

Halogen Free Flame Retardant Based on Organophosphorus Compounds for Expandable Polystyrene Produced by Suspension Polymerization

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Expandable polystyrene (EPS) has been widely used in many fields of engineering but present some inconveniences at higher temperatures. When exposed to a heat source the polymeric material decomposes forming volatile combustible products turning EPS an easily flammable material. During a long time, the halogen-based compounds have been incorporated as an additive flame retardant (FR) for different class of polymeric materials with a good efficiency. Nowadays, plastic industry is suffering hard pressures from health organizations once combustion of halogen-based compounds generates the formation of smoke with a number of negative characteristics. Searching for an environmental safety FR option it was studied two different FR compounds, one of them based on organophosphorus compounds, whose works together to provide efficiency as good as the efficiency provided by halogen-based compounds, like hexabromocyclododecane. Fire retardant effectiveness is obtained through the compounds synergies were each FR has to act in different mechanism complementary. Both FRs are added in situ, during the polymerization reaction. Good flame retardancy was obtained with the FR tested. Results demonstrate a reduction of more than 50% in the burning rate of EPS.

1. Introduction

Expandable polystyrene (EPS) is widely used in many fields of engineering because is one of the most important materials to the industry with a lot of applications. However, EPS present some inconveniences at higher temperatures. When exposed to a heat source the polymeric material decomposes forming volatile combustible products turning EPS an easily flammable material (Brossas, 1989). This higher flammability makes the flame retardancy of EPS be constantly studied. For a long time, the halogen-based compounds have been incorporated as an additive flame retardant (FR) for different class of polymeric materials with a good efficiency. Nowadays, plastic industry is suffering hard pressures from health organizations which are against the use of halogen-based FR. The combustion of halogen-based compounds generates the formation of smoke with a number of negative characteristics (Camino et al., 1991). Searching for an environmental safety FR option studies about different kind of halogen free flame retardant has started (Fu and

Qutubuddin, 2000; Fu and Qutubuddin, 2001). In this paper it was used as FR two different compounds whose works together to provide efficiency as good as the efficiency provided by halogen-based compounds, like hexabromocyclododecane (HBCD). Fire retardant effectiveness is obtained through the compounds synergies were each FR has to act in different mechanism complementary. The most common technique used to add the FR in polymers consists of mixing all compounds by a physical mixture to form polymer/FR blends (Beach et al., 2008). The polystyrene is previously prepared forming PS beads and the product is mixed with FR in mixing bowls. This work proposes a new methodology where both FRs are added in situ, one of them during the polymerization reaction and the other right after polymer is ready, with polystyrene into the reactor. The suspension polymerization is the principal process used in industry to prepare EPS.

A new methodology using free halogen based compound which makes the addition of FR in situ can improve the actual process used by industry and help the product to be in agreement with new regulations adopted by health and environmental organizations.

2. Experimental

In this work it was used as flame retardant two different compounds: triphenylphosphate and elemental sulfur (S). Pure flame retardants were obtained from Sigma Aldrich. EPS was prepared using a batch stirred tank reactor with controlled temperature. It was used to prepare the polymer a total of 1200g of styrene (with *p*-terc-butylcatechol, 12-15 ppm) provided by Innova S. A. (Brazil). Some stabilization compounds and additives were added to the reaction. Organic phase was added in the reactor with the aqueous phase. The temperature was increased until 120°C. During the reaction flame retardant were added to the mixture. N-Pentane was used as expanding agent. The relation of use between TPP 5 % and S 1% was obtained from previous studies (Beach et al., 2008).

2.1 Kinetics Analysis

The first step of this work was the gravimetric analysis to know how the addition of flame retardant compounds could influence the reaction kinetics. Gravimetric analysis was performed thought mass polymerization reaction. Mass polymerization reaction was made in glass tubes with just the organic phase, heated by a thermostatic bath at 90°C. Glass tubes were removed one by one from the thermostatic bath and inserted in a quench bath (ice/alcohol) to discontinue polymerization reaction. A curve of conversion versus time was plotted.

2.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed by Analysis Center of Chemistry Department (Federal University of Santa Catarina) using a thermogravimetric equipment from Shimadzu, TGA – 50. Samples (10-15 mg) for TGA analysis were heated at 10°C/min to 600°C under nitrogen atmosphere. TGA analysis was important to observe the mechanism of action adopted by flame retardants.

2.3 Pentane and residual monomer analysis – Gas chromatography (GC)

Both, pentane and residual monomer has to be analyzed constantly during formulation changes. Analyses were performed by a gas chromatography, GC-2010AF with headspace (AOC-5000 Shimadzu). The equipment has an ionization flame detector working at 270°C. Initially chromatographic column is heated at 50°C for 5 minutes. The heating continue until 100°C with a ratio of 10°C.min⁻¹.

2.4 Flammability analysis

Flammability test was performed in accord with ABNT NBR 11948 - Expanded Polystyrene for Thermal Insulation – Determination of Flammability (horizontal samples). The analysis involves samples of EPS that was cut as plaques that measure 150 mm x 50 mm X 13 mm. The apparatus is manually operated moving a burner ignition source under of the plaque sample to apply a flame from the source to the sample for a period of 60 s. When the heat source (flame) is adjusted under the sample a timer starts. Flammability analysis was realized for pure polystyrene, polystyrene with HBCD (as a reference), and polystyrene with TPP 5%/S 1%.

3. Results and discussion

3.1 Gravimetric analysis

To analyze the influence of flame retardant on the kinetics reaction of polystyrene it was performed two different reactions on glass tubes. Figure 1 show the result of gravimetric analysis. Ball points represent a reaction without flame retardant and star points represent a reaction with flame retardant. Is possible observe that flame retardant cause no significant difference on the kinetics reaction of polystyrene. Data makes possible define the better time to insert flame retardants at the reaction. One of flame retardant has to be inserted on reaction at a specific time. If this clause is not respected reaction cannot finish correctly.

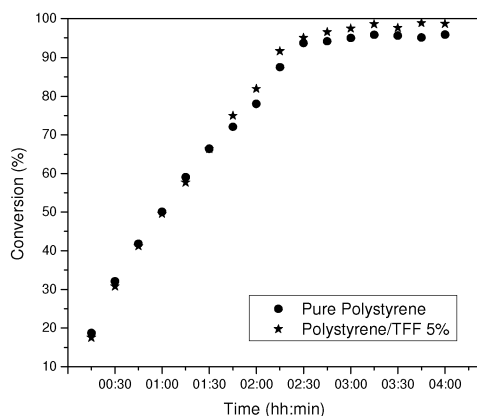


Figure 1 – Gravimetric data of pure polystyrene and polystyrene with triphenylphosphate 5%.

3.2 Thermogravimetric analysis (TGA)

Figure 2, 3 and 4 show TGA analysis for pure polystyrene, polystyrene with TPP 5% and polystyrene with TPP 5% / S 1% respectively.

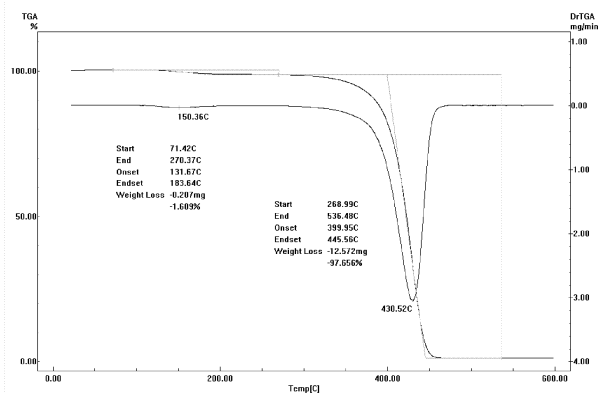


Figure 2: TGA of pure polystyrene

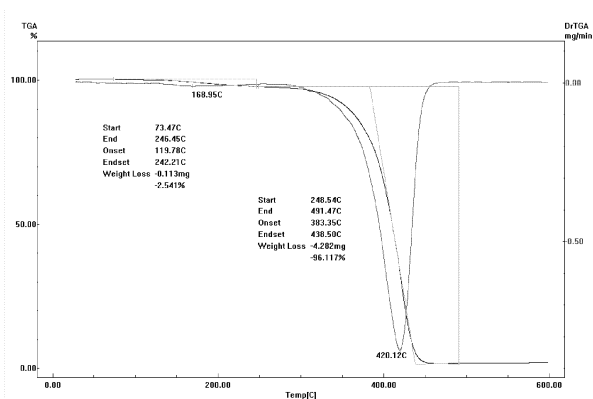


Figure 3: TGA of polystyrene with triphenylphosphate 5%

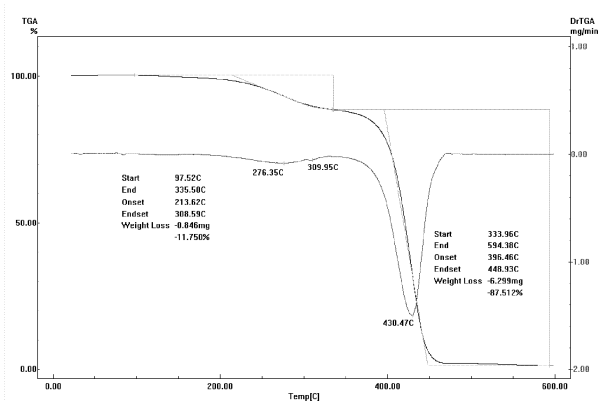


Figure 4: TGA of polystyrene with triphenylphosphate 5% and elemental sulfur 1%

TGA curves in figure 2, 3 and 4 for the pure polystyrene, polystyrene with TPP 5% and polystyrene with TPP 5% / S 1% show a difference in temperature loss. It is possible to observe in figure 3 a negligible enhanced polystyrene degradation. In figure 4 is observed TGA for polystyrene with TPP 5% and sulfur 1%. Polystyrene degradation is probably enhanced by sulfur. Data helps to understand the preferential mechanism of action of each FR. Once elemental sulfur enhances PS degradation, this FR probably prefers the condensed phase mechanism. Phosphorous-based FRs have lower molecular weight and very strong bonds associated. This characteristic suggests that phosphorous-based FRs work preferentially in gas phase as radical scavenger (Babushok and Tsang, 2000).

3.3 Pentane and residual monomer analysis

Analysis of pentane and residual monomer were performed for two reasons, by the importance of a minimum of pentane inside particle to obtain a good expansion of polystyrene and to have a control of maximum quantity of residual monomer. Once EPS is used in many different applications, food storage is one of the main, it is important to maintain residual monomer at a very low level, in accordance with health organization regulations. Production of EPS with a low level of residual monomer is easily reached by end reaction temperature manipulation or by the radical initiator quantity. However, the main objective of this work is to produce an EPS with good fire retardant characteristics and using non halogenated molecules. Concerning about health legislations will be the focus of another part of this work.

Table 1: Residual monomer and pentane

Sample	% monomer	% pentane
Pure EPS	0.190	4.194
EPS/TPP 5%/S 1%	0.323	3.372

Table 1 shows data obtained. The level of residual monomer was higher for EPS with FR. This elevation can be explained by the presence of another compound in reaction. It can be assumed that some unknown reactions of TPP with radical initiator can happen, consuming the initiator. The monomer of reaction will not be totally consumed. The quantity of pentane inside particle was sufficient to expand PS but could be bigger to facilitate expansion particle and produce a better EPS molded specimen.

3.4 Flammability analysis

Results of flammability analysis are shown in table 2. It can be observed the high influence on fire retardancy of polystyrene made by flame retardants, TPP and elemental sulfur.

Table 2: Flammability analysis results

Sample	Extent of burning (mm)	Burning rate (mm.s ⁻¹)	Classification (according ABNT NBR 11948)
EPS	125 (totally burned)	2.55	Not flame retardant
EPS/HBCD	65	1.69	Flame retardant
EPS/TPP 5%/S 1%	30	1.12	Flame retardant

When exposed to a heat source, pure expanded polystyrene present a total burning sample with a burning rate of 2.55 mm.s⁻¹. The sample of EPS with flame retardants presents a slowest burning rate of 1.12 mm.s⁻¹ when compared with pure EPS. Flame was extinguished before sample total burning. Was not observed melt dripping during the analysis for EPS with FR. TPP and elemental sulfur, when used together present a good performance as flame retardants for EPS.

4. Conclusion

Through data obtained it was observed that a combination of gas-phase and condensed-phase activity provides good flame retardancy for PS. From TGA was not observed significant change of degradation mechanism of PS caused by TFF. It is believed that gas-phase activity is produced by organophosphorous compound. This activity is achieved through flame inhibition chemistry of radical scavenging of OH and H radicals. The elemental sulfur would be responsible by condensed-phase activity, enhancing degradation of polystyrene.

Initially elemental sulfur degrades polystyrene improving mass transfer of TPP to the surface of the polymer and the flame region. This facilitates the delivery of TPP on surface, which has a very high level of potential gas-phase activity.

5. References

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