THERMAL CHARACTERIZATION OF ALUMINA TRIHYDRATE (ATH) AND FLAMMABILITY STUDIES OF ATH FILLED LOW DENSITY POLYETHYLENE

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RINGKASAN : *Alumina trihydrate (ATH) sejenis perencat nyalaan yang tidak toksik dan mesra persekitaran dicirikan menggunakan analisis termogravimetrik (TGA) dan analisis pembezaan terma (DTA). Kesan kandungan ATH terhadap sifat kebolehbakaran polietilena berketumpatan rendah (LDPE) ditentukan menggunakan indeks penghadan oksigen (LOI) dan ujian ketumpatan asap. Ujian pencirian terma menunjukkan had suhu ATH yang berfungsi dengan berkesan sebagai perencat nyalaan adalah dari 200 hingga 350°C. Dalam ujian pembebasan air menunjukkan pembebasan air yang bergabung secara kimia dalam ATH bertambah dengan peningkatan suhu. Ujian LOI menunjukkan perencatan nyalaan LDPE bertambah dengan peningkatan kandungan ATH dan pengurangan saiz partikel ATH. Ujian ketumpatan asap membuktikan ATH juga berkesan dalam mengurangkan ketumpatan asap. Kajian juga menunjukkan kelikatan ATH yang diisi LDPE berkurang dengan penambahan saiz partikel ATH.*

ABSTRACT : Alumina trihydrate (ATH) which is a non-toxic and environmentally friendly flame retardant was characterized using Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The effect of ATH content on flammability properties of LDPE was determined using Limiting Oxygen Index (LOI) and smoke density test. The thermal characterization studies showed that the temperature range for ATH to effectively act as a flame retardant is from 200°C to 350°C. In water release test, it was also determined that the release of the chemically-combined water in ATH increased with increasing temperature. The LOI test showed that the flame retardancy of LDPE increased with increasing ATH content and decreasing ATH particle size. The smoke density test of a burning ATH filled LDPE proved that ATH is also effective in reducing smoke density. The study also showed that the viscosity of ATH filled LDPE decreased with increasing ATH particle size.

KEYWORDS: Alumina trihydrate, flame retardant, low density polyethylene, thermal characterization, flammability studies

INTRODUCTION

Low density polyethylene (LDPE) is widely used in the wire and cable industry as insulating materials. However, the flammability of LDPE represents a drawback that restricts their applications (Basfar, 2002). The addition of flame retardants are needed to achieve the properties required by the standards. Flame retardancy of polyolefins can be enhanced by physical incorporation of appropriate flame retardants (Gachter and Muller, 2003).

Halogenated flame retardants in combination with antimony trioxide have been used for many years to impart flame retardancy to plastics (Pritchard, 1998). The use of halogen containing system for fire retarding polymers gives rise to problems of toxicity, corrosion and smoke (Delfosse, 1989). The trend to eliminate halogen-based substances to reduce smoke toxicity during combustion has promoted research on halogen free formulations (Lu *et al.*, 2002). The use of metal hydroxides such as alumina trihydrate (ATH) or magnesium hydroxide has been extensively described by Rothon (1999) and Sauerwein (2002). ATH has been used as a non-toxic, environmentally friendly fire retardant for over thirty years (Zhu *et al.,* 2005).

ATH is one of the less expensive flame retardants used today and has the biggest market share by volume due to the fact that it is cost effective and environmentally friendly. In case of a real fire scenario, it produces low smoke, low carbon monoxide and low toxicity combustion gases. ATH is in reality a crystalline aluminum hydroxide, which on being heated above 200 °C liberates water, leaving aluminum oxide. The release of water as a vapor, absorbs heat from combustion to help extinguish the flame. Also the steam given off, dilutes the combustible volatiles which helps retard the combustion. ATH also helps to form an insulating char. However for ATH to work effectively, it requires ATH loadings in plastic compounds in excess of 30 phr (Dick, 1987).

In this paper, the effect of ATH content and particle size on flame retardancy of LDPE system is reported. Thermal characterization of ATH using Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and water release test was also performed.

MATERIALS AND METHODS

a) Material

Alumina trihydrate (ATH) manufactured by Martinswerk from Germany was used in this research. The chemical composition and physical data of ATH are listed in Table1.

Table 1. Chemical composition and physical data of ATH

Chemical formula	$Al(OH)_3$
Purity	99.6 %
Mohs hardness	2.5
Median refractive index	1.58
Specific heat	1.19 J/g K at 295 K
Density	2.42 g/cm^3
Solubility in H_2O (pH=7)	1.5-10^{-4} g/100 g H_2O

In this research, different particle size of ATH (2, 10, 20 and 55 µm) were purchased from Martinswerk company. LDPE with grade of LH0075 (density of 0.921 g/cm^3 and a melt flow index of 0.89 g/10min) was obtained from the Bandar Imam Petrochemical Company, Iran.

b) Sample Preparation

LDPE and ATH were mixed and melt-blended in a twin-screw extruder model Brabender DSE-25. The length to diameter (L/D) ratio of the screw was 20 with a 150 °C to 160 °C temperature profile. The compound were pre-heated for 5 min, and then compression molded according to ASTM D-1928 into sheets (with dimensions of 150 mm x 150 mm x 2 mm) at 150 °C under a pressure of 10 MPa for 3 min. The LDPE/ATH ratio was varied from 0 to 340 phr for the LOI test with an increment of 50 phr. However, for the smoke density test, the blend ratio is from 0 to 140 phr with an increment of 20 phr. The increment of the LDPE/ATH ratio was different between LOI and smoke density tests because it was expected that the effect of ATH content with an increment of 50 phr on LOI is a steady increase based on a trial study. However, a significant drop is expected for the smoke density test below 50 phr.

c) Differential Thermal Analysis

Differential Thermal Analysis (DTA) was carried out on Netzsch (Simultaneous Thermal Analyzer) STA 509 with S:Pt thermocouple at a heating rate of 5 °C min^{-1} in the temperature range of 30 °C to 1000 °C.

d) Thermogravimetric Analysis

Thermal decomposition behavior of ATH was determined in air environment using TGA model TGD-7000. Specimens were weighed (100 mg) and heated at 10 °C min^{-1} in air at temperatures ranging from 30 °C to 1000 °C. The flow rate of air was 100 cm^3/ min.

e) Water Release Test

ATH can release water when it is exposed at high temperature in an oven ranging from 180 °C to 220 °C. The released water is determined by $W = [(w_2-w_1)/w_2] \times 100$ where w_2, w_1 are the weight of ATH before and after heating and W is the weight percent of water release.

f) Limiting Oxygen Index

Limiting Oxygen Index (LOI) is the minimum concentration of oxygen (expressed as volume percent) in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature. LOI test was performed using an apparatus from Rheometric Scientific, UK in accordance with ASTM D2863. Each sample was placed vertically in a flowing atmosphere of oxygen and nitrogen and ignited at the top. LOI leads to continuous burning of sample. Samples with LOI higher than 21 % can pass this test. Five samples were tested and for each sample, LOI is determined by $LOI = [(O_2 \times 100) / (O_2 + N_2)]$ where O_2 is the volumetric flow of oxygen, cm^3/s and N_2 is the corresponding volumetric flow rate of nitrogen, cm^3/s.

g) Smoke Density Test

Smoke density test was done according to ASTM D 2843. It reveals the loss of light transmission through a collected volume of smoke produced under controlled and standardized conditions. The test employs a (12 x 12 x 31) inch aluminium test chamber with a heat-resistant glass observation door. The chamber was completely sealed except for (1 x 9) inch openings on four sides of the bottom of the chamber. A specimen holder holds the specimen in a horizontal position. A photoelectric cell and a light source were used to measure the light absorption. A test specimen of size (1 x 1 x 1/4) inch was placed in the specimen holder and exposed to a propane-air flame so that the flame is directly under the specimen. The percent light absorbed by the photoelectric cell was measured and recorded at 15 seconds intervals for 4 min. The light absorption data (light absorption in percent) is plotted versus time on a graph recorder. The total smoke produced is determined by measuring the area under the curve. This area under the curve in percent is the smoke density rating. Polymer Laboratories Instrument System SN-2400 was used to measure the smoke evolution.

h) Viscosity Test

Viscosity test is performed in accordance to ASTM D 2393, based on the principles of rotational rheology. In this test, the sample is preconditioned by placing it in a constant temperature bath at the specified test temperature. The proper sized spindle is allowed to rotate in the sample for 30 seconds. The instrument is stopped through the use of a clutch and the reading is taken from the dial. The test is repeated until a constant reading is obtained.

RESULTS AND DISCUSSION

Thermal analysis (TGA and DTA) is a very effective technique for studying the chemical and physical phenomena as a function of temperature. Figures 1 and 2 show the TGA and DTA curves as the ATH powder was heated in air. The data from TGA shows that the decomposition begins slowly at a temperature of about 200 °C. It then accelerates as the temperature exceeds 220 °C and gives a large endothermic peak at 300 °C. The considerable weight loss at 220 °C to 300 °C, gradual weight loss at 300 °C to 500 °C, and slight weight loss above 520 °C are observed by TGA. These results are very similar to the results obtained by Zhu *et al.*, (2005). Saito (1999) reported that the crystalline water of ATH can be liberated twice, respectively, around 300 and 500 °C, as shown in Equations 1 and 2.

$$Al_2O_3.3H_2O \rightarrow Al_2O_3.H_2O + 2H_2O \quad (1)$$

$$Al_2O_3.H_2O \rightarrow Al_2O_3 + H_2O \quad (2)$$

The double dehydrations of ATH resulted in a prominent endothermic peak at 220 °C to 300 °C and the small endothermic peak at 470 °C to 560 °C in the DTA curve. About 90 % of the chemically-combined water was released within the temperature range of 200 °C to 400 °C and followed with a smaller rate until all the chemically combined water released within the 400 °C to 1000 °C range. Therefore the most effective temperature range of ATH for flame retardancy of LDPE is between 200 °C to 400 °C. It could be said that beyond that temperature, the amount of water release is less effective for heat withdrawing from combustion. The reaction required 196 kJ/mol of ATH which means that this amount of heat was removed from the burning system. This slowed down the decomposition of the plastic due to the cooling effect on the system. The water vapour released, diluted the oxygen gases in the vicinity of the burning plastic. The aluminium oxide formed combined with the products of carbonization and built a protective layer, which prevent the diffusion of oxygen and adsorbs harmful products. These results were in agreement with other researchers (Haurie *et al.*, 2006 and Delfosse *et al.*, 1989).

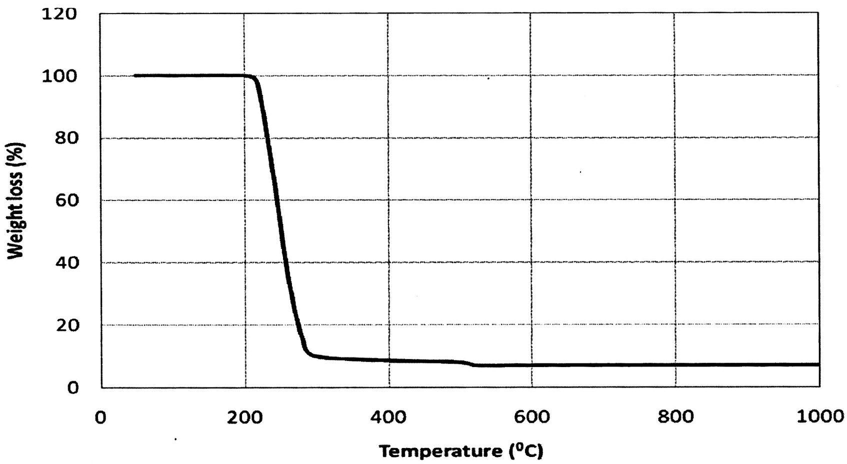

Figure 1. *Thermogravimetric analysis of ATH*

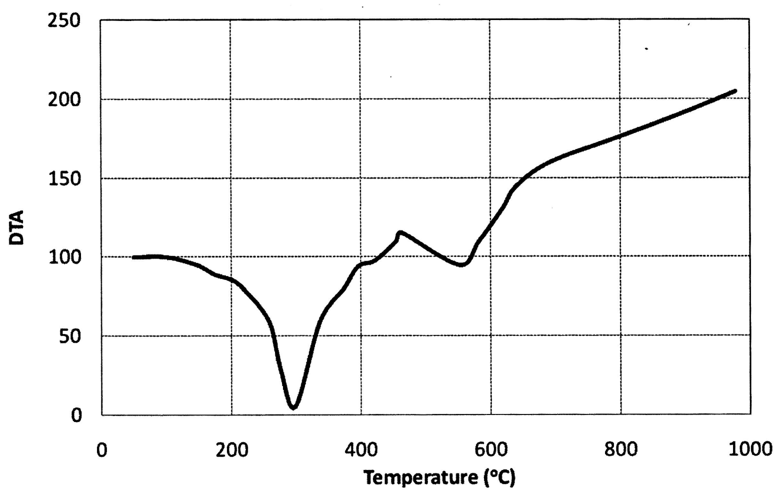

Figure 2. *Differential thermal analysis of ATH*

The flame retardant effect of ATH is based on the endothermic decomposition into aluminium oxide and water respectively. Only non-toxic and non-corrosive decomposition products are formed during these processes. During the decomposition of ATH, considerable quantities of heat are consumed and hence withdrawn from combustion. The water release mechanism begins at approximately 200 °C and consequently the chemically combined water is rapidly released.

Figure 3 shows the water release of ATH versus time at different temperature ranges from180 °C to 220 °C. The median particle size of ATH used in this experiment was 10 μm. Chemically-combined water is released even at 180 °C but the release started to become more significant at approximately 200 °C. For example, when ATH is exposed for 30 minutes at different temperatures (180, 190, 200, 210 and 220 °C) the chemically combined water is released at different amount (0.5, 0.65, 1.7, 2.5 and 3.7 wt% respectively). The result clearly shows that considerable amount of chemically combined water in ATH was released when it is exposed to at least 200 °C. This test is consistent with the data obtained from the thermal analysis which also shows that ATH as a flame retardant will be more effective when it is exposed at the temperature of 200 °C and above.

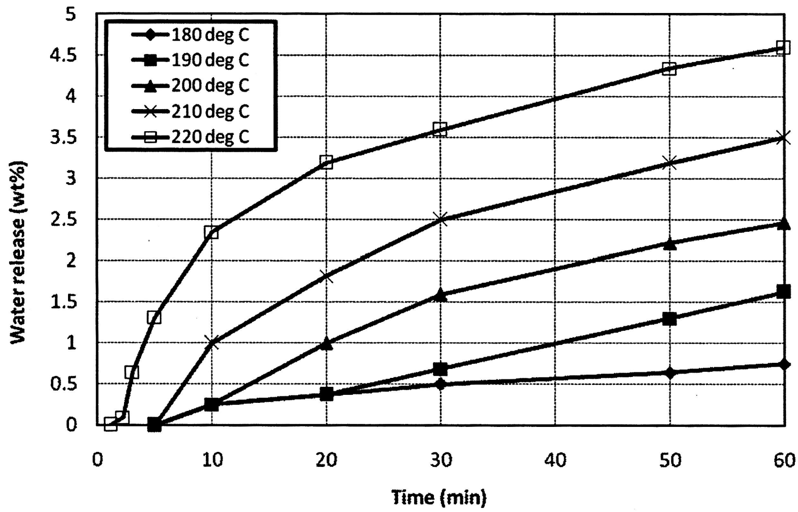

Figure 3. *Effect of time and temperature on water release of ATH*

Figure 4 shows the effect of ATH content on limiting oxygen index. The median particle size of ATH used in this experiment was 10 µm. As expected, the result shows that flame retardancy of the LDPE system increases with increasing amount of ATH as revealed by the LOI values. Similar results were also observed by Haurie *et al.* (2006) and Delfosse *et al.* (1989). From Figure 4, it can be observed that the incorporation of 340 phr of ATH to the blends resulted in the LOI to increase from 18 % (pristine LDPE) to 98 %. The result shows that the LDPE system can pass the LOI test with addition of at least 50 phr.

Figure 5 shows the effect of particle size of ATH on fire retardancy. It can be observed that the particle size of aluminium hydroxide influences the fire retardant effect, i.e. the finer the aluminium hydroxide the greater is the effect. It is interesting and important to know that the finer particle size (less than 10 µm) of ATH has greater effects in LOI test. In addition it was shown that LOI values did not reduce below 30 % even if the particle size of ATH was increased to 55 µm. Therefore, ATH in all domain of particle size of the present study can pass the LOI test. It can be concluded from Figures 4 and 5 that LOI values depend on both median particle size of ATH and the amount of ATH filled in LDPE.

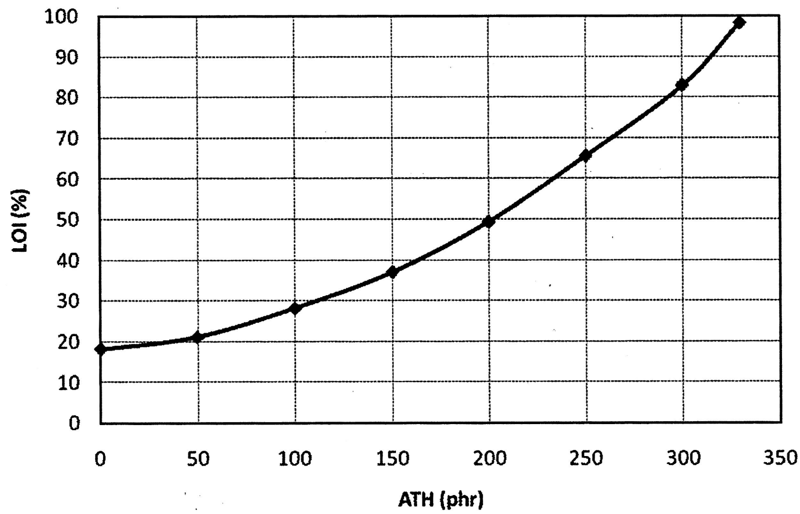

Figure 4. *Effect of ATH content on limiting oxygen index*

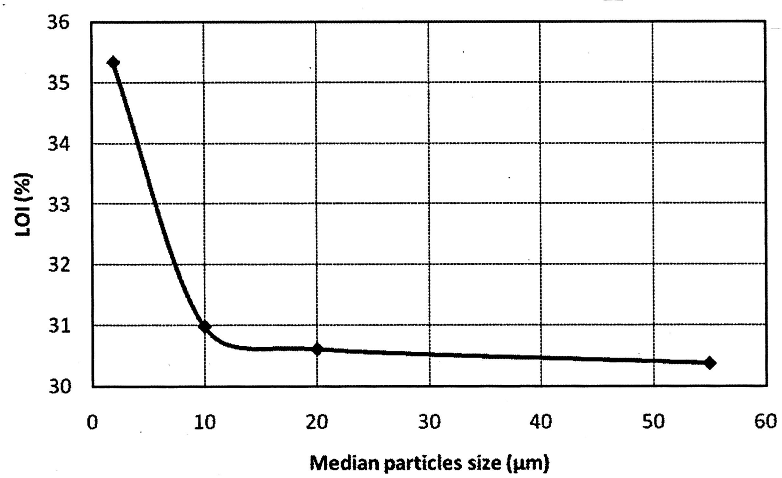

Figure 5. *Effect of median particle size of ATH on limiting oxygen index*

Figure 6 illustrates the effect of ATH concentration on the smoke density of burning ATH filled LDPE system. The study reveals the loss of light transmission through a collected volume of smoke produced under controlled and standardized conditions. The smoke density is proportional to the light absorption. It is shown that the smoke density from burning LDPE decreased with increasing amount of ATH. A drastic reduction in smoke density was observed with addition of 20 phr of ATH whereby the light absorption was reduced from 75 to 27 %. A more gradual reduction was observed on further increase of ATH. This test clearly shows the effectiveness of ATH in reducing the smoke density of a burning LDPE.

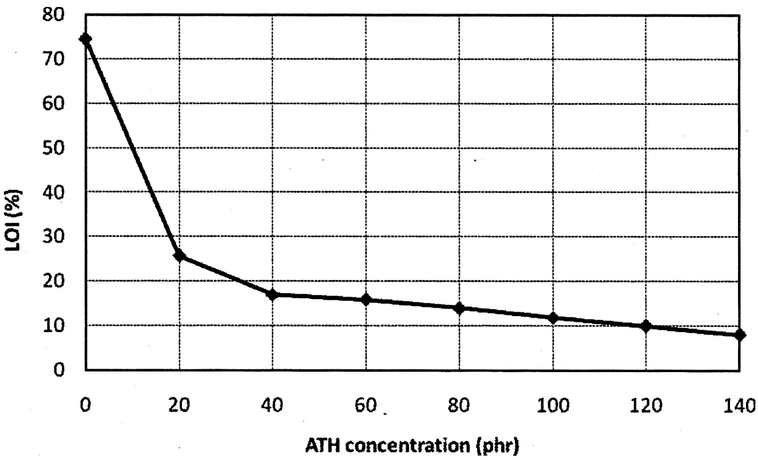

Figure 6. *Effect of ATH content on absorption*

The influence of ATH particle size on viscosity of ATH filled in LDPE is given in Figure 7. This test was done at 140 °C with rotary speed of 50 rpm. The ATH content in this test is 120 phr. The result shows that the viscosity decreased with increasing particle size. As the particle size of ATH increased from 3 to 20 µm, the viscosity reduced significantly from 230 to 90 Pa.S. With a further increase to 53 µm, the viscosity reduced marginally to 50 Pa.S. Low viscosity is an advantage during polymer processing as it lowers the energy consumption. However, in many applications, low flammability is a necessity which requires addition of a significant amount of flame retardants. High ATH concentrations will result in high processing viscosity (Haurie *et al.,* 2006). Interestingly, the present results show that it is possible to incorporate high amounts of ATH without substantially increasing the viscosity behaviour by using large particle size.

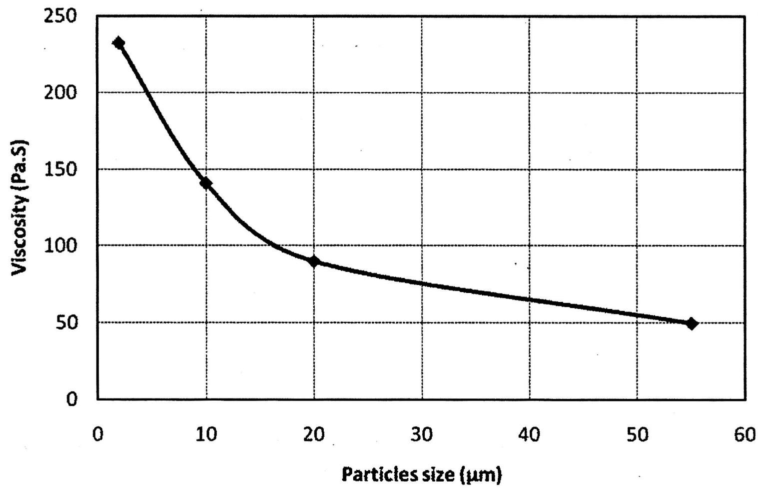

Figure 7. *Effect of particle size of ATH on viscosity behaviour*

CONCLUSION

From the thermal characterization studies of ATH, it was shown that the temperature range for ATH to effectively act as a flame retardant is from 200 to 350 °C. TGA curve showed a significant weight loss of ATH at 230 to 310 °C. The DTA study revealed that double dehydrations of ATH which caused a significant and a small endothermic peak at 230 °C to 310 °C and 470 °C to 560 °C, respectively. In water release test, it was also determined that the release of the chemically-combined water in ATH increased with increasing temperature and started to become significant at 200 °C. The flame retardancy of LDPE increased with increasing ATH content and decreasing ATH particle size. By adding 20 phr of ATH, smoke density of a burning LDPE reduced significantly as revealed by light absorption due to smoke reducing from 75 to 27 %. This clearly proved that ATH is also effective in reducing smoke density. It was also shown that the viscosity of ATH filled LDPE decreased with increasing ATH size.

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