

# Halogen-Free Flame-Retardant Rigid Polyurethane Foams: Effect of Alumina Trihydrate and Triphenylphosphate on the Properties of Polyurethane Foams

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**ABSTRACT:** Rigid polyurethane foam (PUF) filled with mixture of alumina trihydrate (ATH) and triphenyl phosphate (TPP) as fire retardant additive was prepared with water as a blowing agent. In this study, the ATH content was varied from 10 to 100 parts per hundred polyol by weight (php), and TPP was used at a higher loading of ATH (75 and 100 php) in a ratio of 1 : 5 to enhance the processing during PUF preparation. The effects of ATH on properties such as density, compressive strength, morphological, thermal conductivity, thermal stability, flame-retardant (FR) behavior, and smoke characteristics were studied. The density and compressive strength of the ATH-filled PUF decreased initially and then increased

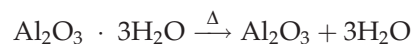
with further increase in ATH content. There was no significant change in the thermal stability with increasing ATH loading. We determined the FR properties of these foam samples by measuring the limiting oxygen index (LOI), smoke density, rate of burning, and char yield. The addition of ATH with TPP to PUF significantly decreased the flame-spread rate and increased LOI. The addition of TPP resulted in easy processing and also improved FR characteristics of the foam. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2260–2268, 2010

**Key words:** fillers; flame retardance; polyurethanes; thermogravimetric analysis (TGA); alumina trihydrate (ATH)

## INTRODUCTION

Rigid polyurethane foams (PUFs) are widely used as thermal insulators and mechanical shock absorbers in transport overpacks and in air conditioning. They are also used as structural materials because of their light weight, greater strength to weight ratio, and energy-absorbing capabilities.<sup>1</sup> PUF, like other organic polymeric materials, tends to be flammable. Thus, the flammability of PUF has long been a factor limiting its use. To improve the flame-retardance properties, different flame retardants (FRs) are added to PUF. However, some of the FR additives used in PUF adversely affect its physical properties and pollute the environment by the evolution of undesirable gases on burning. In recent years, because of the stringent safety standards, both public and environmental, set by statutory authorities across the world, it has become imperative to develop better FR materials with improved FR efficiency that are economical and, at the same time, halogen free.<sup>2</sup>

In general, alumina trihydrate (ATH) is unique in having a high proportion (~ 34%) of water and is used as an FR additive and smoke-suppressant filler. Such inorganic fillers are assuming increasing importance in the industry because of their desirable combination of low cost, low smoke, and relatively high fire-retardant efficiency. ATH decomposes at about 220°C to form Al<sub>2</sub>O<sub>3</sub> and water:



The effectiveness of ATH as an FR additive depends primarily on its endothermic decomposition, which withdraws heat from the substrate and, hence, retards the rate of flame propagation. Water vapor also reduces oxygen supply as it expands and envelops the interface boundary of foam and the environment. The expanding water vapor also cools the surface effectively because it takes away the majority of heat supplied to the foam because of its high heat-carrying capacity at high temperatures. In contrast to the antimony oxide/halogenated fire-retardant system, ATH can provide equivalent fire retardancy at a lower cost and with significantly reduced emission of gases of low toxicity and corrosivity on exposure to a flame environment.<sup>3</sup>

One of the major drawbacks of adding these fillers is that the mechanical properties become inferior

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compared to the bare foam samples. This is possibly due to insufficient interactions between the polymer and the filler, which result in their inferior properties. Bonding interactions between the foam and the FR additives may be improved by various techniques. The surface of the filler can be treated with various species that act as compatibilizers or surface-active agents. In general, ATH is surface-treated with chemicals, such as carboxylic acids, silanes, zirconates, and titanates, to improve its dispersion and distribution within the polymer matrix. Usually, the content of ATH in the formulation is very high (>50%). ATH is used as an FR material in preparing FR rubber products (e.g., cables, conveyor belts) and in plastic materials.<sup>4-13</sup> There have been reports of the use of ATH in polyurethane elastomers<sup>14,15</sup> and flexible<sup>16-19</sup> and rigid PUFs<sup>20-23</sup> as a low-cost FR and smoke-suppressant additive.

In this investigation, we report the use of ATH as an FR nonreactive additive in the preparation of rigid PUF and the effects of ATH on the mechanical properties, thermal conductivity, thermal stability, FR, and smoke-density properties. At higher loadings of ATH, the processing and preparation of PUFs were very difficult because of the resultant high viscosity. Therefore, at higher loadings of ATH, triphenyl phosphate (TPP) was used as a viscosity-suppressant and to improve the flame-resistant properties.

## EXPERIMENTAL

### Materials

Polymeric methane diphenyl diisocyanate (PMDI; NCO = 30.8% and functionality = 2.7) and poly(ether polyol) (OH content = 440 mg of KOH/g, average functionality = 3.0) were obtained from Huntsman International Pvt., Ltd. (Mumbai, India). Distilled water was generated in our laboratory and was used as a chemical blowing agent. *N,N,N',N',N'*-Pentamethyldiethylenetriamine (PMDETA), obtained from Aldrich (St. Louis, MO), was used as a catalyst. Polyether dimethyl siloxane (TEGOSTAB B 8460) supplied by Goldschmidt (Essen, Germany) was used as a surfactant. ATH, with a density of 2.42 g/cm<sup>3</sup> and an average particle size of 200 μm, and TPP, supplied by Phoenix Yule, Ltd. (Kolkata, India), were used as FR additives. All of the chemicals were used as received.

### Preparation of the foam

ATH- and TPP-filled PUF samples were prepared by a one-shot and free-rise method. The chemical compositions of different filled foams are shown in Table I. Except for PMDI, all of the raw materials were well mixed in a plastic beaker, and then, FR was added,

**TABLE I**  
Chemical Composition of ATH/TPP-Filled Water-Blown Rigid PUF

Material	php
Polyether polyol	100.0
PMDETA	0.5
Tegostab B 8460	2.0
Distilled water	0.3
ATH	10-50, 75, 100
TPP	10, 15, 20
PMDI	122.0

and the resulting mixture was thoroughly mixed with the help of a high-speed mechanical stirrer (3000 rpm). Finally, PMDI was added to the mixture for a short duration with vigorous stirring for 10 s. The final resulting mixture was immediately poured into an open mold (30 × 25 × 15 cm<sup>3</sup>) to produce free-rise foams. After preparation, the foam sample was kept in an oven at 70°C for 24 h to complete the polymerization reaction. Different test samples were cut into specific foam shapes after curing. The samples were rubbed with fine emery paper to get the proper dimensions. Different properties of the foams were analyzed with ASTM standard test methods. The amount of PMDI required for the reaction with polyether polyol and distilled water was calculated from their equivalent weight. For the completion of the reaction, excess PMDI (NCO/OH = 1.1) was used. Similarly, all foam samples were prepared by adjustment of the ATH content relative to polyol.

### Measurement of different properties

#### Mechanical properties

The apparent density of the PUF samples was measured as per ASTM D 1622-03; the average value of three samples is reported. The mechanical properties of the PUF samples were measured under ambient conditions with an Instron universal testing machine Hounsfield testing equipment (model H10KS). The compressive stress at 10% strain in the parallel-to-foam rise direction was performed according to ASTM D 1621-00. The size of the specimen was 55 × 55 × 30 mm<sup>3</sup> (Length × Width × Thickness), the rate of crosshead movement was fixed at 2.5 mm/min for each sample and the load cell used was 10kN. The strengths of five specimens per sample were measured, and the average of these values is reported.

#### Scanning electron microscopy (SEM) analysis

The morphology of the PUF samples was studied with a scanning electron microscope (JEOL, JSM 5800, Tokyo, Japan). The samples were gold-coated

before scanning to provide an electrically conductive surface. An accelerating voltage of 20 kV was used while we recorded the scanning electron micrograms.

#### Thermal conductivity test

The thermal conductivity of the PUFs was tested within a week of preparation of the PUFs with a guarded hot plate thermal conductivity meter as per ASTM C 177-97. The size of the specimen was  $100 \times 100 \times 25 \text{ mm}^3$  (Length  $\times$  Width  $\times$  Thickness).

#### Thermogravimetry (TG) study

The decomposition temperature and char residue of the foams were analyzed on a TG analyzer Q50 (TA Instruments, New Castle, DE) under a nitrogen environment at a heating rate of  $20^\circ\text{C}/\text{min}$  over the temperature range  $30\text{--}800^\circ\text{C}$ .

#### Limiting oxygen index (LOI) test

The flammability test was performed with an LOI test instrument (Stanton Redcroft FTA unit, East Grinstead, UK) as per ASTM D 2863-97. The specimens for the LOI measurement were  $120 \times 12 \times 12 \text{ mm}^3$  (Length  $\times$  Width  $\times$  Thickness), five specimens per sample were measured, and their average values are reported.

#### Test for flame propagation

The rate of flame spread was measured as per Federal Motor Vehicle Safety Standard 302.<sup>24</sup> A PUF specimen with dimensions of  $150 \times 10 \times 10 \text{ mm}^3$  (Length  $\times$  Width  $\times$  Thickness) was exposed horizontally at its one end to a small flame for 15 s. The distance and time of burning or the time to burn between two specific marks were measured. The burn rate was expressed as the rate of flame spread according to the following formula:  $B = 60(L/T)$ , where  $B$ ,  $L$ , and  $T$  are the burn rate (mm/min), length of the flame travels (mm), and time (s) for the flame to travel  $L$  mm, respectively. Three specimens per sample were measured, and their average values are reported.

#### Smoke-density test

The smoke density was measured with a smoke-density chamber (made by S. C. Dey and Co., Kolkata, India) as per ASTM D 2843-04. The smoke generated (flaming mode) in the process of burning the sample was measured by the change in light intensity. The size of the PUF specimen was  $100 \times 100 \times 12 \text{ mm}^3$  (Length  $\times$  Width  $\times$  Thickness). The maximum smoke density was measured as the highest

**TABLE II**  
Effect of ATH/TPP on the Density and Compressive Strength of PUF

ATH loading (php)	TPP loading (php)	Density ( $\text{kg}/\text{m}^3$ )	Compressive strength at 10% strain ( $\text{kg}/\text{cm}^2$ )	Reduced compressive strength [ $\text{MPa}/(\text{g}/\text{cm}^3)$ ]
0	0	103	8.1	7.9
10	—	88	5.5	6.3
20	—	81	5.0	6.2
30	—	131	10.5	8.0
40	—	140	11.3	8.1
50	—	153	13.0	8.5
50	10	95	4.1	4.3
75	15	165	14.4	8.7
100	20	207	18.8	9.1

point of the light absorption versus time curve. This smoke-density rating represented the total amount of smoke present in the chamber for the 4-min time and was measured with the following equation:

$$\text{Smoke-density rating} = A/T \times 100$$

where  $A$  and  $T$  are the area under the light absorption versus time curve and the total area of the curve, respectively.

#### Determination of the char yields (CYs)

We measured the CYs of the foams by heating the PUF in a muffle furnace at  $550^\circ\text{C}$  for 30 min. The CY was calculated with the following equation:  $\text{CY} = W_b/W_o \times 100$ , where  $W_b$  and  $W_o$  are the weights of the sample after and before burning.

## RESULTS AND DISCUSSION

### Density

Foam density is a very important parameter that affects the mechanical properties of PUFs.<sup>25</sup> In general, the foam density is dependent on the degree of foaming, which in turn, depends in part on the type and amount of blowing agent. In this study, the amount of chemical blowing agent (distilled water) was kept constant. Table II shows the density of PUFs filled with ATH at different concentrations. It indicates that the density decreased with the addition of small quantities of ATH-filled PUF and then increased with further increase in ATH loading. The density decreased at an initial loading of ATH. This was due to the increase in the cell size, as shown in the SEM figures (discussed later). However, beyond 20 parts per hundred polyol by weight (php) of ATH loading, the density linearly increased with increasing ATH loading. This was due to a decrease

in the cell size and to the higher density of ATH (2420 kg/m<sup>3</sup>) than that of neat PUF. The density of PUF filled with ATH (50 php) and TPP (10 php) was much lower than that of the PUF filled with ATH (50 php) alone. This was because of the diluting effect of TPP. However, with increasing ATH content, the density increased further (Table II). This was because the volume of PUF decreased after expansion as the amount of ATH increased,<sup>22</sup> which led to a greater amount of solid material (polyurethane and ATH) instead of gaseous phase.

### Mechanical properties

The mechanical properties of PUF are important parameters that determine its applications, such as in load bearing and as packaging materials. To study the effect of ATH loading on the compressive properties of PUFs, the effect of foam density and the compressive strength of different foams were normalized by division by their respective densities. Table II shows the effects on the reduced compressive strength and compressive strength at 10% strain of the PUFs filled with increasing loading of ATH and TPP. The table indicates that the reduced compressive strength and compressive strength at 10% strain of PUFs filled with ATH initially decreased and then increased with further increases in the ATH loading. The initial decrease in properties was due to an increase in the average cell size of the PUFs, which also resulted in a decrease in the density. A higher loading of ATH caused a positive effect on the mechanical properties of the PUFs. This was due to an increase in the cell wall thickness and also an increase in the density. It is known that the degree of foaming of PUFs depends on the viscosity and surface tension of the particular formulation.<sup>26</sup> Higher loadings of ATH resulted in an increase in the viscosity (2 Pa s for 20 php ATH from 1.1 Pa s for polyol), and this led to a decrease in the blowing or expansion of the PUFs. The mechanical properties of PUF filled with ATH (50 php) and 10 php TPP decreased drastically compared to those of the PUF filled with only 50 php ATH. This decrease in the mechanical properties was due to the plasticizing effect of TPP with ATH, which was consistent with the change in density, as shown in Table II. In general, the metallic hydroxide of mineral fillers, such as ATH and magnesium hydroxide, act as nonreinforcing fillers, because of its poor wetting or adhesion with the polymer matrix, and also, with inclusion of higher amounts, leads to agglomeration because the filler–filler interaction becomes more pronounced. Pinto et al.<sup>14</sup> observed poor mechanical properties in a polyurethane elastomer filled with ATH. In this case, the mechanical properties of PUF decreased at the initial loading of ATH, but they

increased at higher loadings of ATH. This was due to an increase in the cell wall thickness. The interfacial contact between the polyurethane matrix and ATH modified at its surface improved the polymer–filler interaction and filler dispersion. This resulted in improved mechanical properties in the rigid PUF. Anorga et al.<sup>16</sup> also reported improved physical properties in flexible PUFs with the addition of ATH.

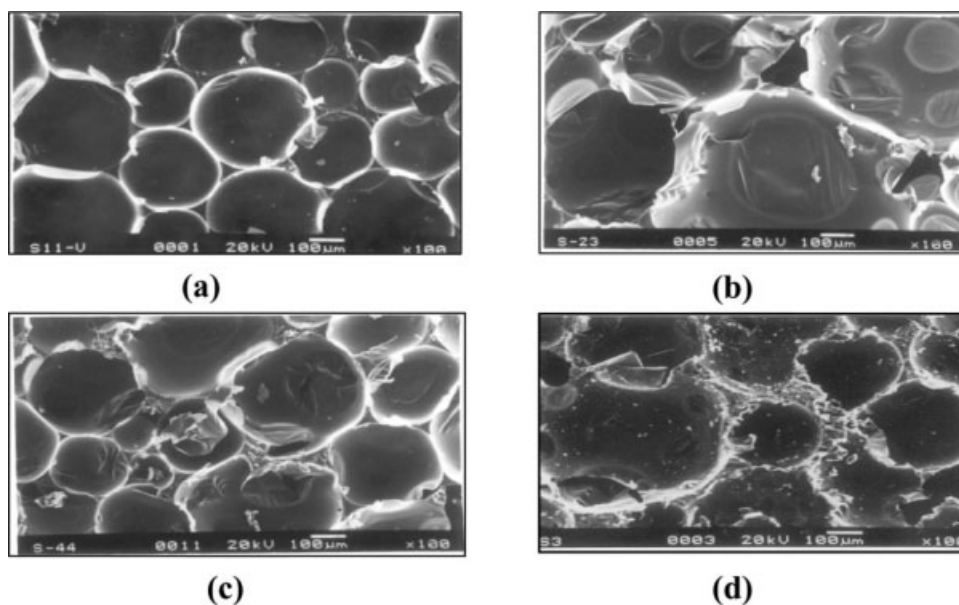
### Morphology

In general, the physical properties of foam not only depend on the rigidity of the polymer matrix but also on the cellular structure of the foam. The morphology of a rigid PUF sample was studied with SEM. Figure 1(a–d) shows the morphology of PUFs filled with ATH and TPP at different loadings. The shapes of the cells in the neat PUF and in the ATH-filled PUF were approximately spherical. As shown in Figure 1(b), the average cell size of the PUF became bigger with the incorporation of lower amounts of ATH compared to the neat PUF [Fig. 1(a)]. This was because ATH did not locate in the cell struts but between the cell walls. This caused an inhomogeneous cellular structure, which was responsible for the lower compressive strength.<sup>26</sup> However, at higher loading of ATH (40 php), the average cell size of PUF decreased because of less blowing [Fig. 1(c)]. This may be due to the addition of a higher amount of ATH, which resulted in an increase in the viscosity (e.g., 2 Pa s for 20 php ATH-filled polyol from 1.1 Pa s for polyol without ATH) of the foam formulation. The increased viscosity of the mixture led to a lower blowing tendency. Also, the morphology of the PUF was not very homogeneous because of the nonhomogeneous dispersion of ATH. The efficiency of foaming of PUF depends on the viscosity and surface tension of a particular formulation.<sup>27</sup> Simioni et al.<sup>22</sup> also observed a decrease in average cell size with the addition of ATH (100 php) in PUF. They found that the amount of polymer was drawn into the cell struts by the filler granules and also confirmed the absence of interaction between the polymer and the filler. In this case, the addition of TPP to the PUF filled with a higher loading of ATH decreased the viscosity. For example, the viscosity of polyol filled with 20 php ATH was 2 Pa s; when TPP (4 php) was added to this system, the viscosity dropped to 1.6 Pa s, which was due to the plasticizing effect of TPP. This decrease in viscosity led to a good blowing efficiency, and thus, it increased the cell size [Fig. 1(d)].

### Thermal conductivity

The thermal conductivity of PUF depends on the average cell size, foam density, cell orientation, ratio of





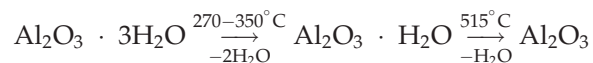
**Figure 1** Microphotographs of the ATH/TPP-filled PUF samples: (a) neat, (b) 20 php ATH, (c) 40 php ATH, (d) 75 php ATH + 15 php TPP.

closed- to open-cell content, and thermal conductivity of filling materials.<sup>28</sup> Figure 2 shows the effect of ATH and TPP on the thermal conductivity of the PUFs. The table indicates that the thermal conductivity of PUF increased with increasing ATH loading. This was due to the high viscosity of the PUF formulation, which increased with increasing ATH loading and led to a nonhomogeneous dispersion of ATH. Therefore, the cellular structure of PUF was not very fine, and the bigger the average cell size was, the more the thermal conductivity increased. In addition, because of the greater volume of solid content (polyurethane and ATH) in the ATH-filled PUF, there was a greater contribution to the thermal conductivity of PUF. Simioni et al.<sup>22</sup> also observed an increase in thermal conductivity with increasing ATH loading with PUFs. At the higher loading of ATH (along with TPP), PUF showed a decrease in the thermal conductivity; this was due to a decrease in the average cell size and an increase in the density. It is well known that the cell size of a PUF depends on the viscosity and surface tension of the mixture. In this study, an increase in viscosity at higher loadings of ATH led to a reduction in the cell size.

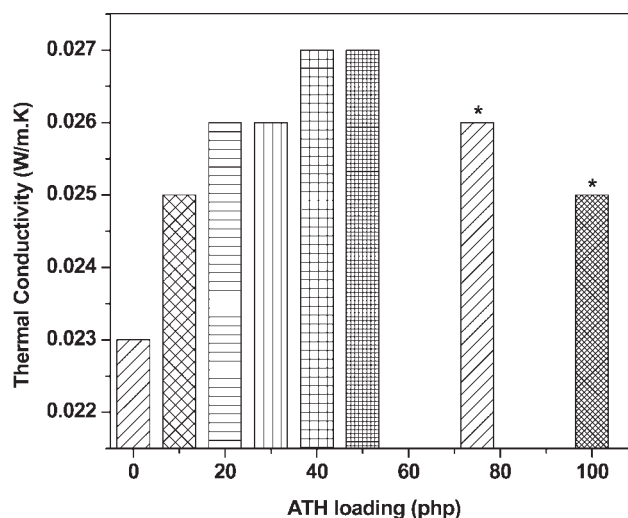
### Thermal analysis

Figure 3 shows the TG/differential thermogravimetry (DTG) thermograms of ATH and TPP FR additives under a nitrogen atmosphere. The figure reveals that the weight loss of ATH took place in three different temperature ranges, at 273, 353, and

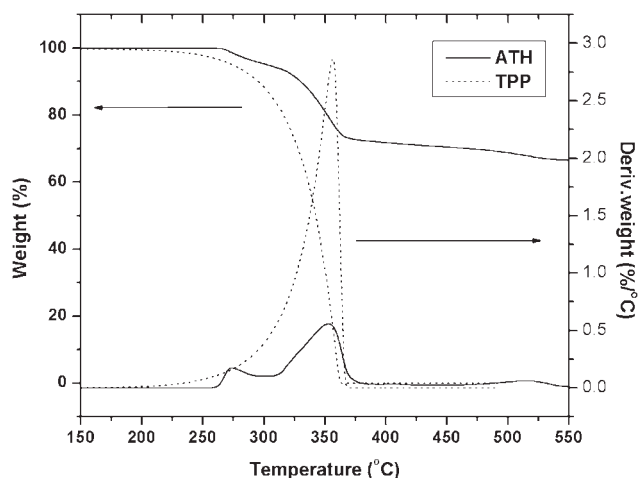
about 516°C, and their corresponding weight losses were about 1.2, 20.5, and 32.2%, respectively. These weight losses were due to the removal of chemically bound water present in the ATH as shown:



This result was in good agreement with the results reported by Simioni and Modesti.<sup>23</sup> The onset temperature (temperature at 5% weight loss) of ATH was 303°C, which was higher than that of TPP (274°C). This indicated that the thermal stability of



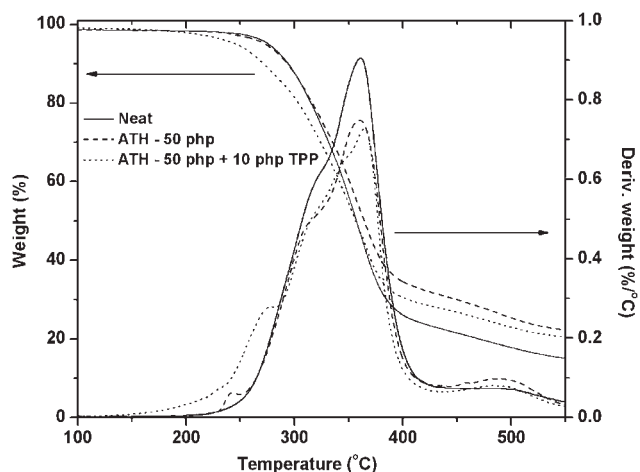
**Figure 2** Effect of ATH and ATH/TPP\* on the thermal conductivity of the PUF.



**Figure 3** TGA/DTG thermograms of ATH and TPP under nitrogen.

TPP was lower than that of ATH. The degradation pattern of TPP indicated that the TPP degraded completely to volatiles by 364°C and left no char residue. However, in the case of ATH, the weight loss was slow at the same temperature. The maximum degradation temperature ( $T_{\max}$ ) of TPP was 356°C and was observed in a single step. The amount of residue (CY) of ATH was greater (67%) than that of TPP, which was almost zero at 550°C.

Figure 4 demonstrates the TG/DTG curves of PUF filled with and without ATH and ATH/TPP. In the neat and filled foam samples, the thermal degradation took place in the range 250–420°C. The DTG curves of the PUFs filled with ATH and ATH/TPP showed a shoulder peak, which was probably due to the elimination of surface-active compounds used in ATH to improve its dispersion in the polymer matrix. With addition of TPP into the ATH, the weight loss of the samples was greater.  $T_{\max}$  for the



**Figure 4** TGA/DTG thermograms of the ATH/TPP-filled PUF under nitrogen.

**TABLE III**  
Effect of ATH/TPP on  $T_{\max}$  of PUF

Sample	ATH loading (php)	TPP loading (php)	$T_{\max}$ in $N_2$ ( $^{\circ}C$ )	CY in TGA at 700°C under $N_2$ (%)
1	0	0	361.7	10.5
2	10	—	361.4	17.3
3	30	—	362.3	18.9
4	50	—	360.2	20.8
5	50	10	364.2	19.3
6	100	20	361.4	17.3

neat and filled PUFs occurred at about 350°C, but CY was greater in case of filled PUFs compared to neat PUF. However, CY of the PUFs decreased with the addition of TPP into the ATH-filled PUF, as expected from the thermogravimetric analysis (TGA) curve of TPP (Fig. 3, which shows no CY). This was probably due to the gas-phase mechanism of phosphate additives. Different other phosphates, for example, ammonium polyphosphate (APP), have shown higher CYs because of the condensed-phase mechanism.<sup>29</sup>

Table III shows the  $T_{\max}$  and CY values at 700°C of the PUFs filled with ATH and TPP under a nitrogen atmosphere. There was no significant change in  $T_{\max}$  of PUF with ATH. Simioni and Modesti<sup>23</sup> also found that ATH did not modify the TGA curves of their PUFs. In general, the degradation temperature of a polymer should increase with ATH loading. This is due to the endothermic decomposition of ATH, which decreases the temperature in the surroundings of the materials. Moreover, the water dilution and the formation of an aluminum oxide protective layer decrease the combustible gases and also act as barrier for transport of oxygen and fuel into polymer. Nachtigall et al.<sup>30</sup> observed an increase in the degradation temperature of modified PP on loading with ATH. In our case, there was no significant change in  $T_{\max}$  of the PUFs with or without the addition of ATH. This was probably due to the reactions between the water molecules released from ATH and the polyurethane degradation products (e.g., isocyanate, carbodiimide), which were exothermic in nature. The CY of ATH filled PUF increased with increasing ATH loading. However, the combination of ATH with TPP decreased CY slightly, which might have been due to the gas-phase mechanism of TPP. In general, the addition of phosphate (APP) additives leads to the condensed-phase mechanism of fire retardation.<sup>29</sup> Thus, it decreases the thermal degradation temperature of the polymer, which results in a greater quantity of CY. However, some phosphorus compounds may also be active in the gas phase by a radical trapping mechanism. In this case, TPP acted as gas phase mechanism,

**TABLE IV**  
Effect of ATH/TPP on LOI, Smoke Density, Rate of Flame Spread, and CY of the PUF

Sample	ATH loading (php)	TPP loading (php)	LOI (%)	Maximum smoke density (%)	Smoke density rating (%)	Flame spread rate (mm/min)	CY in the muffle furnace at 550°C for 30 min (%)
1	Neat	—	22.0	63	62	200	0.05
2	10	—	22.2	—	—	182	3.2
3	20	—	22.5	54	51	150	6.0
4	30	—	23.0	—	—	113	12.2
5	40	—	23.7	—	—	103	13.4
6	50	—	25.0	45	30	94	17.3
7	—	10	23.2	—	—	158	1.3
8	50	10	27.2	54	36	88	12.4
9	75	15	28.0	64	61	SE <sup>a</sup>	18.2
10	100	20	29.5	—	—	NB <sup>b</sup>	26.0

<sup>a</sup> Self-extinguished after 15 s.

<sup>b</sup> Not burning (did not catch fire).

thereby decreasing CY of the PUF filled with ATH/TPP compared to the same with ATH alone.

### FR behavior

We analyzed the FR behavior of PUFs filled with ATH and TPP at different loadings by determining the LOI, rate of flame spread, smoke density, and CY measurements. Table IV shows the effect of ATH on the LOI of PUF. It clearly shows that the LOI value slightly increased from 22 to 25% with the addition of ATH in PUF. This lesser beneficial effect of ATH on the flame retardation of PUF occurred, because the initial water elimination process of ATH was hampered, as discussed in Thermal Analysis section. It may also have been due to the fact that lower amounts of ATH in the PUFs protected the dehydrating effect of ATH. An endothermic effect is only effective in PUFs having a higher amount of ATH.<sup>23</sup> The fact that the ATH did contain bound water is very important for its flame retardation in polymers. The slight increase in the LOI was due to the endothermic decomposition of ATH and water elimination from the third stage and also the formation of aluminum oxide char on the surface of the polymer, which acted as an insulative protective layer. Table IV indicates that the LOI of PUF sample filled with 50 php ATH and 10 php TPP was higher than the PUF filled with same amount of ATH only. This was due to the volatilization of TPP and the formation of phosphorus acid at higher temperatures. The addition of APP improved the flame retardance of the polymers via the condensed-phase mechanism. In this case, APP first decomposed to produce polyphosphoric acid, which accelerated the formation of char via ester formation on reaction with hydroxyl precursor.<sup>29</sup> In this case, TPP first decomposed to form phosphorus acids (as shown in

the following equation), which reacted with the —OH-containing moiety formed on the depolycondensation of PUF at higher temperatures:<sup>31</sup>



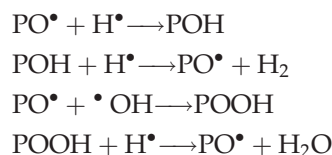
For a combination of additive systems, the numerical values of LOI may be shifted from those of the theoretically calculated ones. The upward shift is called *synergism*, and the downward shift is known as *antagonism*. The theoretical LOI values of the flame-retarded PUFs filled with ATH/TPP were calculated from knowledge of their experimental values under identical conditions with the individual additives and without additive. For instance, the LOI values of a polymer with binary combinations (LOI<sub>ab</sub>) can be calculated from the following equation:

$$\text{LOI}_{ab} = \text{LOI}_a + \text{LOI}_b - \text{LOI}_c$$

where LOI<sub>a</sub>, LOI<sub>b</sub>, and LOI<sub>c</sub> are the LOI values for samples containing “a” additive, “b” additive, and without additives, respectively.<sup>32</sup> According to the previous relationship, the experimental value of LOI of the ATH/TPP filled PUFs was greater (27.2%) than the theoretical value of LOI (26.2%). Hence, the PUFs filled with these combinations of additives showed synergistic behavior. The mechanism for this behavior may have been due to the combination of gas-phase (volatilization of TPP) and condensed-phase mechanisms of TPP and ATH. Simioni and Modesti<sup>23</sup> also found beneficial behaviors of fire retardants and easy processing of higher loaded ATH and dimethyl methyl phosphonate (DMMP) fire-retardant additives in PUF.

Table IV shows the effect of ATH in the presence of TPP on the rate of flame spread of PUF at room temperature. The rate of flame spread or the rate of

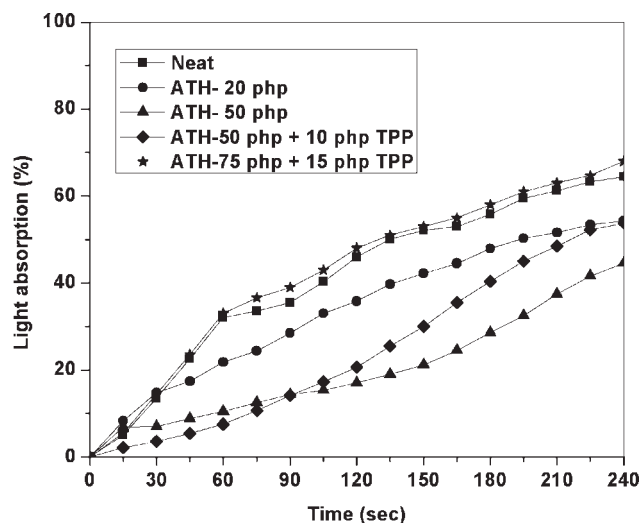
burning depends on the physical and thermal properties of the material, the method of mounting and orientation of the specimen, the type and magnitude of fire and heat exposure, the availability of air, and the properties of the surrounding area.<sup>2</sup> Table IV indicates that PUFs filled with only ATH burnt completely, but the rate of flame spread decreased with increasing ATH content. The addition of TPP to ATH further lowered the rate of the flame spread compared to PUF filled with the same amount of ATH (50 php) alone (i.e., without TPP; samples 6 and 8). Moreover, the PUF filled with 75 php ATH in combination with 15 php TPP extinguished after 15 s of burning, and interestingly, the PUF with 100 php ATH and 20 php did not catch fire at all at room temperature. This was attributed to the synergistic effect of the ATH and TPP. This was probably due to the following volatilization of TPP, the condensed-phase mechanism of TPP, the diluting effect of ATH, and the formation of carbonaceous alumina oxide hybrid char at higher temperatures:



The decomposition of TPP imparted certain amount of  $\text{PO}^\bullet$  free radicals, which effectively captured  $\text{H}^\bullet$  and  $\text{HO}^\bullet$  highly active free radicals in the flame zone, which induced the chain degradation of the polymer and were responsible for the flame propagation.<sup>33</sup> In this way, it decreased the rate of fuel formation and retarded the flame propagation.

### Smoke-density measurements

Smoke is a visible suspension of solid and liquid particles resulting from the combustion of materials. In general, smoke development depends on the source of ignition, oxygen availability, heat intensity, and composition and properties of the combustible materials.<sup>34</sup> Figure 5 shows the effect of ATH and TPP on the smoke density of the PUFs. The important values of the maximum smoke evolution in a chamber at 4-min time intervals and the smoke-density rating are presented in Table IV. This clearly shows that the maximum smoke density (amount of smoke generation) decreased with increasing ATH content. This was due to the action of ATH decomposition intermediates in the gas phase<sup>23</sup> and also to the adsorption of carbonaceous materials on the surface of the oxide residue and subsequent oxidation to carbon dioxide. This process was related to the efficiency of the residual alumina as oxidation catalysts.<sup>29</sup> However, on the addition of TPP with ATH, the smoke density



**Figure 5** Effect of ATH/TPP on the smoke density of the PUF.

slightly increased compared to that of the neat PUF because of insufficient combustion. Bonsignore<sup>17</sup> and Simioni and Modesti<sup>23</sup> also reported similar results with the addition of organophosphates to ATH.

### Char formation

There is a strong correlation between CY and flame resistance. Char formation occurs at the expense of combustible gases, and the presence of a char inhibits the further spread of flame by acting as a thermal barrier and a diffusion barrier.<sup>35</sup> Table IV shows the effect of ATH and TPP on CY when the PUF was burnt in muffle furnace at 550°C for 30 min. CY increased linearly with increasing ATH loading. However, with the addition of TPP to the same amount of ATH, the char residue slightly decreased. The ATH decomposition generated a ceramic layer of  $\gamma\text{-Al}_2\text{O}_3$  residue with a relatively high heat capacity, and it reduced the amount of thermal energy available for further degradation of the substrate.<sup>36</sup> The addition of TPP (15 and 20 php) in combination with ATH at a very higher loading (75 and 100 php) further improved the char residue. This was probably because the formation of a greater amount of phosphoric acid (precursor for char) from TPP increased at higher temperatures as result of the catalytic function of alumina oxide. In addition, we observed that CY did not increase proportionally with the addition of ATH in PUF. This was because the alumina oxide might have undergone ablation at higher temperatures.

### CONCLUSIONS

ATH and TPP were used as additives to improve the mechanical and fire-retardant performance of



PUFs with suitable formulations. The addition of ATH slightly increased the LOI, CY, and rate of flame propagation. The addition of TPP improved the processing of different raw materials during PUF preparation at higher loadings of ATH. Interestingly, the FR properties of the PUFs improved because of the synergistic effect of ATH and TPP.

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