

# Flammability and Mechanical Properties of Al(OH)<sub>3</sub> and BaSO<sub>4</sub> Filled Polypropylene

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**ABSTRACT:** The flammability and mechanical properties of Al(OH)<sub>3</sub>/BaSO<sub>4</sub>/polypropylene (PP) composites were investigated. The flow, morphological, and thermal properties were also analyzed by melt flow index (MFI), Scanning electron microscopy (SEM), and Differential scanning calorimeter (DSC) studies, respectively. Total filler amount was fixed at 30 wt % to optimize physical characteristics of the composites. In addition to the flame retardant filler Al(OH)<sub>3</sub>, BaSO<sub>4</sub> was used to balance the reduction in impact strength at high filler loadings. Substantial improvement in mechanical prop-

erties was achieved for 20 wt % Al(OH)<sub>3</sub> (i.e., 10 wt % BaSO<sub>4</sub>) composition while maximum flammability resistance was obtained for 30 wt % Al(OH)<sub>3</sub> composite. SEM studies showed that the presence of aggregated Al(OH)<sub>3</sub> particles led to low interfacial adhesion between them and PP matrix ending up with decreased mechanical strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3034–3040, 2010

**Key words:** flammability; polypropylene; mechanical properties; aluminum hydroxide; barium sulfate

## INTRODUCTION

Flammability of polymers has received much attention due to increased demand for flame retardant polymers in many applications, such as construction, textiles, home appliances, and furnishings.<sup>1,2</sup> Polypropylene (PP), a well known commodity thermoplastic, is highly flammable experiencing rapid decomposition rate, high dripping, no shoot and residual char formation during combustion. Like other polyolefins, it is difficult to make PP flame retardant because of its self-ignition (550–570°C) and surface pyrolysis (480°C) temperatures.<sup>3–5</sup> To impart flame retardancy, the mostly applied method is the addition of flame retardant fillers.<sup>6</sup> The history of these chemicals used to control the flammability properties of fabrics and textiles dates back early 19<sup>th</sup> century. In 1820s Gay-Lussac, after 34 years of study to protect the fabrics of the theaters, found that ammonium salts of phosphoric, sulfuric, and hydrochloric acid, especially the mixtures of ammonium phosphate, ammonium chloride, and borax, were very effective in flame retarding of hemp and linen fabrics.<sup>7</sup>

Halogenated and inorganic compounds, phosphorus and nitrogen based formulations are the main flame retardants for polymer matrices.<sup>8,9</sup> Hydrogen halides can be used efficiently because they inhibit

the radical formation during the propagation and chain branching steps of the combustion. When antimony trioxide is used with halogen containing compounds, produced antimony halides are thought to be a good trap for the radicals in the flame.<sup>10,11</sup> Nitrogen and phosphorus are two important elements found in the structures of many flame retardant additives. Phosphorus based flame retardants are generally effective when used with nitrogen or halogen containing compounds. For example; an intumescent flame retardant system is a result of a reaction between a polyol and a phosphorus and nitrogen containing compound.<sup>12,13</sup>

Despite their high usage rate, halogenated flame retardants are toxic, cause corrosion, emit smoke, and toxic fumes during processing.<sup>14,15</sup> Fortunately, nonhalogenated flame retardants are environmental friendly, nontoxic, and noncorrosive. Among them, aluminum hydroxide (Al(OH)<sub>3</sub>) is a well known metal hydroxide flame retardant, which starts to break down around 250°C to alumina and water endothermically. This endothermic decomposition forms the basis of its flame retardant behavior. The water released dilutes the combustible gases and acts as a barrier by preventing oxygen from supporting the flame. In addition, the oxide forms an insulating protective layer with the charring products.<sup>16,17</sup> However, high loading, i.e., in excess of 60% by weight, of metal hydroxide fillers is necessary to obtain satisfactory flame retardancy results.<sup>18</sup>

In some recent works the use of nano clay has become very popular to have better flame retardant polymeric composites.<sup>19–23</sup> Although some advantages

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**TABLE I**  
**Compositions of Prepared Samples**

Designation	Weight fraction (%)			Volume fraction (%)		
	PP	Al(OH) <sub>3</sub>	BaSO <sub>4</sub>	PP	Al(OH) <sub>3</sub>	BaSO <sub>4</sub>
Neat PP	100	–	–	100	–	–
0-A	70	–	30	92	–	8
10-A	70	10	20	90	4.8	5.2
15-A	70	15	15	89.1	7.1	3.8
20-A	70	20	10	88.1	9.4	2.5
30-A	70	30	–	86.2	13.8	–

were discussed in terms of substantial improvements as increase in limiting oxygen index (LOI)<sup>19</sup> the combinations of nano clays with other materials like nano clay-Al(OH)<sub>3</sub>,<sup>20</sup> layersilica-carbon nanotube,<sup>21</sup> nano clay and charring agents,<sup>22</sup> and organo phosphorous and nano-clay<sup>23</sup> were proved to enhance particularly char formation and lowering heat release to some extent.

In this study, since high loadings have inferior effect on mechanical properties of polymers, the total amount of used filler was kept at 30% by weight and Al(OH)<sub>3</sub> was main filler as flame retardant replaced by barium sulfate (BaSO<sub>4</sub>) filler. BaSO<sub>4</sub> incorporation was aimed to provide PP with better toughness and impact strength.

## EXPERIMENTAL

### Materials and preparation of samples

Hostalen (former Hoechst, Germany) PPR 4142 grade PP was used as the matrix material. Both Al(OH)<sub>3</sub> and BaSO<sub>4</sub> were obtained from Riedel De Haen (Germany) and used as supplied. The measured average particle sizes of Al(OH)<sub>3</sub> and BaSO<sub>4</sub> were 70 and 4 μm, however; agglomerated particles were also observed at 400 and 100 μm, respectively. Table I shows the compositions of samples; where A stands for Al(OH)<sub>3</sub>. The volume fractions were based on the densities of PP, Al(OH)<sub>3</sub>, and BaSO<sub>4</sub> for all composites studied in the work.

Melt blending was performed in a mixing head of a Brabender Plasti-Corder (Duisburg, Germany) at 190°C with 45 rpm of rotor for 15 min. Solid inorganics were added after PP melted in the mixing head of the plasti-Corder. Sample sheets of 2 mm thickness were obtained by compression molding after complete mixing at the same temperature and used for subsequent mechanic and flammability tests.

### Characterization experiments

Melt flow properties of samples were characterized by Coesfeld Material Test, Meltflixer LT (Dortmund, Germany) at 230°C/2.16 kg according to ASTM D

1238-90b. Tensile tests were performed in a computer controlled tensile testing machine (Lloyd LR 5K) on standard dumbbell shaped specimens at room temperature. The testing gauge length was set as 8 cm and the draw rate was 5 cm/min. Unnotched Charpy impact testing was carried out on samples having the dimensions of 60 × 7.5 × 3.5 mm by Pendulum Impact Testing Machine, Coesfeld Material Test PSW 4 J (Dortmund, Germany) at room temperature. In all static tests, for every composition at least seven specimens were sampled.

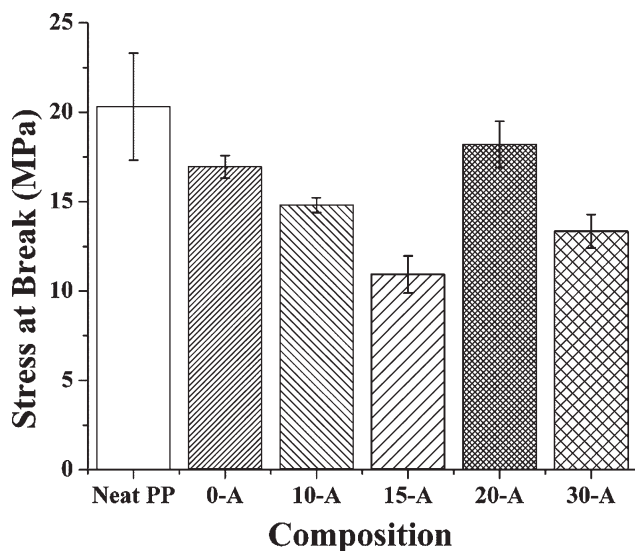
Impact-fractured surfaces of all compositions were analyzed via scanning electron microscopy (SEM) (JEOL, JSM-840A, and Tokyo, Japan) to interpret the distribution of filler throughout the matrix and to study the morphology of the samples. DuPont Thermal Analyst 2000 DSC 910 S (New Castle, DE) was used to follow thermal behavior of samples under air and nitrogen atmospheres between 30 and 300°C with a 10°C/min heating rate. To investigate thermal stability of Al(OH)<sub>3</sub>, isothermal (at 190°C for 40 min) and nonisothermal (from 35 to 350°C) analyses were carried out by Dupont 951 Thermogravimetric Analyzer.

LOI and horizontal flammability tests (HFT) were performed to investigate flammability properties of composites. In LOI test, specimens were top ignited in a glass column with different gas combinations by changing the flow rates of nitrogen and oxygen according to ASTM D 2863-77. For HFT, specimens were marked with lines at 25 and at 100 mm from the end of the specimen. They were clamped supporting the longitudinal axis horizontally and holding the transverse axis with a 45° to the horizontal axis. Specified height of flame was exposed to the free end of the specimen. The burner was removed at 30 s and the time, in seconds, for a flame to reach the 25 mm marked line was measured and recorded as *t*<sub>1</sub>. The chronometer was stopped when the flame front reached to the 100 mm marked line and burning time was recorded as *t* in accordance with ASTM D 635-91.

## RESULTS AND DISCUSSION

### Flow properties and mechanical testing

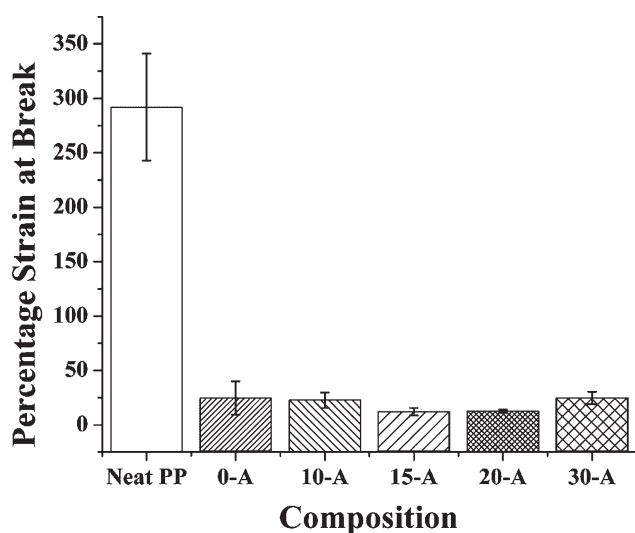
Filler addition changes the flow properties of matrix material; typically in highly filled compounds the increase in viscosity is inevitable. The MFI values of neat PP, 0-A, 10-A, 15-A, 20-A, and 30-A were measured as 4.3, 5.6, 5.5, 5.3, 4.8, and 4.7 g/10 min, respectively. Effect of Al(OH)<sub>3</sub> filler on MFI can be seen from 0-A to 30-A composites. It is apparent that replacing BaSO<sub>4</sub> by Al(OH)<sub>3</sub> caused MFI to decrease slightly parallel to the increase in the amount of Al(OH)<sub>3</sub>. This can be a consequence of



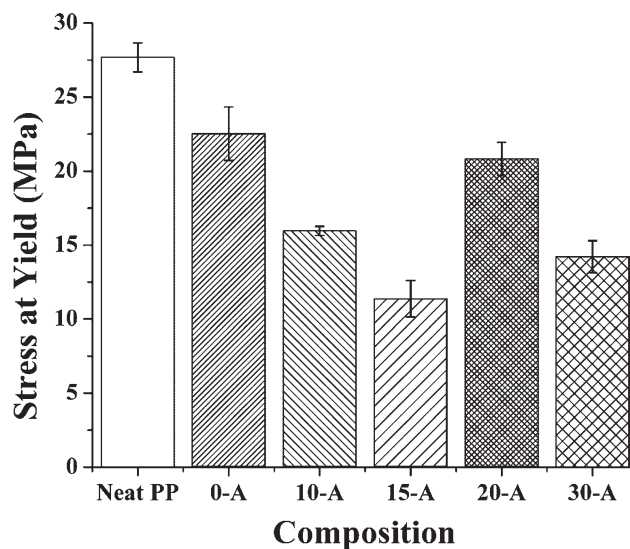
**Figure 1** The variation of stress at break with respect to composition. (For abbreviations of compositions see Table I and the same composition abbreviations were used for the rest of the figures).

morphology (size and shape) of  $\text{BaSO}_4$ , which gave rise to improved filler dispersion and higher MFI values, i.e., easy flow, contrary to  $\text{Al}(\text{OH})_3$ . Apparently, we did not observe any distinguishing change in flow properties with the amount of filler and compositions.

Figures 1–6 present the results of the tensile and impact testing of  $\text{Al}(\text{OH})_3/\text{BaSO}_4/\text{PP}$  composites with error bars. The stress at break decreased with increasing  $\text{Al}(\text{OH})_3$  content in Figure 1, but up to 20-A. Incorporation of only  $\text{BaSO}_4$  to PP decreased the stress at break to a slightly lower value than that of neat PP. Also, when  $\text{Al}(\text{OH})_3$  was added into the polymer replacing  $\text{BaSO}_4$ , stress at break values con-

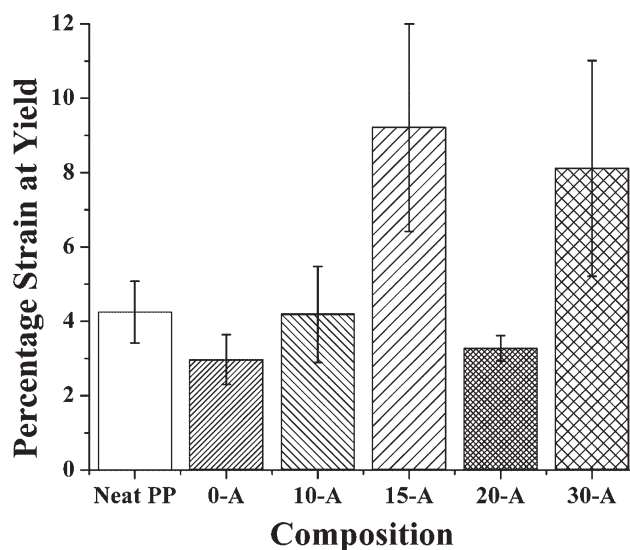


**Figure 2** The variation of percentage strain at break with respect to composition.

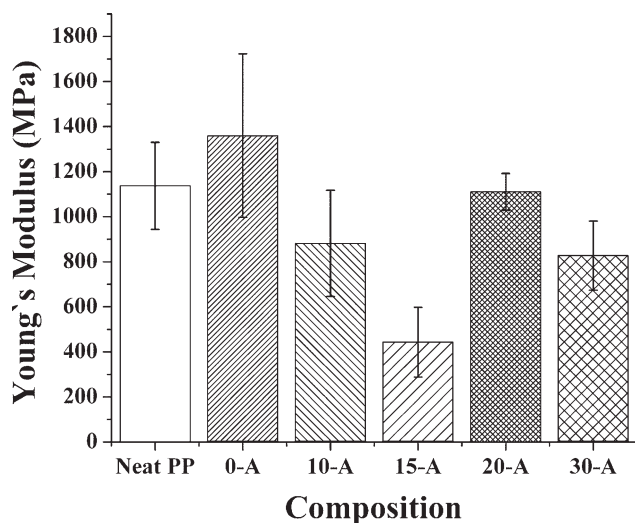


**Figure 3** The variation of stress at yield with respect to composition.

tinued to decrease up to 15-A composite. Compositions from 0-A to 15-A, there is an antagonistic effect leading to very low stress at break values while an improvement can be seen for 20-A among the others. Finally, 30%  $\text{Al}(\text{OH})_3/\text{PP}$  composite gave slightly better value at an average, than 15-A; nonetheless it is still lower than the other two compositions, 0-A and 10-A. Neat PP has a very high percentage strain at break value, typical of this polymer. However, with the addition of filler, the strain at break values dropped suddenly, as it was expected due to loss of continuity in the main matrix to very low values and never recovered again with the change of the filler composition, as shown in Figure 2.



**Figure 4** The variation of percentage strain at yield with respect to composition.



**Figure 5** The variation of Young's modulus with respect to composition.

All filled samples failed just after the yield point, as seen in Figure 3. The variation of yield strain at elastic deformation is presented in Figure 4. Figure 5 illustrates an improved modulus for the case of BaSO<sub>4</sub>/PP composite, while it was the lowest for 15-A. Despite the addition of rigid filler into a comparatively soft polymeric material the Young's modulus showed a decreasing trend, except 0-A composition, rather than the expected increase in moduli. However, the moduli within the limits of standard deviation decreased with slight changes after 10-A composition. This may be attributed to the differences in the shapes and size of particles where Al(OH)<sub>3</sub> (flake-like) has rather large particles compared to BaSO<sub>4</sub> (spherical). The impact strength of BaSO<sub>4</sub>/PP (sample 0-A) was higher than that of Al(OH)<sub>3</sub> (Fig. 6), and the neat PP did not break at all. It was obvious that presence of even small amount of Al(OH)<sub>3</sub> was enough to decrease impact strength to very low values.

### Morphology of filled PP

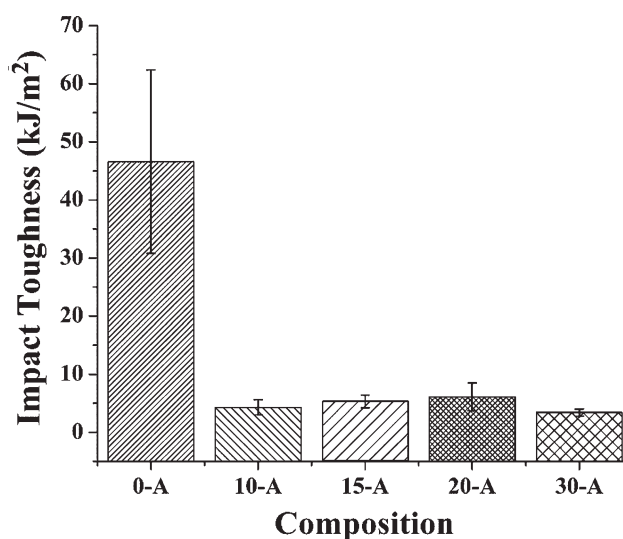
Impact fracture morphology was investigated by SEM. It is apparent that shapes of the two fillers, BaSO<sub>4</sub> and Al(OH)<sub>3</sub> are totally different, i.e., spherical and flake-like, respectively. SEM pictures given in Figure 7(a–d) show the impact fracture surfaces of samples. BaSO<sub>4</sub> particles have smaller size, mostly lower than 1 μm compared to the average 10 μm particle size of Al(OH)<sub>3</sub>. As depicted in Figure 7(a) big spherical agglomerates of BaSO<sub>4</sub> coexist with the well distributed smaller BaSO<sub>4</sub> particles. When the content of one filler was increased, then agglomeration became inevitable for that filler. Some stacked Al(OH)<sub>3</sub> particles were pulled off from the matrix leaving empty holes that proves poor interfacial

adhesion between the filler and the matrix, Figure 7(c). Impact properties of filled polymers depend on number of factors; such as particle geometry, size, and distribution and filler matrix interfacial adhesion. It can be suggested that, Al(OH)<sub>3</sub> lowered the impact strength of PP composites due to its plate like shape and high aggregation tendency. Addition of BaSO<sub>4</sub> to PP gave better impact strength and also Young's modulus than the other filler. No debonding was observed for BaSO<sub>4</sub>, which may be the indicative of presence of good wetting between the filler and the polymer. If BaSO<sub>4</sub> had been distributed very homogeneously without agglomeration in the matrix and interacted with PP, it would have raised the impact strength even better.

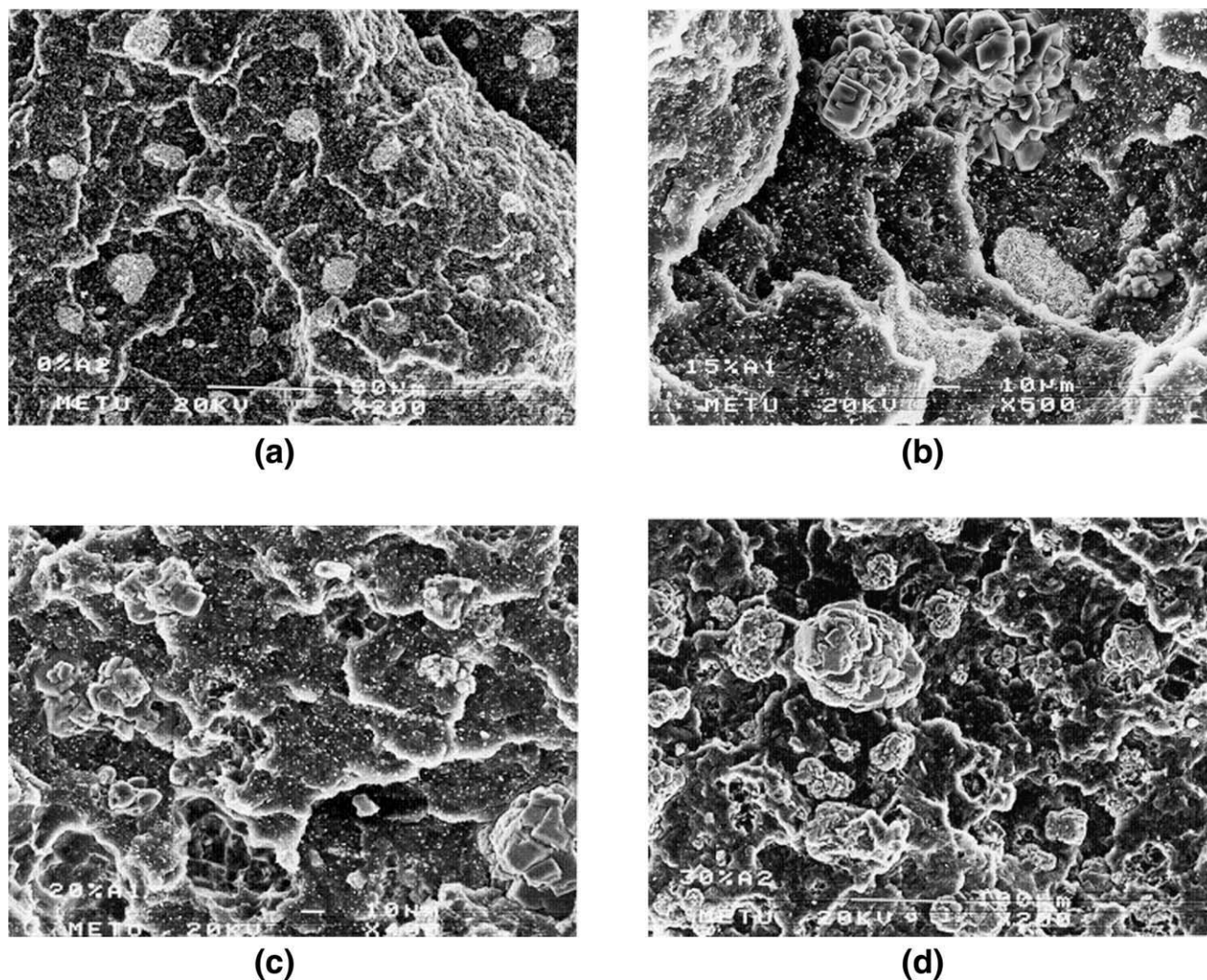
### Thermal analysis

The thermal stability of Al(OH)<sub>3</sub> filler was characterized by TGA as shown in Figure 8. In the same plot the isothermal TGA thermogram of Al(OH)<sub>3</sub> was also shown. There was no change in Al(OH)<sub>3</sub> for 40 min at the study temperature (190°C) which indicated that Al(OH)<sub>3</sub> was stable for the processing temperature. The weight loss of Al(OH)<sub>3</sub> starts around 250°C, which is well above the processing temperature. The risk of decomposition of Al(OH)<sub>3</sub> during processing at 190°C therefore appears to be very low even at longer processing times.

Thermal analyses of composites were given in Figures 9 and 10 in N<sub>2</sub> and air atmospheres, respectively. Endothermic melting peak of neat PP was observed at 167.5°C in air and 166.5°C in N<sub>2</sub>. The addition of filler of both kind did not cause any alteration in the crystallinity of the matrix since, melting point of PP was found to be almost the



**Figure 6** The variation of impact toughness with respect to composition.

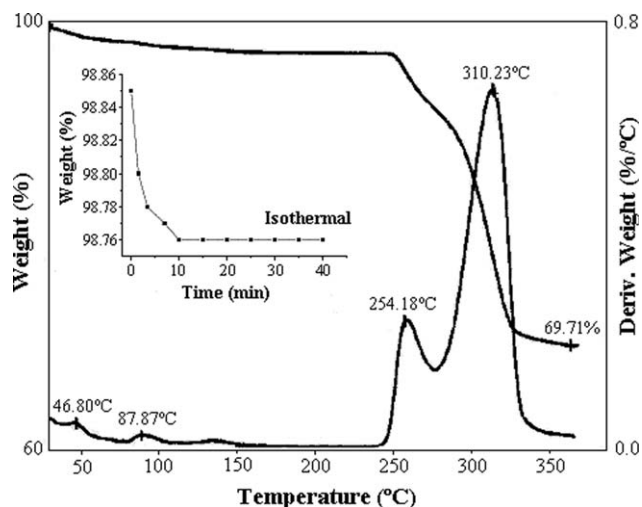


**Figure 7** Impact fracture surfaces of (a) 0-A, (b) 15-A, (c) 20-A, (d) 30-A where neat PP did not break.

same. When the thermogram of  $\text{BaSO}_4/\text{PP}$  composite i.e., 0-A, is compared to that of neat PP, it can be seen that  $\text{BaSO}_4$  does not show any thermal transitions, e.g., decomposition, within the temperature range studied.

However, on heating,  $\text{Al}(\text{OH})_3$  loses water turns into alumina ( $\text{Al}_2\text{O}_3$ ) without melting. Figure 9 also shows two peaks at 230 and 315°C corresponding to endothermic loss of water from  $\text{Al}(\text{OH})_3$ . At 230°C, 15-A composite shows little amount of heat release while the amount is more pronounced for  $\text{Al}(\text{OH})_3/\text{PP}$ . The peak at 315°C is more endothermic therefore, it cools the specimen's surface better and at this temperature  $\text{Al}(\text{OH})_3$  completely turns to alumina.

The exothermic oxidation of PP started at about 260°C (oxidation induction temperature), Figure 10. Oxidation peaks were seen in thermograms of all PP composites taken in air. Therefore, the oxidation induction temperature would be expected to



**Figure 8** The isothermal and nonisothermal TGA thermograms of  $\text{Al}(\text{OH})_3$ .

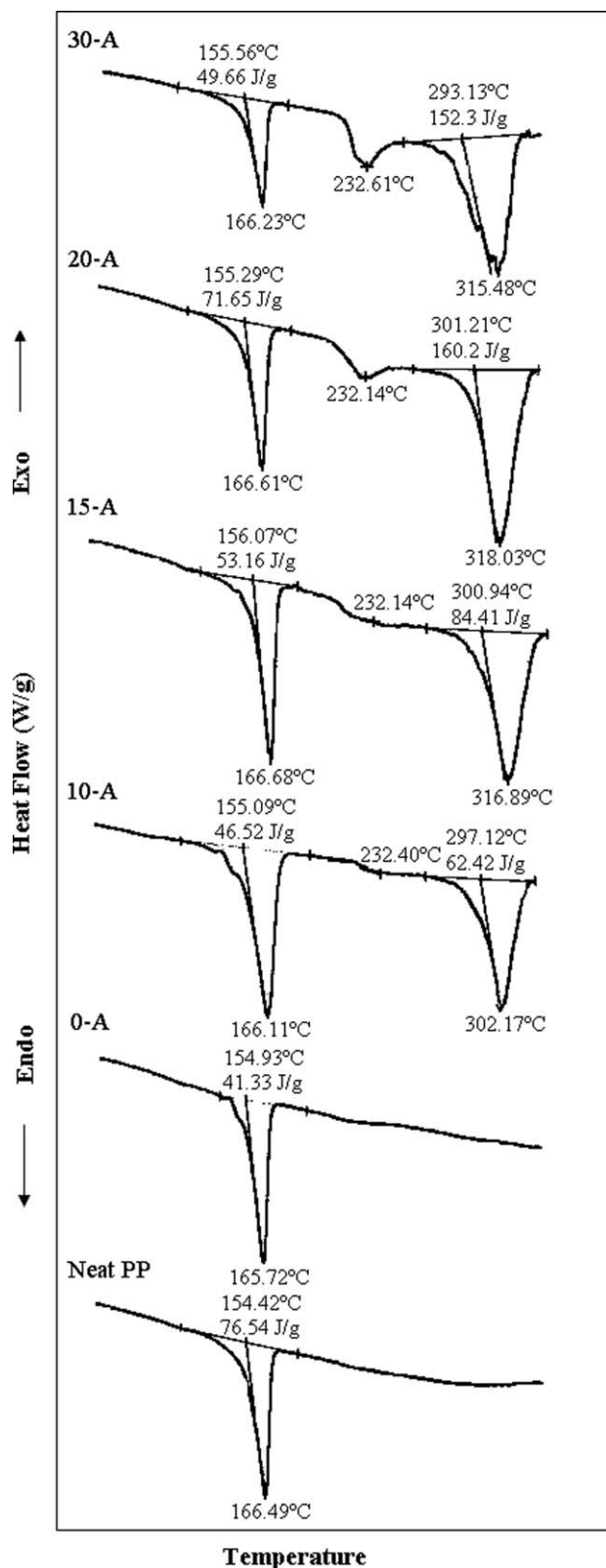


Figure 9 The DSC thermograms in N<sub>2</sub>.

increase to the higher temperatures through better stabilization. With the increase of the amount of Al(OH)<sub>3</sub> filler from 10% to 30%, the thermal oxida-

tion onset temperature of PP shifted to higher temperatures and broadened as illustrated in Figure 10.

**Limiting oxygen index**

Table II shows an improvement in LOI values of all composites compared to neat PP. While performing

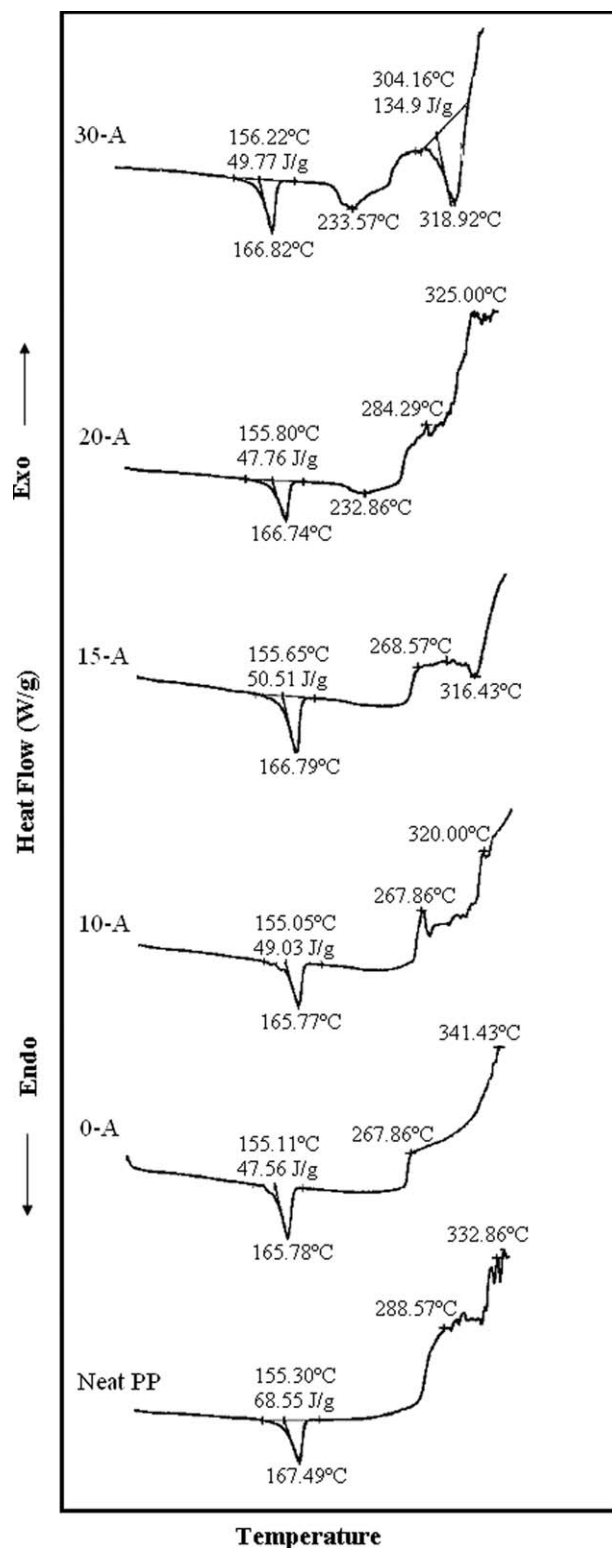


Figure 10 The DSC thermograms in air.

**TABLE II**  
The Results of Horizontal Flammability and LOI Tests

Composition	$t_1$ (s)	$t$ (s)	$t-t_1$ (s)	Ave. Burning Rate (cm/min)	LOI
Neat PP	48	209	161	2.80	17
0-A	54	162	108	4.17	21
10-A	50	192	142	3.17	20
15-A	56	199	143	3.14	21
20-A	78	224	146	3.09	20
30-A	92	339	247	1.82	20

The abbreviations are defined in the text.

the test, one of the problems was excessive dripping. During combustion, specimen burning parts broke out by bending and these broken parts also continued to burn for a short time. Since air comprises about 20.95% oxygen by volume, any material with LOI less than 20.95 burn easily in air then any material having this threshold LOI is defined as being marginally stable. Therefore, when LOI of filled samples (20–21 g/10 min) are compared with that of neat PP (17 g/10 min), it can be stated that obvious flame retardancy has been achieved.

#### Horizontal flammability test

Tested specimens gave the results as shown in Table II. Since all the samples burned to the 100 mm mark, burning rate calculated as  $450/(t-t_1)$ (cm/min). As in LOI test, dripping was a problem even pronounced for composites. When the filled grades of PP were considered, with the addition of 30% BaSO<sub>4</sub> (0-A), average burning rate increased suddenly almost twice of that neat PP. As the amount of Al(OH)<sub>3</sub> replaces BaSO<sub>4</sub> burning rate gradually decreased and 30-A [30% Al(OH)<sub>3</sub>] showed the smallest burning rate, even lower than that of neat PP. Al(OH)<sub>3</sub> alone is without any doubt, the best, whereas the loss in mechanical properties should also be considered.

#### CONCLUSIONS

20-A composite gave the most substantial improvement in stress at break, Young's modulus, and stress at yield values. Since better characteristics of BaSO<sub>4</sub> (size and shape) gave improved filler dispersion and high MFI values, i.e., easy processing, BaSO<sub>4</sub>/PP composite showed the highest impact strength. Among Al(OH)<sub>3</sub> containing composites, 20-A showed slight improvement in impact strength but flake-like shape and possible high aggregation of Al(OH)<sub>3</sub> lowered the impact strength of PP matrix.

An improvement of LOI for filled-PP samples revealed that at least ambient oxygen concentrations needed to initiate and maintain the combustion com-

pared to very low LOI of PP. Al(OH)<sub>3</sub> was effective in changing the burning rate of the matrix material. For the composites, as Al(OH)<sub>3</sub> content increased, burning rate of filled-PP decreased proportional to the amount of the filler. It should also be remembered that to obtain sufficient flame retardancy by using metal hydroxides high filler loading is necessary. If only both flammability tests are considered, the best result was achieved for 30-A composite. Because it gave higher LOI and lower average burning rate than those of neat PP. However, if both mechanical and flammability properties are the main concern, 20-A composite is definitely the optimum choice. This situation also confirms that since the total amount of filler in 20-A and 30-A is the same, BaSO<sub>4</sub> is effective in improving the mechanical properties of the composites.

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