages of Sb_2O_3 like discoloration, high cost, increasing smoke and afterglow. In this research we have compared the synergistic effect of antimony trioxide and aluminium trihydroxide in the presence of tetrabromobisphenol-A in the flame-retardancy of HIPS. The synergism mechanism of antimony trioxide has been known [14,15], but according to our knowledge, there is no specific study about the synergistic effect of aluminium trihydrate in presence of brominated flame-retardants in the literature.

EXPERIMENTAL

Materials

High impact polystyrene (HIPS) obtained from Iranian Petrochemical Industries (Tabriz Petrochemical Co.) was used in this research work. Tetrabromobisphenol-A (TBBA) as the halogenated flame-retardant was obtained from Fluka Chemical Co. Antimony trioxide (Sb_2O_3) and Aluminium trihydrate (ATH) were purchased from Merck Chemical Co. and used without further purification.

Equipments

Mixing of samples was performed with 60 cc Haake internal mixer with banbury rotors (HBI- System 90). The bulk of compounds were compression moulded in order to prepare sample sheets.

Limiting oxygen index (LOI) measurements were carried out by using of FTA flammability unit, Stanton Redcroft. Vertical burning test was applied for evaluation of LOI in accordance with ASTM D2863, with $10^* 7^* 0.2$ cm specimen dimensions.

Thermal gravimetric analyses (TGA) were performed with a PL instrument and a heating rate of 10°C/min in the region of 25-600°C. The sample weight was 5-10 mg in each run.

The morphological studies were carried out by using scanning electron microscopy (SEM, Stereoscan 360, Cambridge Instrument). Each sample was evacuated, flushed with argon gas, evacuated again and coated with powdered gold for SEM analysis.

Table 1. Formulation of samples with Sb_2O_3 and ATH as the synergist.

Sample No.	HIPS (wt %)	TBBA (wt %)	Sb_2O_3 (wt %)	ATH (wt %)
S0	85.0	15.0	0.0	-
S1	84.0	15.0	1.0	-
S2	82.0	15.0	3.0	-
S3	80.5	15.0	4.5	-
A0	85.0	15.0	-	0.0
A1	84.0	15.0	-	1.0
A2	82.0	15.0	-	3.0
A3	80.0	15.0	-	5.0

Sample Preparation in the Presence of Sb_2O_3 as a Synergist

HIPS, TBBA and Sb_2O_3 were mixed in a Haake internal mixer with different amount of Sb_2O_3 at 170°C (Table 1). The rotor speed was set at 60 rpm and the residence time was 4 min. The obtained bulk compounds were compression moulded at 190°C under 160 bar pressure to form the corresponding sheets with $10 \times 7 \times 0.2$ cm dimensions.

Samples Preparation in the Presence of ATH as a Synergist

The procedure in these experiments were similar to the previous one (samples containing Sb_2O_3), except that ATH was used instead of Sb_2O_3 . The reagent's quantities are listed in Table 1.

RESULTS AND DISCUSSION

Here we have performed simple mixing of HIPS, TBBA and the synergist (Sb_2O_3 or ATH) by using a Haake internal mixer at 170°C during 4 min residence time. Then the obtained products were compression moulded at 190°C and 160 bar to produce sheets, which were used for some identification tests.

Flammability Studies

The variation of limiting oxygen index (LOI) quantities versus weight percent of synergists (ATH and Sb_2O_3) in each compound has been plotted in Figure 1 (Table 2). These results show that by increasing the

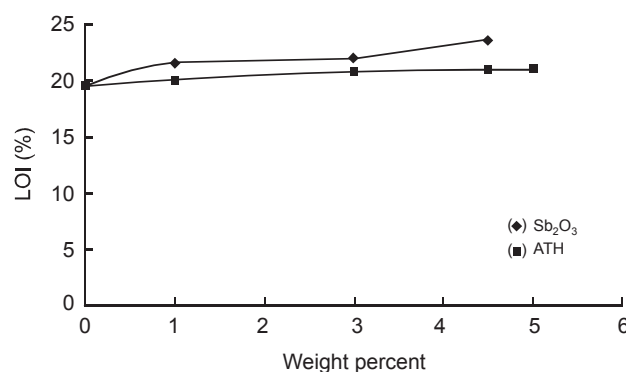


Figure 1. Limiting oxygen index amounts for samples containing different weight percent of Sb_2O_3 & ATH.

weight percent of a synergists, there is a slight increase in LOI amount in both cases. The flame-retardancy for samples containing Sb_2O_3 is more than those containing ATH. This could be concluded from the greater amount of the obtained LOIs given in Table 2.

It was observed that the LOI amount will increase about 20.5% in comparison with the blank sample [without any Sb_2O_3 (sample S0 in Table 2)] by addition of 4.5% Sb_2O_3 . This increase for ATH was about 7.7%.

Antimony oxide is a known synergistic agent and several mechanisms have been proposed due to its effect in the presence of halogenated flame-retardants [14,16-18]. One of its most common mechanisms was introduced before [11].

According to the above mechanism, antimony oxide is changed to antimony oxychloride in the presence of hydrogen halides that is the effective intermediate. This intermediate produces SbCl_3 through the

Table 2. The LOI values of samples containing Sb_2O_3 and ATH.

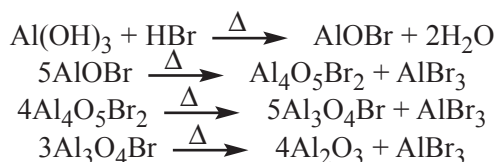
Sample NO.	LOI(%)
S0	19.5
S1	21.5
S2	22.0
S3	23.5
A0	19.5
A1	20.0
A2	20.7
A3	21.0

chain reactions, which is a gas product and it is excluded from the system.

ATH has a different mechanism. It has been proved that it plays the role of a flame-retardant by itself via an endothermic and thermal degradation process [11,12]. The product of this degradation (i.e., Al_2O_3) on the substrate acts as an insulating protective layer together with the charring product.

Consequently, antimony oxide enters the flame-retardancy mechanism in the presence of a halogenated compound as a synergist during chain reaction mechanism. However, according to the known mechanisms for ATH, it does not need any halogenated compound. Therefore, large amounts of ATH are required in order to obtain optimum and somewhat efficient flame-retardancy effect (up to 65% by weight).

Here, we observed that ATH also could have synergistic effect in the presence TBBA according to the increase in LOI amount of the corresponding compound. This means that it could have another degradation mechanism plus to its previously known and conventional proved one. This would be explained as below (Scheme I).



Scheme I

It is notable that the above mechanism is similar to the proposed mechanism by Pitts et al. for antimony oxide [18].

Accordingly, the observed synergistic behaviour of ATH in the presence of TBBA would be explainable. But at the same conditions it could not effectively act as antimony oxide. This may be due to the more susceptibility and reactivity of Sb_2O_3 to contribute in the chain reactions than ATH.

Thermal Properties

In order to study thermal properties of samples, TGA thermograms of the samples containing ATH (Figure 2) and also antimony oxide (Figure 3) as the synergist with different weight percents have been shown here. It could be concluded that their

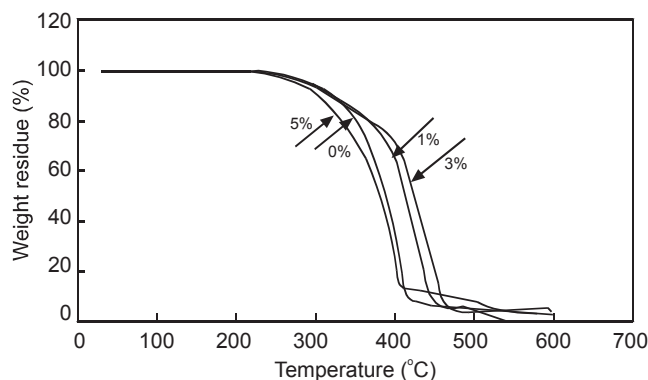


Figure 2. TGA Thermograms of samples with different weight percent of ATH.

thermal degradation is about the same and does not change with varying the amount of synergist remarkably. Also the weight percent residue of samples after heating up to 600°C in the air atmosphere were determined by TGA and the obtained data was plotted versus weight percent of synergist (Figure 4). Samples containing ATH are thermally stable after heating process. But those including Sb_2O_3 have less or at most equal thermal stability relative to the primary compound. This could be because of some chemical reactions originating from the antimony oxide, which cause its easier and faster thermal degradation. Of course, after the critical amount of Sb_2O_3 (i.e., 1% by weight), this effect is diminished and the residual weight percent increases as usual.

However, the temperature relating to 10% weight loss is almost identical for each sample containing ATH

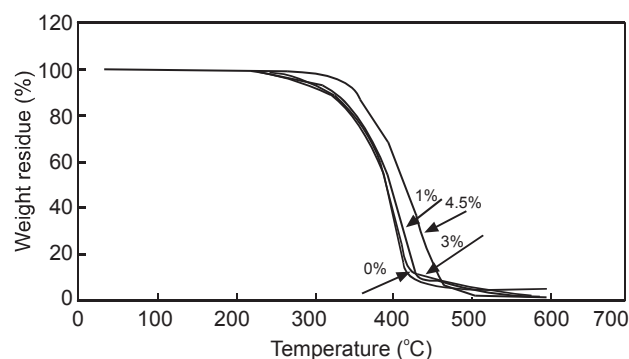


Figure 3. TGA Thermograms of samples with different weight percent of Sb_2O_3 .

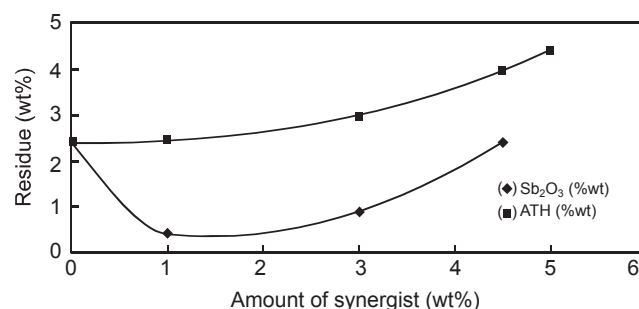


Figure 4. Weight percent residue of samples at 600°C versus the amount of synergy.

(Figure 5). Except for the sample containing 4.5% Sb₂O₃, this trend could also be observed (Figure 5). 10% Weight loss will occur at higher temperature in this sample than the others. Similar behaviours were found for the temperatures at which 90% weight loss would occur with different amounts of the synergist (Figure 6).

This means that ATH and Sb₂O₃, as synergists in this research work, have the same effects on the ther-

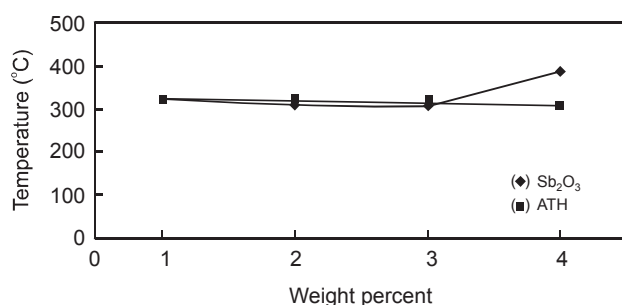


Figure 5. Temperatures for 10% weight loss versus the amount of synergist.

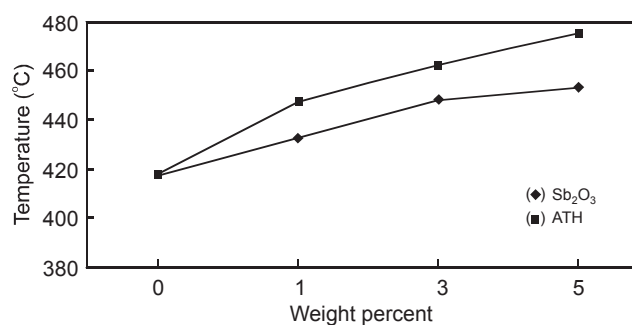


Figure 6. Temperatures for 90% weight loss versus the amount of synergist.

mal properties of their corresponding compounds.

Morphological Studies

Figures 7 and 8 show the SEM of samples with ATH and Sb₂O₃, respectively. With attention to melting point of TBBA (178-180°C) and processing temperature, it is clear that mixing of this material, is melt-melt mixing and HIPS/TBBA form a continuous phase. Therefore, as shown in SEM micrographs, ATH and Sb₂O₃ are dispersed phase in TBBA/HIPS continuous phase. Although the amounts of synergistic agents are not too much, SEM micrographs show good dispersion and distribution during mixing process. The reason could be related to less surface activity of these fillers. Good dispersion, distribution and mixing of the synergistic agents in TBBA/HIPS are very important in flame conditions in order to make fast cooling and flame-retardancy of the system homogeneously.

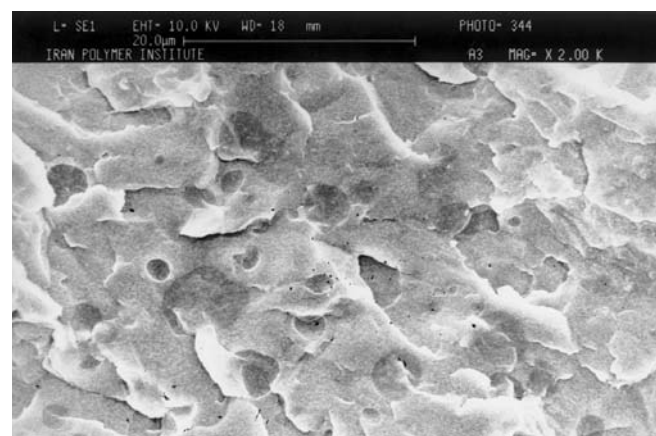


Figure 7. SEM Micrograph of the sample containing 5% ATH.

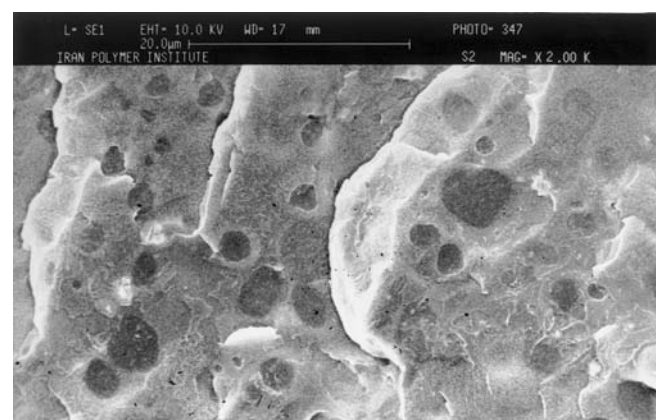


Figure 8. SEM Micrograph of the sample containing 4.5% Sb₂O₃.

CONCLUSION

In this research the effect of two mineral components, antimony trioxide and aluminium trihydrate, for creation of synergism effect in flame-retardant high impact polystyrene with tetrabromobisphenol-A was studied and also compared. The obtained results from thermal analysis and limiting oxygen index measurements show that ATH like Sb_2O_3 has synergistic effect in the presence of TBBA. But its effect is less and the optimum amount of this component should be more than Sb_2O_3 . Thermal stability of samples containing ATH is improved in comparison with samples containing Sb_2O_3 . Morphological studies reveal that each of the above two mineral components has good dispersion and distribution in HIPS/TBBA system through the mixing process.

ACKNOWLEDGEMENTS

Authors wish to thank Iran Polymer and Petrochemical Institute for financial support of this work, Grant No. 803P416.

REFERENCES

1. Pal G. and Macskasy H., *Plastics: their behavior in fires*, Elsevier, Ch. 2, (1991).
2. Fire F.L., *Combustibility of Plastics*, New York, Van Nostrand Reinhold, Ch.7, (1991).
3. Asseva R.M. and Zaikov G.E., Fabrikant T, Ed., *Combustion of Polymer Materials*, Hanser, 347-351 (1981).
4. Lewin M., Atlas S.M., and Pearce E.M. (Ed.), *Flame-retardant polymeric materials*, **2**, New York, Plenum, 194-197 (1978).
5. Edenbaum J., (Ed.), *Plastics and Modifiers Handbooks*, New York, Van Nostrand Reinhold, 1034-1050 (1991).
6. Zhu J., Start P., Mauritz K.A., and Wilkie C.A., Silicon-methoxide modified clays and their polystyrene nanocomposites, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1498-1503 (2002).
7. Zilg C., Thomann R., Baumert M., Finter J., and Milhaupt R., Organic/ inorganic hybride materials and nano composites based upon layered silicates modified with cyclic amidines. *Macromol. Rapid Commun.*, **21**, 1214-1219 (2000).
8. Zilg C., Dietsch F., Hoffmann B., and Mulhaupt R., Nanofillers based upon organophilic layered silicates, *Macromolecule*, **169**, 65-77 (2001).
9. Morgan A.B., Gilman J.W., Harris R and Jackson CL., Flammability of polystyrene-clay nanocomposites, *ACS Polym. Mat. Sci. Eng.*, **83**, 53-54 (2000).
10. Yang C.P., Sheen B.S., Effect of tetrabromobisphenol- A diallyl ether on the flame-retardancy of high impact polystyrene., *J. Appl., Polym. Sci.*, **37**, 3185-3194 (1989).
11. Muller H. and Gachter R., (Eds.), *Plastics Additives Handbook*, Hanser, Ch. 12, (1990).
12. Dufto P.W., *Fire: Additives and Materials*, RAPRA Technology Ltd., Ch. 4, (1995).
13. Radloff B., Spiess H.W., Books J.T., and Dowling K.C., Interaction between polybrominated flame retardants and high impact polystyrene, *J. Appl. Polym. Sci.*, **60**, 715-720 (1996).
14. Karak N. and Maiti S., Antimony polymers: III. Flame retardant behaviour of chloroprene and natural rubber vulcanizates with antimony polymer. *J. Appl. Polym. Sci.*, **98**, 927-935 (1998).
15. Boryniec S. and Przygocki W., Polymer combustion process: flame retardants of polymeric materials. *Int. Polym. Sci. Technol.*, **27**, 83-93 (2000).
16. Siddhamalli S.K. and Lee W.W., Injection moldable FR-HIPS formulation based on blends of chlorinated wax and non- diphenyl oxide-brominated flame retardant in conjunction with metal oxide metal sulphide synergists, *J. Vinyl & Additive Technol.*, **4**, 117-125 (1998).
17. Lewin M., Synergism and catalysis in flame retardancy of polymers, *Polym. Advan. Technol.*, **12**, 215-222 (2001).
18. Starnes W.H., Kamg Y.A., and Payne B., Interaction of antimony oxide with a chlorinated organic fire retardant in nylon 6.6., *ACS Polymeric Materials*, Fall Meeting, **83**, Aug. 94-95 (2000).