



## Modification of montmorillonite and its effect on the thermal stability of PP/APP

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The effect of montmorillonite (Mt) and the treated montmorillonite (MtT) with sulfuric acid on the efficiency of nanoparticles of ammonium polyphosphate (APP) has been studied. Five samples containing different percentage of montmorillonite are prepared and other five samples containing treated montmorillonite also prepared. The chemical analysis (XRF), the spectroscopic measurements (XRD and IR) and the morphology (SEM) studied have been performed to identify the sulfuric acid treatment for the montmorillonite on the chemical composition and on the structure of the montmorillonite layers. The results have been revealed that the acid treatment changes the layered structure of montmorillonite and no effects on the chemical composition. The thermogravimetric analysis (TGA) is used to evaluate the ammonium polyphosphate (APP)/ montmorillonite (Mt) or APP/ montmorillonite treatment (MtT) as flame retardants for Polypropylene (PP). The results show that both treated and untreated montmorillonite when mixed with APP accelerate the first step of the thermal degradation. Also, it is indicated that the time of degradation increased by adding treated or untreated montmorillonite to APP in the following sequence PP<PP/APP<PP/(APP/Mt)<PP/(APP/MtT). Overall, the results indicated that the modification of added montmorillonite to App improves the flammability of the PP.

**Keywords:** Acid modification, Ammonium Polyphosphate, Flammability, Montmorillonite, Thermal Stability

In the previous works, the preparation, the improvement and evaluation of some inorganic materials and natural ores as flame retardant for polypropylene (PP) were studied. In this strategy, nano-sized ammonium polyphosphate (APP) was prepared by mixing certain amount of ammonium dihydrogen phosphate with urea solution and accompanied with heat treatment. Ammonia solution was used for precipitation the (APP). The chemical and spectroscopy studies were used for the characterization process<sup>1</sup>. Thermogravimetric analysis (TGA and DTA) and the cone calorimeter measurements were applied for evaluation the nano-sized APP as flame retardant for PP<sup>2</sup>. The characterization methods proved that the prepared APP is a nano-sized ranging from 5-85 nm and it is in form I. The analysis of TG, DTA and the cone calorimeter test proved that when 10% APP is added to PP delays the time of degradation by an amount equals to 51%. This finding leads to conclude that APP can be used successfully as flame retardant for PP. On the other hand an improvement was carried to increase the efficiency of APP as flame retardant for PP. This improvement includes mixing natural kaolin with APP. The analysis indicates that the mixture with 6% kaolin and 4% APP increases the time of degradation for PP

71%. It is noteworthy that the increase in the time of degradation gives a suitable chance for the workers to escape and the fire men work.

In the present work, another modification for APP was carried out by using another structure of clay material to increase the efficiency of APP as flame retardant. In general clays were incorporated into an intumescent flame retardants (IFR) system containing APP as an acid source to improve the thermal stability and flame retardancy of PP<sup>3-5</sup>. But there is a great difference, when the clays added to APP and did the structure of clays have any effects on the retardancy. Any how the addition of clays act as an added value because at high temperature the clays materials decomposed to produce SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> where these oxides use as flame retardants for PP. Also the fine structure of the clay compounds can penetrate through the particles of APP and also it can coat the APP particles. As reported in the previous literature, the beneficiation of the clay materials is highly related to its reactivity and the surface properties, which depended strongly on surface modifications<sup>4</sup>. Several methods such as mechanochemical activities<sup>6-13</sup>, intercalation<sup>14,15</sup>, thermochemical treatment and chemical activation<sup>13</sup> were

introduced to improve the surface behaviour of clays. Among these methods, acid treatment has been widely used as a chemical treatment route to improve the surface activity of clays. On the other hand, among the acid treatment,  $H_2SO_4$  is the preferable acid because the clay materials are more soluble in  $H_2SO_4$  than other acids and  $H_2SO_4$  is relatively cheap and has a simple route<sup>2,16</sup>.

## Experimental Section

### Materials and methods

#### Ammonium polyphosphate (APP)

IT was prepared in earlier work as described earlier<sup>1</sup>. It is an APP form I and having particles size ranging from 5nm to 85nm. Polypropylene (PP) (LG Chem, LTD Seetc, N 1600 Boo 1046M, Korea) was used in the preparation of tested samples.

#### Montmorillonite

The montmorillonite in this study was supplied from Wadi El Hamadiya region, Egypt. The sample was used as it is without further treatment. For untreated montmorillonite, it contains  $SiO_2=42.02$ ,  $Al_2O_3=47.07$ ,  $MgO=0.028$ ,  $CaO=0.035$ ,  $K_2O=0.013$ ,  $ZnO=0.006$ ,  $TiO_2=0.76$  and  $Fe_2O_3=0.005$ . For treated montmorillonite, it contains  $SiO_2=55.32$ ,  $Al_2O_3=28.88$ ,  $MgO=0.021$ ,  $CaO=0.013$ ,  $K_2O=0.011$ ,  $ZnO=0.006$ ,  $TiO_2=0.25$  and  $Fe_2O_3=0.004$ .

#### X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns were performed with power D8 ADVANCE diffractometer (Germany) using CuK $\alpha$  radiation (1.542 $\text{\AA}$ , 40 KV, 40mA) in the  $2\theta$  range of 4–80. The acquisition parameters were as: a step size of 0.02 and a step time of 0.4s.

#### X-Ray Fluorescence spectroscopy (XRF)

The XRF analyses of the samples were done by using a Model-PW2400 of Phillips with X-ray tube of rhodium anode and scintillation detector with a current 40 mA and voltage 40 mV.

#### Fourier transforms infrared (FTIR) spectroscopy

FTIR spectra of the samples were obtained using a KBr disk and FTIR 6500 spectrometer (JASCO, Japan) in the range of 400-4000 $cm^{-1}$

#### Thermal analysis

The thermal analysis (TGA, DTA) were performed by USA Perkin – Elmer thermogravimeter samples of approximately 10 mg was heated from 50 to 800 $^{\circ}C$  with heating rate 10/m under a nitrogen

atmosphere, and the flow of nitrogen was 50 mL/min.

#### Scanning electron microscope

The surface morphologies of the samples were carried out using a JEOL JSM t20 scanning electron microscope (SEM) (JEOL, Japan) at an accelerating voltage of 5 kV.

#### BET measurement

Nitrogen adsorption–desorption measurements (BET method) were performed at liquid nitrogen temperature ( $-196^{\circ}C$ ) with an Autosorb BET apparatus from Quanta chrome Corporation. The BET analysis procedure is automated and operates with the static volumetric technique. Before each measurement, the samples were degassed firstly at 200 $^{\circ}C$  for 2 hours, at  $5 \times 10^{-3}$  torr and then at room temperature for 2 hours, at  $0.75 \times 10^{-6}$  torr. The isotherm methods were used to determine the specific surface areas using the BET equation.

#### Chemical modification of montmorillonite

The chemical modification of montmorillonite ore was carried out by adding 50 g of the montmorillonite ore to 500 ml of sulfuric acid solution (10M) and refluxing at 110 $^{\circ}C$  under the atmospheric pressure in a round bottled flask equipped with a reflux condenser for 4 h. The resulting suspension montmorillonite was then rapidly quenched by adding 500 mL ice- cold water. The content was then filtered, cleaned with distilled water to remove any unspent acid, then dried in an oven, after that it was calcined at 500 $^{\circ}C$  for 1 h and grounded in mortar pastel to get the powder form.

#### Preparation of the samples (APP/ Montmorillonite /PP)

Table 1 contains the composition of APP/ montmorillonite (treated and untreated) with PP.

Table 1 — The chemical composition of APP/(MMT or MMTT)/ PP system

Sample	PP	APP	Montmorillonite
PP	100	0	0
APP	90	10	0
MMT 2	90	8	2
MMT 3	90	6	4
MMT 4	90	4	6
MMT 5	90	2	8
MMT 6	90	0	10
MMTT 2	90	8	2
MMTT 3	90	6	4
MMTT 4	90	4	6
MMTT 5	90	2	8
MMTT 6	90	0	10

Table 2 — Chemical analysis of montmorillonite ore and treated montmorillonite

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	ZnO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
(MMT)	42.02	47.07	0.028	0.035	0.013	0.006	0.76	0.005
(MMTT)	55.32	28.88	0.021	0.013	0.011	0.006	0.25	0.004

MMT refers to montmorillonite ore and MMTT refers to treated montmorillonite.

**Results and Discussion**

**Chemical analysis and surface area**

Montmorillonite is an hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca)<sub>0.33</sub> (Al, Mg)<sub>2</sub> (Si<sub>4</sub>O<sub>11</sub>) (OH)<sub>2</sub>.nH<sub>2</sub>O. It is a very soft phyllosilicate mineral that typically form in microscopic crystals. Its particles are plate-shaped forming a layers trapped with H<sub>2</sub>O<sup>17,18</sup>. The chemical composition of montmorillonite and the modified montmorillonite were represented in Table 2. The XRF analysis showed that the parent montmorillonite contains 42.02 %SiO<sub>2</sub> and 47.07% Al<sub>2</sub>O<sub>3</sub> with other inorganic oxides. While the montmorillonite treated with H<sub>2</sub>SO<sub>4</sub>, the chemical analysis indicate that the SiO<sub>2</sub> content increased to 55.32% causing an increase about 31%, while Al<sub>2</sub>O<sub>3</sub> content decreased to become equal 28.88%. The other inorganic oxides changes slightly by acid treatment of montmorillonite. Table 3 shows the change of surface area by acid treatment. The results of measurements show that applying of montmorillonite the surface area increased from 12 to 47 M<sup>2</sup>/g. This increase of may due to the increase of SiO<sub>2</sub> content, where SiO<sub>2</sub> having high surface area and it has a great effects on the behaviour of montmorillonite<sup>19</sup>.

**XRD measurements**

The XRD patterns of untreated and treated montmorillonite were presented in Fig. 1. For the untreated montmorillonite, the XRD profile shows series of the peaks at 2 theta equal 5, 12, 20, 25, 34, 40. The appearance of the peak at 2 theta equals 5 is characterized the montmorillonite clays as that observed by Alexander *et al.*<sup>20</sup>. These peaks have small intensity indicating to the low crystallinity of montmorillonite. The appearance of the two peaks at 12 and 25 correspond to the reflect form of (001) plane, which is specified to the clay materials. On the other hand the peak at 34 and 40 may was attributed to the ore of clay materials. For the acid treatment montmorillonite, the X-ray pattern exhibits the same peaks as that observed for untreated montmorillonite but more sharpens and high intensity. In the two case

Table 3 — BET measurements montmorillonite ore and treated montmorillonite

Sample	Surface area(m <sup>2</sup> /g)
Montmorillonite ore (MMT)	12
Treated montmorillonite ( MMTT)	47

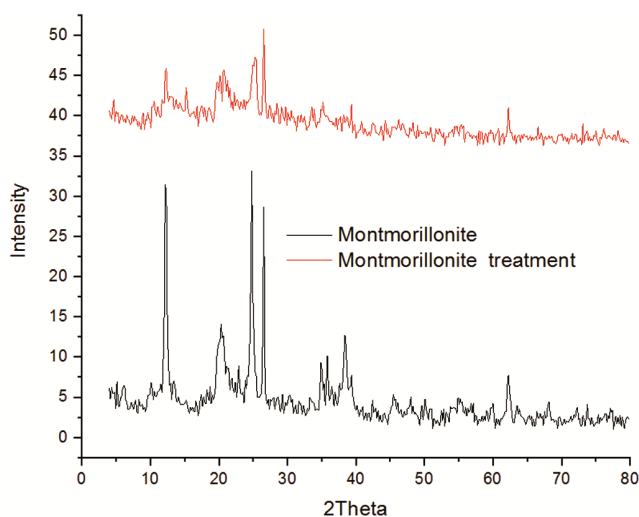


Fig. 1 — XRD of the untreated and treated montmorillonite.

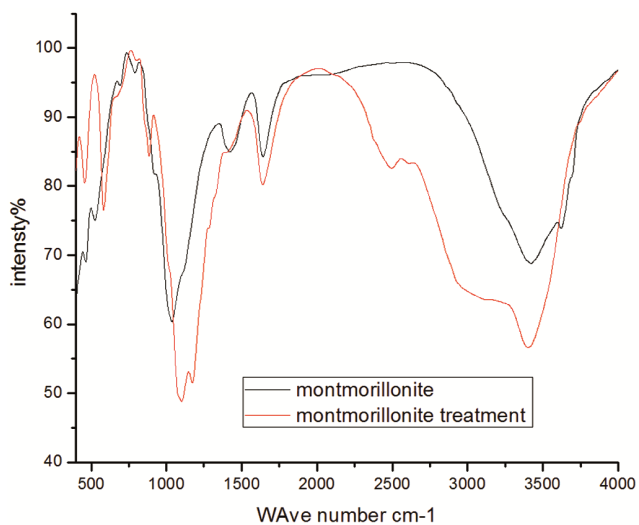


Fig. 2 — IR of the untreated and treated montmorillonite.

of the treated and untreated montmorillonite, the X-ray profiles indicates that the structure is poor crystalline and have slight effect of the structure and crystalline by acid treatment<sup>2</sup>.

**IR measurements**

Figure 2 represents the IR absorption of both the untreated and treated montmorillonite. From the IR

analysis, it is observed that the main groups of absorption are appeared in both cases with some changes in the position and the intensity as follows<sup>6,21</sup>:

- 1) The strong peak which appeared at  $3500\text{ cm}^{-1}$  which specified the Al-OH bond becomes more clearness with acid treatment while the sample shoulder at  $3650\text{ cm}^{-1}$  was specified to the physico-water between the layers also due to the acid treatment.
- 2) Appearance of small peak by acid treatment of montmorillonite at  $3250\text{ cm}^{-1}$ .
- 3) The band which specified the binding and appeared at  $1630$  is not affected by acid treatment, where the peak that appeared  $1200\text{ cm}^{-1}$  in the parent montmorillonite converted to small shoulder by acid treatment.
- 4) The series of bands which appeared at  $912, 820, 600$  and  $540$  which specified the Al-Al-OH, Si-O Si-O-Al and Si-O-Al become more sharpness with acid treatment. This results indicate that the acid treatment of montmorillonite don't affects on the chemical composition but change the structure and the layers of the built. Also the results indicate that the acid treatment causes a change in the surface area of the layers which by turn increases the activity of montmorillonite. In general, the IR profiles of the treated and untreated Mt are finger reprints obtained by other investigation.

#### TGA and DTA

Figure 3a represents the TGA of the untreated and treated montmorillonite. The TGA curve of the parent montmorillonite can be classified into three categories of degradation. The first one starts from the room temperature till to  $100^\circ\text{C}$ , the second step start from  $100$  to  $500^\circ\text{C}$  and the third one up to  $800^\circ\text{C}$ . The first two steps may attribute to the evaporation of the physisorbed water and the dehydroxylation of the coordinated water between the montmorillonite layers. The last step may be related to the condensation and dehydration of the hydroxyl groups of the montmorillonite structure. These behaviours are nearly identical for the clay materials, where they contain three types of water. The physisorbed of the interlayer water on the surface and they are loosely bounded and it (evaporate) at low temperature less than  $100^\circ\text{C}$ . The second type of water is present in the coordination structure of the inter layer ions and it is strongly

bonded and evaporated at high temperature range  $500^\circ\text{C}$ . The third one occurred at high temperature between  $500$  to  $800^\circ\text{C}$  are attributed to the condensation and dehydration of the hydroxy groups which present in the main structure of the clay materials. For the treated montmorillonite with  $\text{H}_2\text{SO}_4$  acid, it is possible to distinguish four steps of the TGA curves. The behaviours of these steps are clearer than that observed for the untreated montmorillonite. The first step ended at  $60^\circ\text{C}$ , the second step take place at  $200^\circ\text{C}$ , the third step ended at  $550^\circ\text{C}$  and the last step which represent the condensation and dehydrogenation of OH groups joining the layers of montmorillonite starts at  $700^\circ\text{C}$  and continue to  $800^\circ\text{C}$ . These observations are in agreement with the results obtained by Yei *et al.*<sup>21</sup>, and Chen *et al.*<sup>22</sup>. For DTA curves, Figure 3b, the

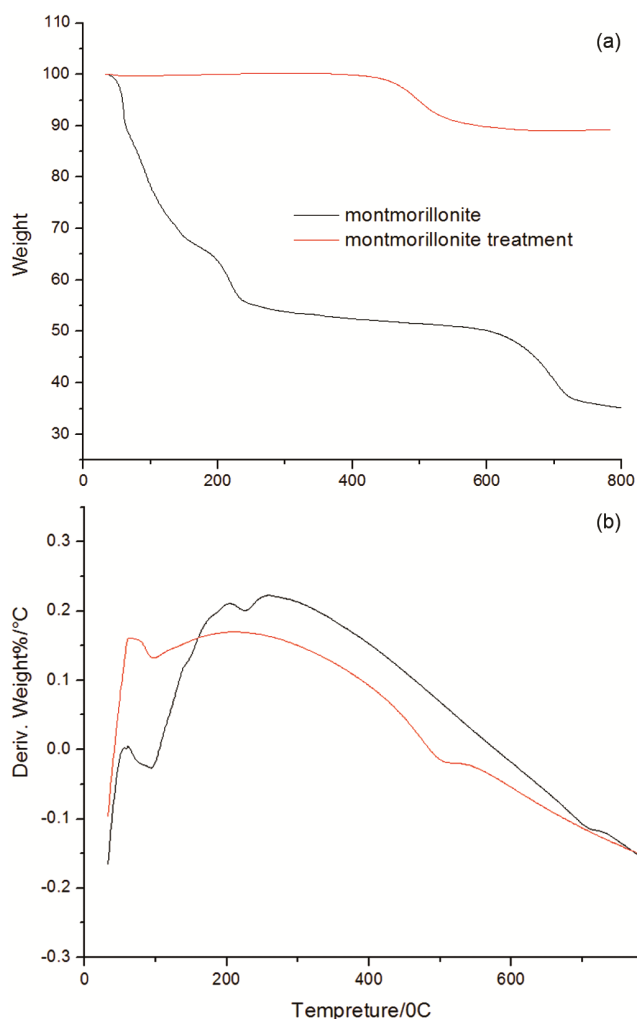


Fig. 3 — (a) TGA and (b) DTA of the untreated and treated montmorillonite.



appearance of the steps of degradation was clarified. It was observed that the DTA of the untreated montmorillonite shows endothermic peaks at 50 and two at 500°C, while for treated samples four endothermic peaks were appeared. These peaks focused at 50, 120, 200 and 600°C. The obtained results for the DTA of treated and untreated montmorillonite confirmed the results of the DTA.

**SEM measurements**

The SEM measurement of treated and untreated montmorillonite is shown in Fig. 4a. For the untreated montmorillonite, the photographs reveals that montmorillonite consist of layer particles appeared as flaky particles stacked together in the form of agglomerates. With acid treatment, it is observed that there were rearrangements to the particles forming layered structure Fig. 4b.

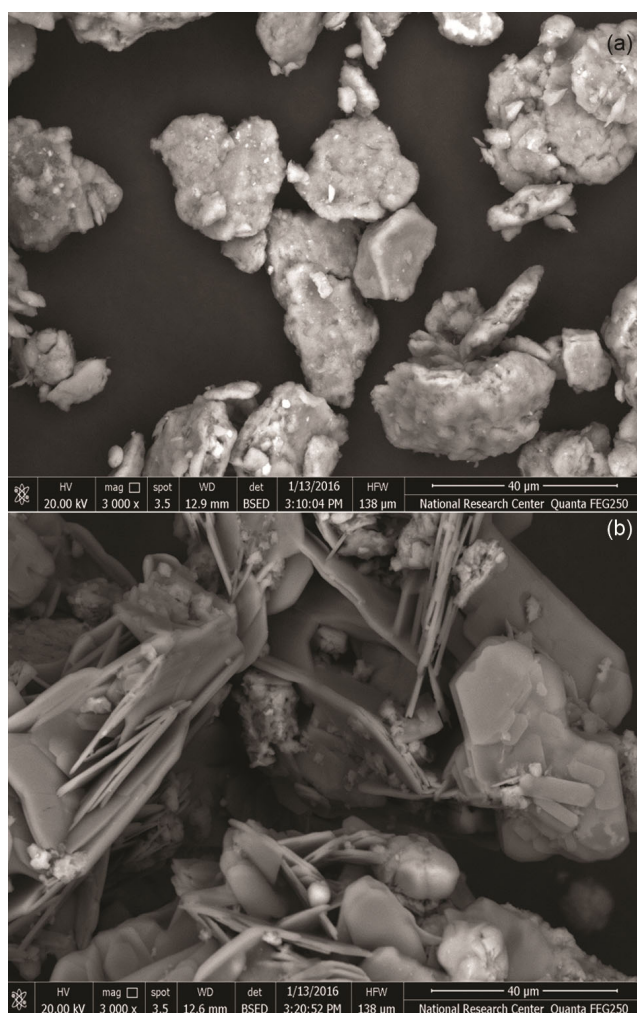


Fig. 4(a-b) — (a) SEM of the untreated montmorillonite and (b) SEM of the treated montmorillonite

**Evaluation of APP/ Montmorillonite as flame retardant for PP**

There are different methods for evaluation the materials as flame retardants such as Limiting oxygen index (LOI) and Cone Calorimeter test. Among these methods, the thermo- gravimetric analysis represents an acceptable method for evaluation because it gives complete information about the thermal behaviour from the room temperature till to the high temperature and it gives information about the thermal stability of the materials. Also, it gives information about the different steps of the thermal degradation. In the present work, both the thermo gravimetric analysis (TGA) and the DTA are used for evaluation the APP/ montmorillonite as flame retardant to PP. Figure 5 represents the TGA behaviours of both start materials (PP) and APP. From the profile of TGA of APP, it is clear that APP starts to decomposed at 350°C and ending at 450°C. According to the literature survey APP decomposed to give nitrogen and poly phosphoric acid. On the other hand the TGA profile of PP shows that it decomposed between 300 to 450°C gives a residual ash. The TGA profile of the treated and untreated montmorillonite shows that they decomposed at 200°C up to 600°C. Our target in this work to increase the efficiency of APP as flame retardant for PP in presence of montmorillonite through following the TG curves. Figure 6 represent the TGA behaviours of five samples containing (APP/ montmorillonite) and PP with different percentage of APP and montmorillonite as shown in Table 1, while Figure 6 represent the TG curves of other five samples containing (APP/treated

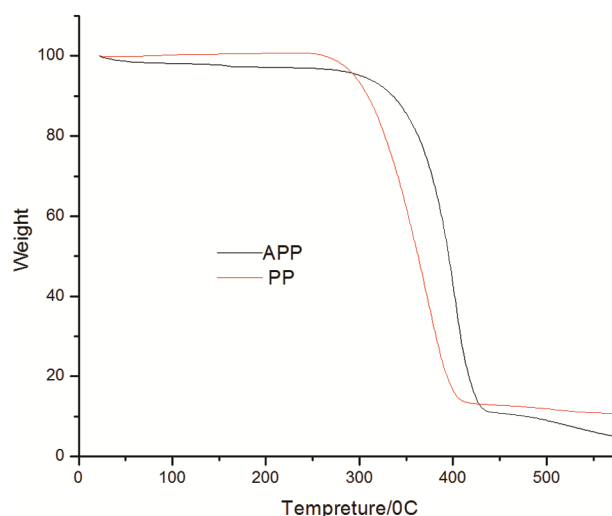


Fig. 5 — TGA of PP and APP

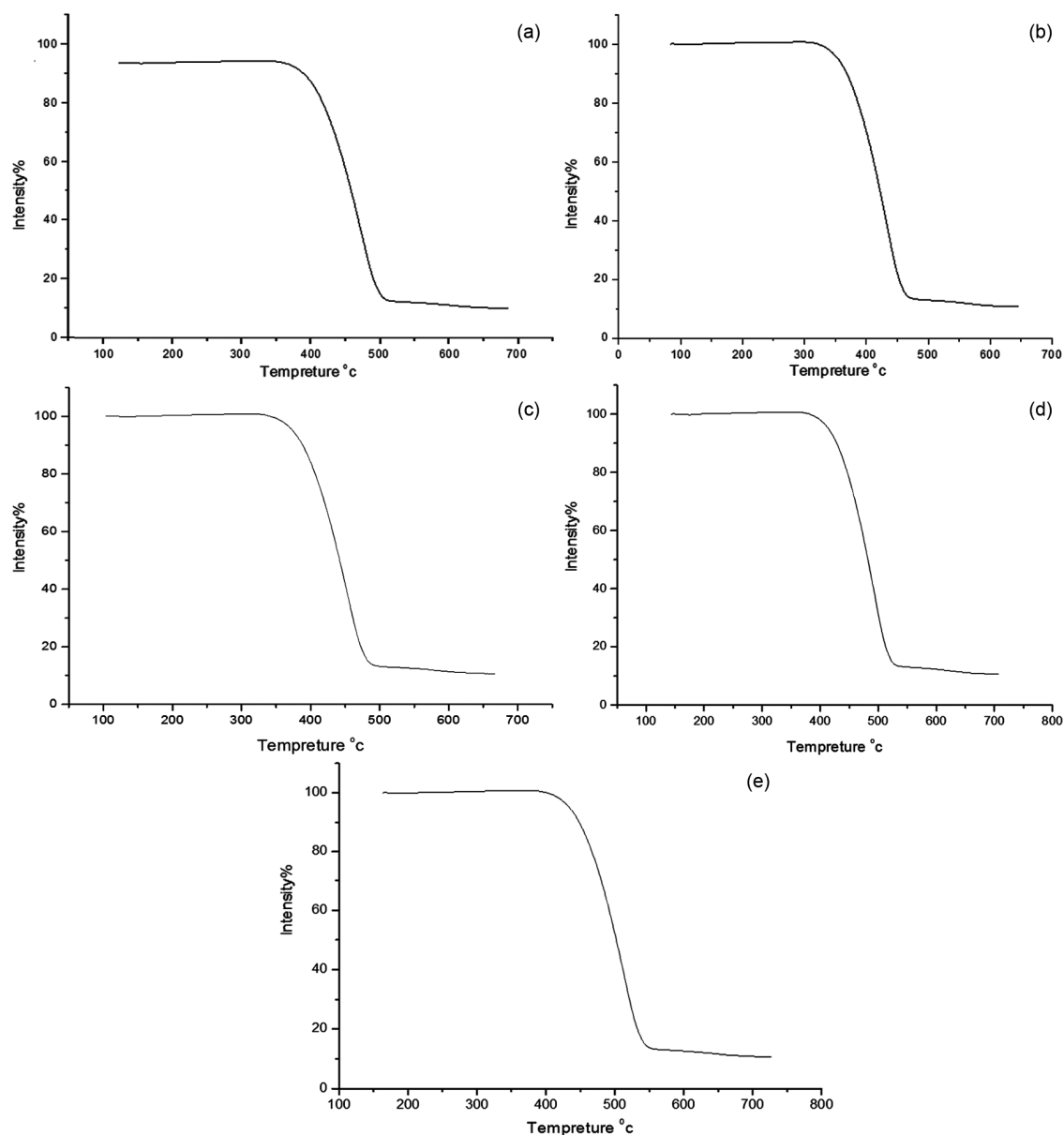


Fig. 6 — TGA of untreated montmorillonite

montmorillonite) with PP. In all samples the percentage of PP remains constant equals to 90%. By taking the initial temperature of thermal decomposition of the samples ( $T_{\text{onset}}$ ) as the start point of the flammability and taking the end of the thermal decomposition ( $T_{\text{outset}}$ ) as the end of the flammability of PP, Table 4 summarized the  $T_{\text{onset}}$ ,  $T_{\text{outset}}$  and time of degradation which calculated from the temperature range of the thermal decomposition between  $T_{\text{onset}}$  and  $T_{\text{outset}}$ . The analysis of the results as shown from Figs 5 and 6 and Table 4 show that for sample MtT2 which contain 8% APP, 2% montmorillonite and 90%PP the initial temperature

Table 4 —  $T_{\text{onset}}$  and  $T_{\text{outset}}$  and Time of degradation of treated and untreated montmorillonite.

Samples	$T_{\text{outset}}/^{\circ}\text{C}$	$T_{\text{onset}}/^{\circ}\text{C}$	Time of degradation/min
PP	375	330	4.5
APP	471	416	5.5
MMT2	472	400	7.2
MMT3	485	375	11
MMT4	490	365	12.5
MMT5	475	390	8.5
MMT6	475	425	5
MMTT2	485	400	8.5
MMTT3	490	355	13.5
MMTT4	520	370	15
MMTT5	495	400	9.5
MMTT6	485	435	5

reduced from 416 to 400°C, while the end of decomposition increased slightly in comparison with the sample contains APP only. This means that the presence of MtT accelerated the first step of degradation to produce nitrogen and polyphosphoric acid early. The time of degradation increased from 2 to 5.5 to 8 min for the samples contain PP, PP/APP and PP/ montmorillonite /APP. This behaviour continues till the sample MtT4, while the time of degradation recorded 14 min. This observation means that the time of degradation increased till the sample contains 4%APP/6% montmorillonite /90%PP. By increasing

the percentage of montmorillonite the time of degradation decreased from 14 to 9 min, this meaning that the more effective to elongate the time of ignition that sample contains 4%APP/6% montmorillonite. For the samples containing APP and treated montmorillonite and containing the same composition that proceed for untreated montmorillonite, as shown Table 4, the results show that both the  $T_{onset}$  and  $T_{outset}$  behave the same trend as that observed for untreated, while there is a considerable changes for the time of degradation. By following the results recorded in Fig. 7 and tabulated in Table 4, it was observed that

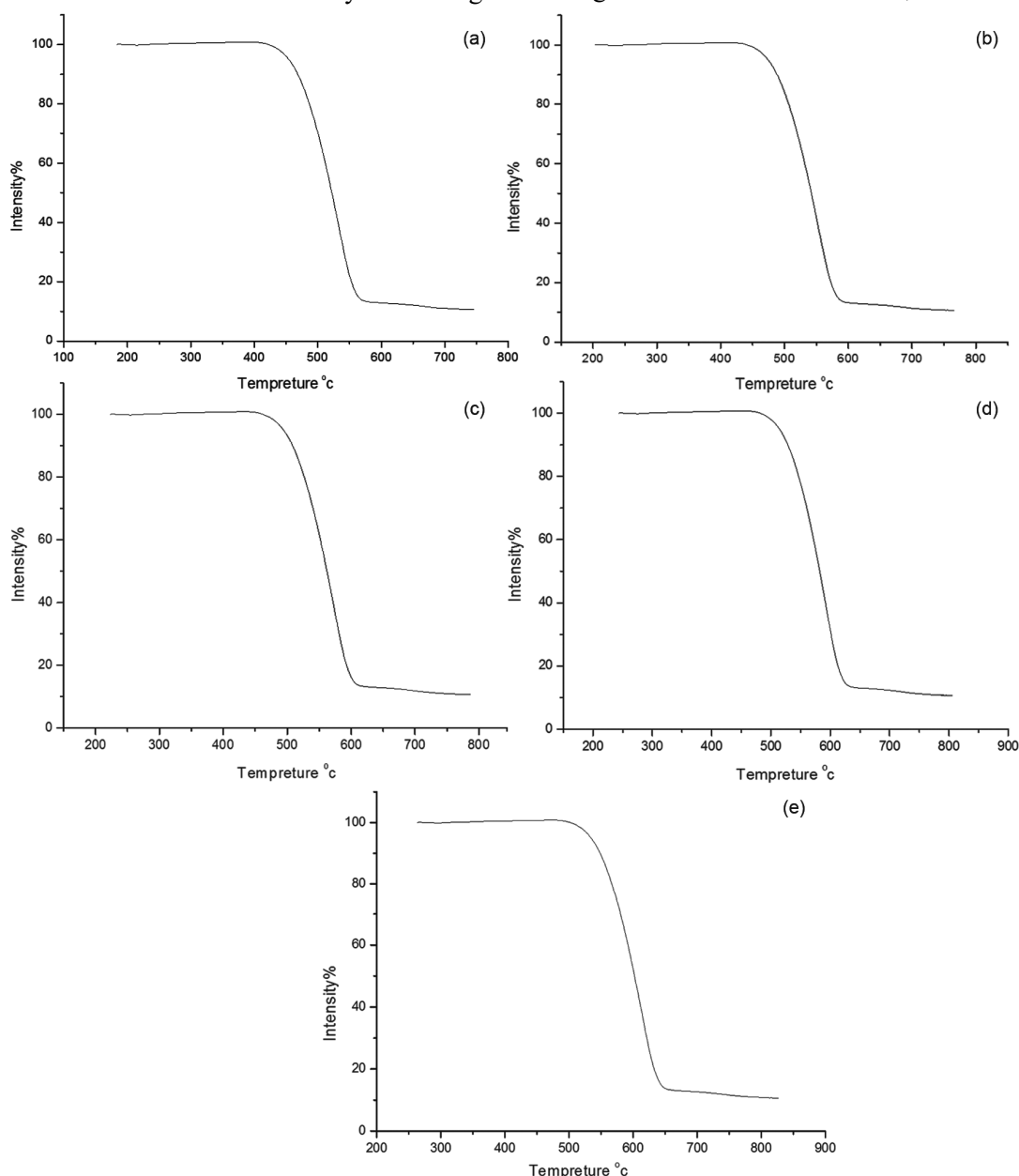


Fig. 7 — TGA of treated montmorillonite.

the time of decomposition for sample which containing 4% APP/6% montmorillonite increased to become 15 minutes showing an increase when compared by the samples containing APP only or APP/ montmorillonite. This means that the modification of montmorillonite increases the efficiency of APP when it used as flame retardant for PP. This increase follow the following sequence PP<PP/APP<PP/Mt<PP/MtT. To interpretate the effects of APP or APP/ montmorillonite as flame retardant for polymer, it should retain to the mechanism of the flammability. In this respect there are three mechanism for interpretation, the barrier mechanism, radical trapping causing by presence some oxides in the clay materials such as Fe<sub>2</sub>O and the catalytic effect on the clay formation. These three mechanisms depend on the nature of polymer, the percentage of the clays and their structure and particle size of clays. In the light of these mechanism and our results, it may suggest that by lowering the T<sub>onset</sub> and raising the T<sub>outset</sub>, the time of degradation increase due to the thermal decomposition of APP at lower temperatures and producing nitrogen which inhibit the spread of fire and poly phosphoric acid which forming an isolated layer between the flame and the bulk of polymer. The increase of the time of degradation in presence of untreated montmorillonite and treated montmorillonite may be explain that there are a mutual effect between the APP and montmorillonite where the nano-particle of APP penetrated through the layers of montmorillonite and the montmorillonite particles coated the APP montmorillonite. This mutual effect causes an elongation of the time of degradation leads to give a chance for controlling on the spread of flame.

### Conclusion

From the analysis of the obtained results, it may conclude that the acid treatment for montmorillonite increases the SiO<sub>2</sub> content which is high surface area and decrease the Al<sub>2</sub>O<sub>3</sub> content with rearrangement of the layers. When the treated or untreated montmorillonite mixed with APP for using as flame retardant for PP, the results indicate that the treated montmorillonite is more effective than that for ore montmorillonite. Also, it is revealed that the presence of treated montmorillonite accelerated the first step

of the thermal decomposition which represents the APP and evolved nitrogen and poly phosphoric components. It is concluded that the presence of treated montmorillonite or untreated montmorillonite changed the thermal time of degradation, which gives a chance for controlling on the spread of flame.

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