

Preparation of Flame Retardant Polystyrene via In-Situ Bulk Polymerization Method and Evaluation of its Flammability Properties

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ABSTRACT

In this study, in-situ bulk polymerization was investigated for obtaining flame retardant polystyrene (PS). The halogenated and phosphoric compounds were used as flame retardant additives and Perkadox 30 was used as a synergist. The flammability of the PS was evaluated by thermogravimetric analyzer (TGA), limiting oxygen index (LOI) and UL-94 tests. The results show that polymerization process for production of flame retardant polystyrene requires lower amount of flame retardant additives compared with the process for production of flame retardant composites. Furthermore, using Perkadox 30 as a synergist lowers the loading of flame retardant additives. LOI tests show that flame retardant polystyrene is synthesized by adding at least 0.35 % (w/w) hexabromocyclododecane (HBCD) during polymerization. TGA analysis confirms that with addition of HBCD the degradation temperature decreases and weight loss occurs quickly. The degradation temperature of the sample consisting of 0.8 % (w/w) HBCD was lower than the sample that consists of 0.35 % (w/w) HBCD and 0.45 % (w/w) triphenylphosphate (TPP). The pure polystyrene did not pass the UL-94 test because of inflammability and greater dripping. For samples with HBCD, less time is needed to quench the flame and these samples passed the UL-94 test. On the other hand, greater dripping of polymer melt led to transmission of UL-94 rate from V0 to V2. It is also observed that flaming rate for samples with TPP was very low and dripping did not occur.

1. Introduction

Polystyrene (PS) is one of the most widely used polymers due to its lower density, higher chemical resistance, high performance-price ratio and convenience of processing and

molding. As compensation for the high flammability and serious dripping during burning, brominated compounds such as hexabromocyclododecane (HBCD), etc. are imparted into the PS products in industrial

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scales [1]. Most styrenic polymers are easily flammable in air with 21 % oxygen because of their carbon building. Some additives are mainly used as flame retardants in order to increase the resistance of polymer to burning. Using flame retardants can prevent fire from aggravating. Flame retardant materials are not designed to inhibit the flame; however, they are used to minimize flame spread and to prevent continuous burning. The most regular styrenic flame retardants are total organic halogens. These halogens are analyzed under the heat and form halogenated radicals which are involved in oxidation of volatile fuels. These compounds generate toxic gases (such as vapors of hydro bromic acid and hydro chloric acid) and high amounts of smoke [2]. These gases are very corrosive and are environmental pollutants. Retardants including halogens can hardly be disposed in the environment and they are environmental pollutants.

In this research in-situ bulk polymerization is used to obtain flame retardant polystyrene. For the flame retardancy of the polymer, we used the halogenated and phosphoric compounds as flame retardant additives and Perkadox 30 as a synergist. The purpose of this research was to reduce the amount of halogenated flame retardant materials and to increase the efficiency of these materials in retarding synthesized polystyrene. We prepared samples with three different methods. In the first method, phosphate flame retardants in combination with halogenated flame retardants were used; in the second method, flame retardant materials were used while synthesizing in order to have better placement in polymer matrix; and in the last

method, Perkadox 30 (Dicumene) was used as a synergist. Limiting oxygen index (LOI), UL-94 and thermogravimetric analysis (TGA) tests were applied on synthesized flame retardant polymers to investigate inflammability and heat resistance.

2. Experimental procedure

2.1. Materials

Tabriz Petrochemical Co. (Tabriz, Iran) supplied styrene. Hexabromocyclododecane (HBCD) flame retardant was supplied by Star Chemical and Catalysts Co. (Hangzhou, China) and triphenylphosphate was obtained from Merck (Germany).

2.2. Sample preparation

150 g of styrene monomer was placed in a 250 ml jar. HBCD was added in accordance with proposed weight percentage. The jar was settled in an oil bath above magnetic hotplate stirrer. The polymerization was carried out for 6 h at temperature ranging from 110°C to 140°C. The polymer was then dried in a vacuum oven at 200°C and 4000 Pa for 2 h to detach the residual monomers. There were different reasons for synthesizing samples at low temperatures (i.e. 110°C). The main reason was the fact that when polymerization occurs at high temperatures, styrene monomer boils and overflows the jar. However, by initiating polymerization at low temperature around 110°C, with little polymerization, viscosity increases and boiling will be prevented. Another reason is related to the exothermic reaction during polymerization which releases sudden and rapid heat at high temperatures, making it very difficult to control the process. In contrast, when polymerization occurs slowly at low

temperatures, it is much easier to control the process. The reason is related to average molecular weight of produced polymer. As the polymerization temperature increases, the number of radicals increase, the chains' length and average molecular weight of produced polymer decrease.

2.3. Characterization methods

After polymerization of styrene monomer, the synthesized samples were hot pressed at 200°C under 1500 psi (10.34 MPa) for 2 min in order to achieve the polymer sheets. The sheets were then cut into small samples with suitable size according to the standard of LOI and UL-94 tests. 15 mg of samples were placed in a thermogravimetric analyzer (TGA/Lineis Instrument - A 1750). The temperature ramp was set at 10°C min⁻¹ and the final temperature was 600°C and air was fed to the TGA at 20 mL min⁻¹. LOI is the minimum concentration of oxygen that supports flaming combustion in a flowing mixture of oxygen and nitrogen according to ASTM D2863 and was carried out using Dynisco instrument. A small test specimen was supported vertically in a mixture of oxygen and nitrogen flowing upwards through a transparent chimney that supported combustion conditions. At least three samples were tested in different oxygen concentrations and the average minimum value was determined. UL-94 burning test, developed by Underwrites Laboratory Inc., was performed using Atlas Instrument (HVFAA Horizontal-Vertical Flame Chamber, USA). The specimen is classified as V-0, V-1 and V-2 in vertical burning test according to ASTM D3801. To achieve the class of UL-94 V0, the flame should self-

extinguish within 10 s. after each ignition and the total burning time for 5 samples should be less than 50 s., also there should be no burning drips. In UL-94 V2 and V1, these times were 30 s and 250 s respectively and burning drips were allowed in UL-94 V2. Horizontal burning test was also performed according to ASTM D635. Dimensions of specimens were 100×10×4 mm³ in LOI and UL-94 burning test. Table 1 shows the weight percentage of different materials for polymerization of styrene monomer.

3. Results and discussion

3.1. Flammability studies of synthesized samples

Figure 1 shows the effect of increasing flame retardant material Hexabromocyclododecane (HBCD) on LOI data. With increasing the concentration of HBCD the required oxygen increases for flaming sample. It should be noted that when flame retardant materials are added during polymerization, weight percentage of halogenated flame retardant was very low which is confirmed considering environmental matters. The results of adding different concentrations of triphenylphosphate (TPP) on LOI data of synthesized polystyrene are shown in Fig. 2 indicating that addition of TPP during polymerization had no effect on increasing amount of required oxygen for flaming polystyrenic samples. In other words, TPP did not prevent flaming of polystyrene. To be more specific, flaming with TPP was very little and samples started to flame very slowly and orderly from the top. Regarding the results of previous sections, bromic compounds had an effective role in retarding the flammability of polystyrene. However, as

Table 1

Code name and composition of synthesized samples (wt. %).

Sample Number	Sample Code	HBCD	TPP	Dicumene
0	PS	0	0	0
1	PS H0.35	0.35	0	0
2	PS H0.6	0.6	0	0
3	PS H0.8	0.8	0	0
4	PS H0.45 T0.35	0.45	0.35	0
5	PS H0.35 T0.45	0.35	0.45	0
6	PS H0.6 T0.25	0.6	0.25	0
7	PS H0.25 T0.6	0.25	0.6	0
8	PS H0.35 D0.06	0.35	0	0.06
9	PS H0.35 D0.12	0.35	0	0.12
10	PS H0.6 D0.06	0.6	0	0.06
11	PS H0.6 D0.12	0.6	0	0.12
12	PS H0.8 D0.06	0.8	0	0.06
13	PS H0.8 D0.12	0.8	0	0.12
14	PS T0.35	0	0.35	0
15	PS T0.6	0	0.6	0
16	PS T0.8	0	0.8	0
17	PS H0.45 T0.35 D0.06	0.45	0.35	0.06
18	PS H0.45 T0.35 D0.12	0.45	0.35	0.12
19	PS H0.6 T0.25 D0.06	0.6	0.25	0.06
20	PS H0.6 T0.25 D0.12	0.6	0.25	0.12

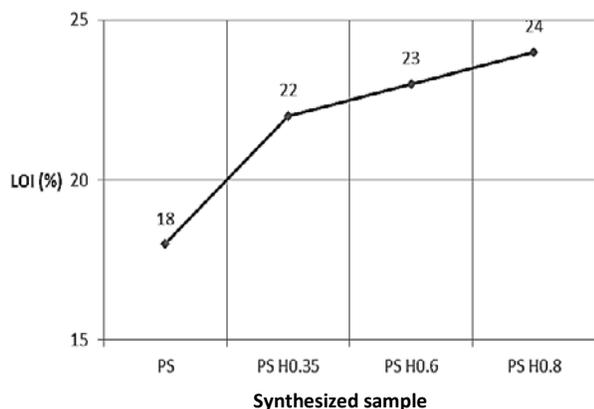


Figure 1. The variation of LOI value in polystyrene with different weight percent of HBCD.

mentioned before, using halogenated materials has limitations considering environmental matters because of contamination and toxicity of materials resulted from their analyses. Therefore, sufficient care must be taken while

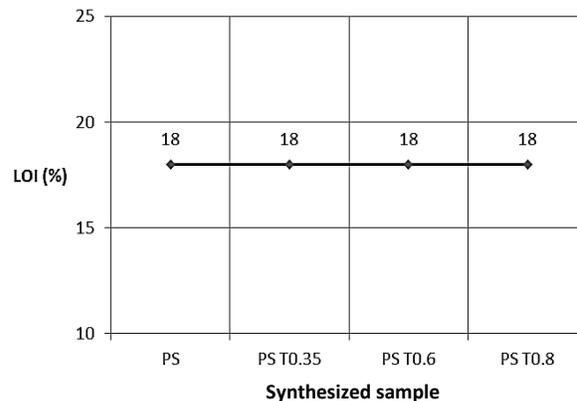


Figure 2. The variation of LOI value in polystyrene with different weight percent of TPP.

using these materials. The strategy to decrease the amount of halogenated flame retardants is to use phosphorous compounds in combination with halogenated compounds [1]. For this purpose, samples with different weight percentages of HBCD and TPP were

synthesized. According to Fig. 3, as the amount of these compounds increases, the required oxygen or flaming polystyrene increases. It is observed that samples with more TPP concentration have greater limiting oxygen index. This is due to the fact that HBCD, in addition to acting in gas phase generation, increases polystyrene degradation at lower temperatures. This leads to polymer softening and transmitting active parts of TPP to gas phase and increasing its performance. According to Fig. 3, it is observed with increasing TPP and decreasing HBCD, limiting oxygen index of 23 was reached and it is almost equal to LOI of sample containing 0.8 % (w/w) HBCD. In LOI test, comparing these amounts with samples containing HBCD, it is observed that the addition of TPP reduces the amount of HBCD. Another way to reduce HBCD concentration is addition of Perkadox 30 (Dicumene) as a synergist [3]. Figure 4 compares limiting oxygen indices of the sample that consists of HBCD with sample comprising both HBCD and Perkadox 30. It can be seen that increasing the amount of Perkadox 30 from 0.06 % (w/w) to 0.12 % (w/w) led to an increase of 1 to 2 units in LOI. An explanation for this could be related to the annular structure of Perkadox 30 and aromatic cycle structure of polystyrene which can cover this additive material and it can be easily placed in the structure of the produced polystyrene leading to increased amounts of oxygen required for its inflammability. Therefore, Perkadox 30 can be used in order to decrease the concentration of harmful substances in flame retardant compounds to control the environmental threat of

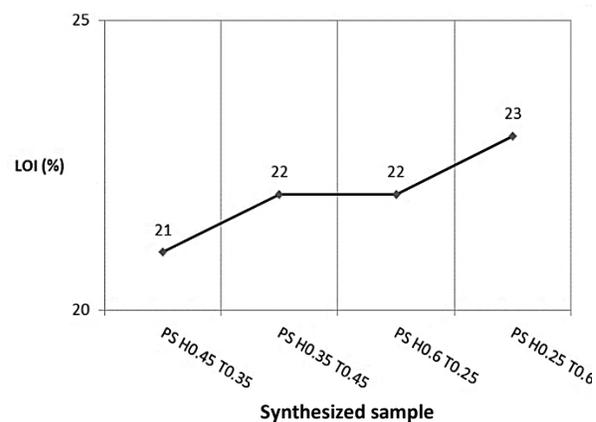


Figure 3. The variation of LOI value in polystyrene with different weight percentage of HBCD and TPP.

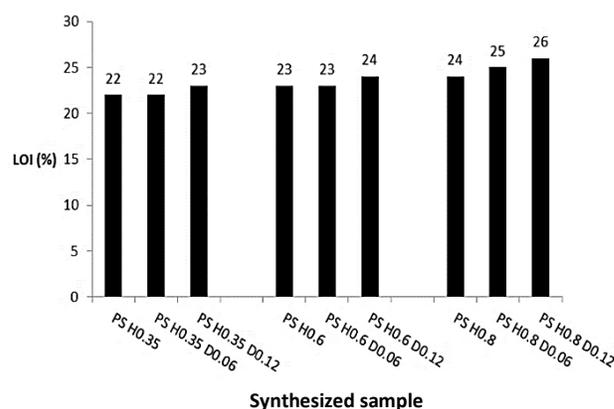


Figure 4. The variation of LOI value in polystyrene with different weight percentage of HBCD, TPP and Perkadox30.

halogenated additives. In Fig. 5, the effects of three additives of HBCD, TPP and Perkadox 30 on LOI values were investigated simultaneously. It is observed that in the presence of HBCD and TPP, increasing of Perkadox 30 from 0.06 % (w/w) to 0.12 % (w/w) caused an increase of 1 to 3 units in LOI value. Furthermore, in total weight percentage of HBCD and TPP in the presence of Perkadox 30, the high amount of HBCD had no effect on LOI values. Therefore, it can be concluded that TPP and Perkadox 30 could be satisfactorily used to decrease

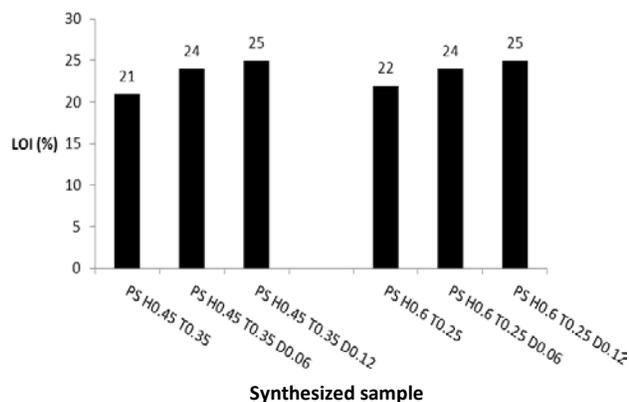


Figure 5. The variation of LOI value in polystyrene with different weight percentage of perkadox30.

environmental threat of halogenated flame retardants. LOI results also showed that two samples, one incorporating 0.6 % (w/w) HBCD, 0.25 % (w/w) TPP and 0.12 % (w/w) Perkadox 30 and the other containing 0.45 % (w/w) HBCD, 0.35 % (w/w) TPP and 0.12 % (w/w) Perkadox 30 had the highest LOI values. Considering the environmental matters, the latter sample is more acceptable because of lower concentrations of halogenated additives. UL-94 flame rating test is commonly used to show polymers inflammability. There are important factors involved in UL-94 flame rating test such as time of quenching, speed of flaming and drop of flaming melt [6]. According to results from Table 2, pure polystyrene did not pass the test because of inflammability and greater dripping. In samples with HBCD, less time was required to quench the flame and they passed the UL-94 test. However, more dripping of polymer melt in these samples led to transmission of UL-94 rate from V0 to V2. It is observed that in samples with TPP despite inflammability effect, the flaming was slow and free of dripping. In other words,

Table 2

The data of UL-94 burning test for different flame retardant samples.

Sample Number	Sample Code	UL-94	Dripping
0	PS	Fail	Yes
1	PS H0.35	V-2	Yes
2	PS H0.6	V-2	Yes
3	PS H0.8	V-2	Yes
4	PS H0.45 T0.35	V-0	No
5	PS H0.35 T0.45	V-0	No
6	PS H0.6 T0.25	V-0	No
7	PS H0.25 T0.6	V-0	No
8	PS H0.35 D0.06	V-0	No
9	PS H0.35 D0.12	V-0	No
10	PS H0.6 D0.06	V-0	No
11	PS H0.6 D0.12	V-0	No
12	PS H0.8 D0.06	V-0	No
13	PS H0.8 D0.12	V-0	No
14	PS T0.35	Fail	No
15	PS T0.6	Fail	No
16	PS T0.8	Fail	No
17	PS H0.45 T0.35 D0.06	V-0	No
18	PS H0.45 T0.35 D0.12	V-0	No
19	PS H0.6 T0.25 D0.06	V-2	Yes
20	PS H0.6 T0.25 D0.12	V-2	Yes

flaming rate was very low in samples with TPP. Comparing compound samples of HBCD and TPP with samples with HBCD showed that adding TPP firstly decreased the concentration of HBCD and, secondly prevented the melt dripping, in which UL-94 test rate of these samples was V0. Investigating samples with HBCD and Perkadox 30, it is observed that one way to prevent dropping of polymer melts is using Perkadox 30, and UL-94 test rate in these samples was V0.

3.2. Thermogravimetric analysis (TGA)

TGA was used to investigate thermal stability and degradation of prepared samples. Fig. 6 shows that TGA curves were related to pure

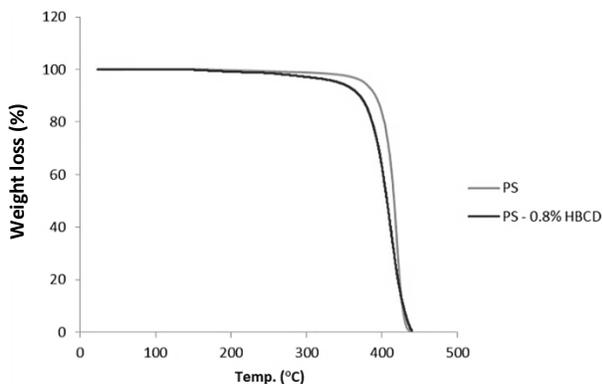


Figure 6. TGA curves of pure polystyrene and polystyrene with 0.8 weight percent of HBCD.

polystyrene and the sample with 0.8 % (w/w) HBCD. Incorporating HBCD to polystyrene decreased the degradation temperature. This is due to the fact that degradation temperature of HBCD is less than that of pure polystyrene and starts to degrade at 215 °C [4]. Moreover, less viscosity of HBCD led to decrease in degradation temperature. TGA analysis curves of pure polystyrene and the sample with 0.8 % (w/w) TPP are shown in Fig. 7. Because of lower evaporation temperature of TPP in comparison with degradation temperature of polystyrene, weight decrease occurs fast in sample with TPP. According to the diagram, as the amount of TPP is low, decrease in degradation temperature is also low.

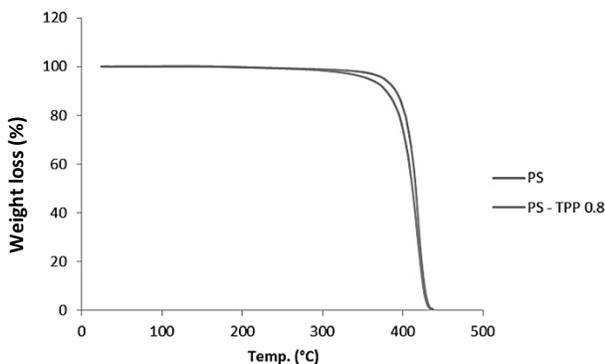


Figure 7. TGA curves of pure polystyrene and polystyrene with 0.8 weight percent of TPP.

In Fig. 8, TGA curves of the sample with 0.8 % (w/w) HBCD and the sample with 0.8 % (w/w) TPP are compared. It shows that degradation temperature of HBCD containing sample is less than that of TPP containing sample. The reason is the low degradation temperature of HBCD in comparison with evaporation temperature of TPP. Degradation temperature of HBCD is about 215 °C and evaporation temperature of TPP is about 230°C [4-5]. Figure 9 represents TGA curves of a sample with 0.8 % (w/w) HBCD (in blue) and another sample containing 0.35 % (w/w) HBCD and 0.45 % (w/w) TPP (in red). In equal weight percentage of additives, the

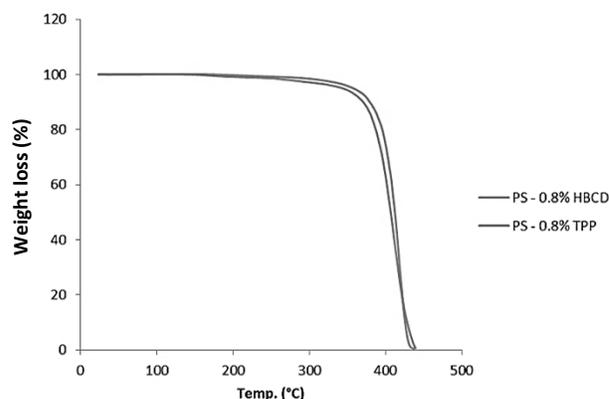


Figure 8. TGA curves of polystyrene with 0.8 weight percent of HBCD and TPP.

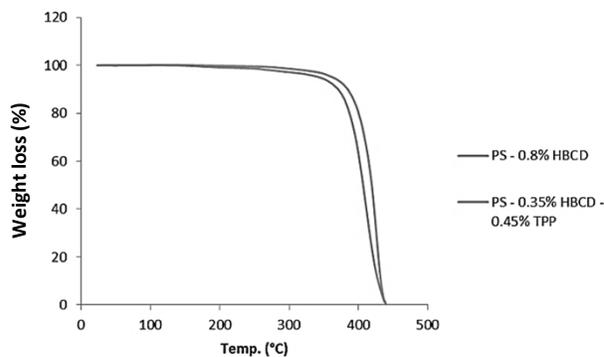


Figure 9. Effect of TPP Addition on the thermal degradation behavior of synthesized polystyrene containing HBCD.

sample that consists of HBCD and TPP has higher thermal stability compared with the sample prepared by HBCD.

4. Conclusions

In this study flame retardant polystyrene was produced via in-situ bulk polymerization and its inflammability properties were investigated using LOI, TGA and UL-94 tests. Bromic, phosphate and synergist Perkadox 30 compounds were used in order to relate flame retardancy behavior in synthesized polystyrene. LOI test showed that the most important solution to decrease the amount of halogenated flame retardant and to control environmental threat is using non-halogenated materials during polymerization. It was also shown that bromic retardant of HBCD is very effective in decreasing inflammability of polystyrene and better results were obtained at low concentrations. Comparing the samples shows that as the concentration of flame retardant material increases, the inflammability of synthesized polymer decreases. The results showed that phosphate flame retardant of TPP solely has no effect on retarding flame and only reduces flaming rate of the polymer. However, when it is used as an additive to HBCD, it decreases the concentration of HBCD and increases LOI values. Perkadox 30 as a synergist additive was used to decrease the concentration of HBCD retardant. Samples with HBCD, adding 0.06 to 0.12 weight fraction of Perkadox 30 increase oxygen index from 1 % to 2 %. Also, adding 0.06 to 0.12 weight fraction of Perkadox 30 increases oxygen index from 1 % to 3 % in the presence of HBCD and TPP. The results of TGA tests confirmed that using

HBCD and TPP decreased degradation temperature of samples.

Acknowledgments

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