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Studies on The Effects of Kaolin and Modified Kaolin on the Flammability of APP/PP System

A. A. Hanna[1], Eglal, R. Souaya[2], Marwa, A. Sherief[*1], A.S. Abdelmoaty[1]
[1]Inorganic Chemistry Department, National Research Centre, Dokki, P.O. Box: 12622, Postal code: 11787,and [2]Chemistry Department, Ain Shams University, Cairo, Egypt.

THIS WORK is a continuation of the previous works by the authors to increase the efficiency of ammonium polyphosphate (APP) as flame retardant for polypropylene(PP). In this work a more abundant kaolin was used. Also to improve the efficiency of kaolin, an acid modification by sulfuric acid was used. XRD, XRF, IR, SEM and BET were used to characterization the samples. TGA and DTA were used to evaluate the prepared samples as flame retardant. For comparison, five samples of (APP/ Kaolin ore)/PP were prepared and other five samples (APP/Modified kaolin)/PP have the same composition also were prepared. The analysis of the XRD, IR and SEM results indicate that the acid treatment of kaolin increases the SiO_2 content which lead to increase the surface area. In the same time the acid leaching causes some distortion in the crystalline and the layers. The evaluation of the flammability of the system by using the TGA indicate that the presence of kaolin increases the time of degradation of PP. On other hand, the modification of kaolin by sulfuric acid improves the role of the kaolin when added to the APP.

Keywords: Ammonium polyphosphate, Kaolin, Flame retardant, Thermal analysis, Characterization, Modification.

During the last few years, the demand of the polypropylene (PP) has been increased as a special technical material. It exhibits excellent properties through the applications such as it is low cost, inert, low density, hydrophobic, resist the chemical reactions and resist the biological degradation by some organisms. On other hand it has acceptable mechanical properties such as good tensile strength and the other dynamics properties. Also, , it is used in wide range of fibrous and nonwoven applications [1] . The main drawback of polypropylene in some industries its flammability which put some restriction for uses in some industries such as electrical devices [2], So that different trails were done to overcome on this point. These trails included the addition of some organic or inorganic materials through the fabrication of the polymers. Among the inorganic materials a special attention was drawn towards the ammonium polyphosphate (APP), because it degrades thermally to produce nitrogen and

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*Corresponding author: Tel: +20.10.5249230; fax: +20.2.33335968.
E-mail: gohamora@yahoo.com, or marwa-nrc@hotmail.co.uk

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poly phosphoric acid. The nitrogen gas acts as inert medium which inhibit the spread of fire and the poly phosphoric acid forms an isolated layer between the flame and the bulk of the polymers.

In the previous works, the authors synthesized and characterized nano-particles of APP[3]. The characterization by using X-ray diffraction, IR absorption and scanning electron microscope proved that the prepared particles have a structure belong to form I. Also, the authors evaluated the prepared form as a flame retardant for polypropylene. They used both the thermo- gravimetric analysis (TGA, DTA) and the cone calorimeter to study the effects of APP when added to the PP. The analysis of the obtained data proved that APP can be used successfully as flame retardant for PP when mixed with about 10% APP [4].

In this field, different trails were done to raise the efficiency of APP to inhibit the spread of the flame through the materials. In general two ways were followed in this respect, the first one is physically treatment and the second chemically by addition some other materials. These materials may be organic or inorganic such as metal oxides, metal salts and natural ores such as zeolite, sepiolite and clays.

The aim of the present work is a continuation of our earlier works to improve the role of APP as flame retardant by using the natural kaolin as it is or after modification.

Experimental

Materials

Ammonium polyphosphate (APP)

It is prepared in earlier work as described before [3]. It is an APP form I and having particles size ranging from 5nm to 85nm.

Polypropylene (PP)

Polypropylene (PP) (LG chem, LTD seetc, N 1600 Boo 1046M, Korea) was used in the preparation of tested samples.

Kaolin

The kaolin in this study was supplied from Wadi El Hamadiya region, Egypt. The sample was used as it is without further treatment.

Instruments

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns were performed with power D8 ADVANCE diffractometer (Germany) using CuKa radiation (1.542°A, 40 KV, 40mA) in the 2ϴ 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 (Germany).

Fourier transform infrared (FTIR) spectroscopy

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

The thermal analysis

The thermal analysis (TGA, DTA) were performed by USA Berkin – Elmer thermogravimeter. Samples of approximately 10 mg was heated from 50^oC to 800^oC with heating rates 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 °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 out gassed first at 200 °C for 2 hr, at 5×10^{-3} torr and then at room temperature for 2 hr, at 0.75×10^{-6} torr. The isotherm methods were used to determine the specific surface areas using the BET equation.

Chemical modification of kaolin[5]

The chemical modification of kaolin ore was carried out by adding 50 g of the kaolin ore to 500 ml of sulphoric acid solution (10M) and refluxing at 110◦C under the atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 hr. The resulting suspension kaolin was then rapidly quenched by adding 500ml ice- cold water. The content was then filtered, repeated washed with distilled water to remove any unspent acid, dried in an oven, calcined at 500°C for 1 hr and grounded in mortar pastel to powder form.

Preparation of the samples (APP/Kaolin/PP)

The addition of APP with kaolin to PP was proceed as described in the previous work [3]. Different samples of APP/kaolin were prepared as illustrated in Table 1 owing to the recommended process, where K refer to Kaolin and Km refer to the modified kaolin.

TABLE 1. The composition of APP/Kaolin(treated and untreated) with PP.

No of sample	PP	APP	Kaolin
PP	100	0	0
APP	90	10	0
K2	90	8	2
K3	90	6	4
K4	90	4	6
K5	90	2	8
K6	90	0	10
Km2	90	8	2
Km3	90	6	4
Km4	90	4	6
Km5	90	2	8
Km6	90	0	10

Results and Discussion

The chemical analysis of kaolin

The chemical analysis of the kaolin samples were performed by using XRF technique. Table 2 represents the chemical analysis of treated and untreated kaolin. The chemical analysis of the kaolin indicated that it contain 42.02 SiO_2, 47.07 Al_2O_3, 0.013 K_2O, 0.028 MgO, 0.035 CaO, 0.006 ZnO, .76 TiO_2 and 0.005 F_2O_3. The leaching by H_2SO_4 leads to increase the SiO2 content to become equal 55.32 and decrease the Al_2O_3 to become equal 28.88and the other compounds also decreased. It is found that the acid treatment increases the surface area from 16 to 18 m^2/g as shown from BET measurements (Table 3). This may due to the increase of the silica content.

TABLE 2. Chemical analysis of kaolin and kaolin treatment.

Sample	SiO_2	Al_2O_3	MgO	CaO	K_2O	ZnO	TiO_2	Fe_2O_3
Kaolin	42.02	47.07	0.028	0.035	0.013	0.006	0.76	0.005
Kaolin treatment	55.32	28.88	0.021	0.013	0.011	0.006	0.25	0.004

TABLE 3. BET measurement of kaolin and kaolin treatment.

Sample	Surface area(m^2/g)
Kaolin	16
Kaolin treatment	18

Modification of Kaolin

The literatures survey on the modification of the clay materials are related to the reactivity and the surface area, which by turn depend on the structure and the surface modification. To improve these properties, several trails were done including mechano-chemical activation [5] intercalate with some organic materials and thermo-chemical routs or chemical activation. Acid activation is the more familiar methods for modification of the kaolin materials which involves the leaching of the kaolin ore with the minerals acids [6-13]. Most of the acid treatment has indicated that the kaolin is more soluble in H_2SO_4 than the other acids. For this reason in the present work, the sulphuric acid treatment was used. Figure 1 represent the XRD of both the kaolin ore and that treated with H_2SO_4.

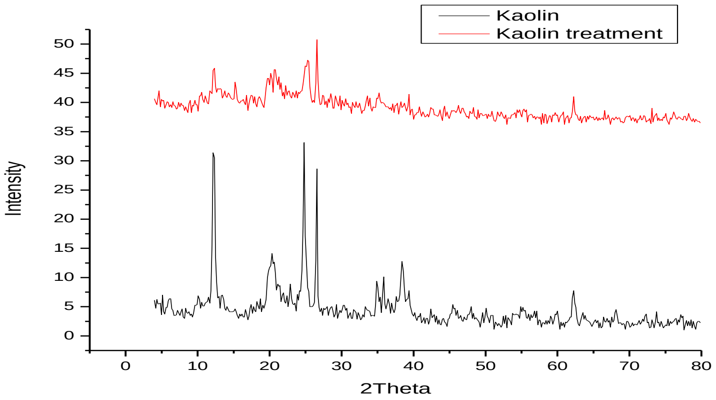


Fig.1. XRD of kaolin and treated kaolin.

For the kaolin ore the XRD chart exhibits two sharp peaks at 2 theta = 12 and 25. These peaks corresponding the reflection of (001) which specified the presence of kaolin [14]. While the appearance of other peaks at 2 theta =26, 28, 36 and 38 may due to the depending of the structure of kaolin on the origin and the geological regions of it formation as reported by B.N. Dudkin [15].

For the sample treated with H_2SO_4, the XRD profile shows that the sharpness of the two main peaks tend to decrease. Also the intensity of the other peaks decreased. This behavior indicates that the acid treatment of kaolin leads to strongly change in the crystalline and the structure of the layers.

Figure 2 represents the IR spectrum of the treated and untreated kaolin. The IR of the kaolin ore shows different absorption peaks at 3443, 3650, 1634, 912, 1100, 795, 750, 800, 550 and 480 cm^{-1}. The two first peaks corresponding the Al-OH bond which link between the tetrahedral and the octahedral sheets, and the physo-sorbed water respectively [16]. The appearance of the absorption peaks at 1634, 912, 795 and 750 specified clay materials, the peak at 1634 cm^{-1} may due to the bending vibration mode of the absorbed water on the surface of the silica and the peaks at 912, 795 and 750 cm^{-1} can be assigned to the Al-Al OH, Al-Mg-OH and Si-O-Al vibration of the clays structure [17]. By acid treatment of the kaolin there are indication for the appearance of the previous peaks which characterized the untreated kaolin, but these peaks become flatted and strongly decreased in their intensities. These observations may lead to concluded that there are a distortion in the crystalinity and the layers by acid treatment due to the leaching as observed for XRD measurements.

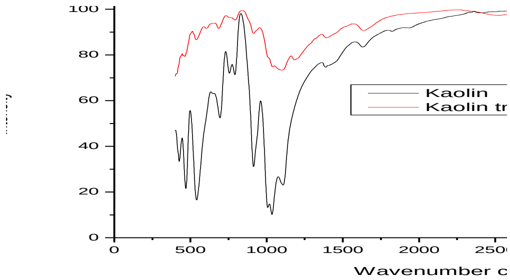


Fig.2. FTIR of kaolin and treated kaolin.

Figure 3 represents the TGA profiles of treated and untreated kaolin. For the untreated kaolin, The TG curve shows that the sample goes to thermally degraded in three steps at 120, 460 and 720°C in sequence. The first step may due to the physo-sorbed water on the surface of the kaolin layer, while the second step may due to the dehydroxy of the coordinate and structure water between the layers of the kaolin. The third step on the TGA profile of the untreated sample at 720°C may due to the condensation of the structural hydroxyl groups in the built of layer. For the sample treated with acid, the boundaries of the three steps become well defined and shifted to higher temperature for the distortion and the water content on the surface or between the layers. This finding may due to the fact that the leaching with acid increases the silica content as indicated by the chemical analysis, (Table 2), which have surface area and have high absorption water. In Fig. 4 the DTA curves supported the results of TGA where three endothermic peaks at 90, 120 and 530^{0}C were appeared for the untreated kaolin. The appearance of the three peaks corresponding to the liberation of the physo-sorbed, the coordinated water and the distortion in the structure of kaolin. For the treated kaolin the presence of the three endothermic peaks become flatted and less intensity, this may due to the change in the structure of the kaolin which leads to increase the physic water and decreased the coordinate water as obtained from the TG measurements.

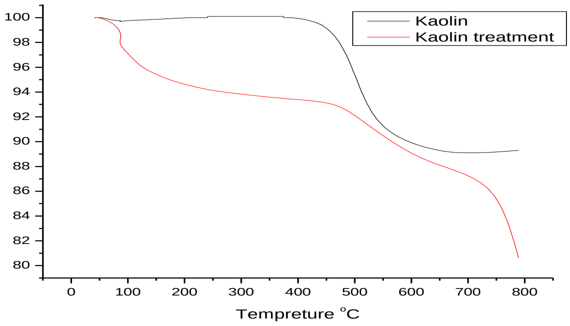


Fig.3. TGA of kaolin and treated kaolin.

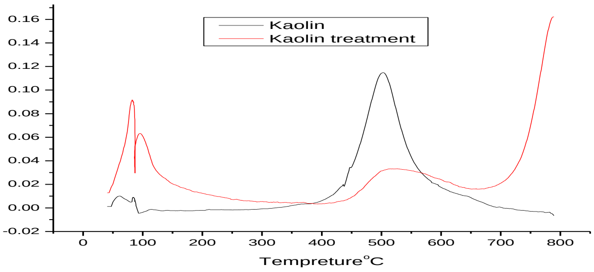


Fig. 4. DTA of kaolin and treated kaolin.

The photos of the SEM of the treated and untreated kaolin are represented in Fig.5a and 5b respectively. For the untreated kaolin, the photo shows that the morphology of the structure formed from large particle size. By acid treatment these particles converted to small particles size with some aggumulated, this leads to concluded that the acid treatment of kaolin causes the distortion of the layers and crystals. These findings are in agreement with XRD and IR measurements.

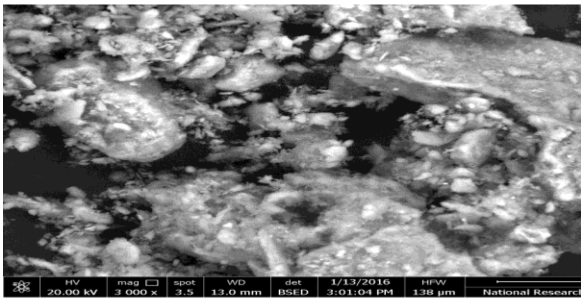


Fig. 5a . SEM of kaolin.

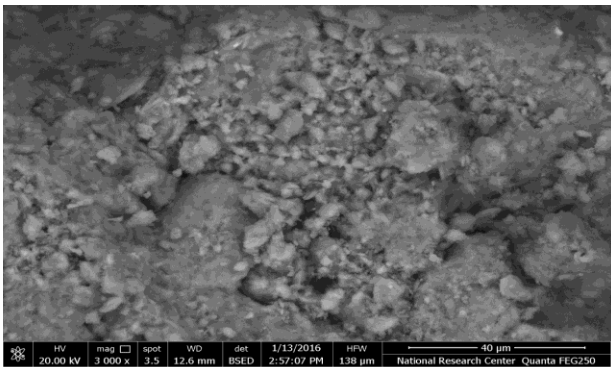


Fig. 5b. SEM of treated kaolin.

Evaluation of APP/kaolin as flame retardant for PP

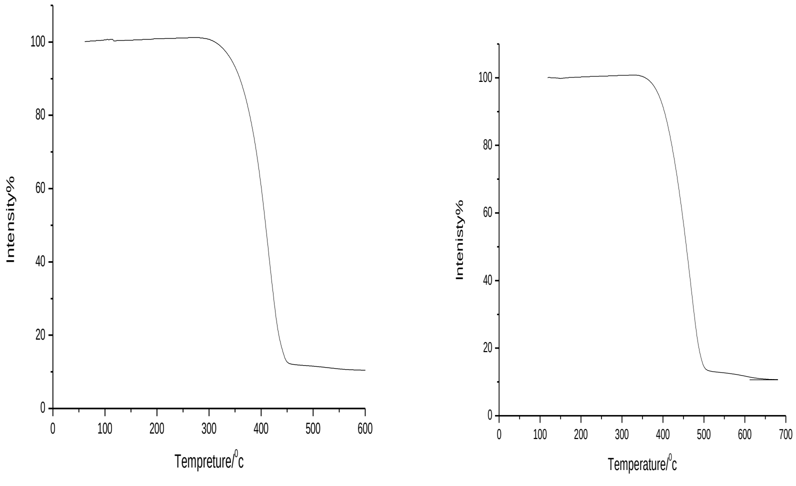
The thermo-gravimetric analysis was used to evaluate the (APP/kaolin) mixtures as flame retardant for PP. In the earlier work [4], the authors found that the mixing of APP with different percentage (1, 3, 5, 10) leads to decrease in the T_{onset} and increase in the T_{outset} and the calculated time of the complete degradation of the polymer increases. This increase in the time of degradation release two targets, the first one gives the chance to the workers to escape and the second gives the chance to the firemen works. Also, they conclude that the addition of APP improves the flammability without remarkable effect on the mechanical properties of the polymer [4]. As continuation of this work, the author used natural kaolin with APP as flame retardant of PP (Table 4).

TABLE 4. of T_{onset} , T_{outset} and time of degradation of kaolin and kaolin treatment.

Sample	T_{onset}	T_{outset}	Time of degradation/min
APP	471	416	5.5
K2	472	400	7.2
K3	485	375	11
K4	495	385	11
K5	475	405	7
K6	450	425	2.5
Km2	475	400	7.5
Km3	490	370	12
Km4	510	380	13
Km5	480	400	8
Km6	465	435	3

T_{onset}= the start degradation temperature.
T_{outset}= the end degradation temperature.

Figures 6&7 show the TGA profile of the prepared samples with that for PP pure as a reference sample. The TG profiles show that there are three steps of degradation for all samples but there are some changes in the initial of degradation. The TGA of pure PP showed that the pure polymer starts to degraded at temperature equals 440^{o}C and ending at temperature equals 460 ^{0}C with time of degradation equals to 2 min. By adding 10% APP to PP only it observed that there is some change where the T_{onset} decreased to become equals 416 ^{o}C and ending at T_{outset} equals 471 ^{0}C (5) and time of degradation equals 5.5 minutes as shown in Table 4.

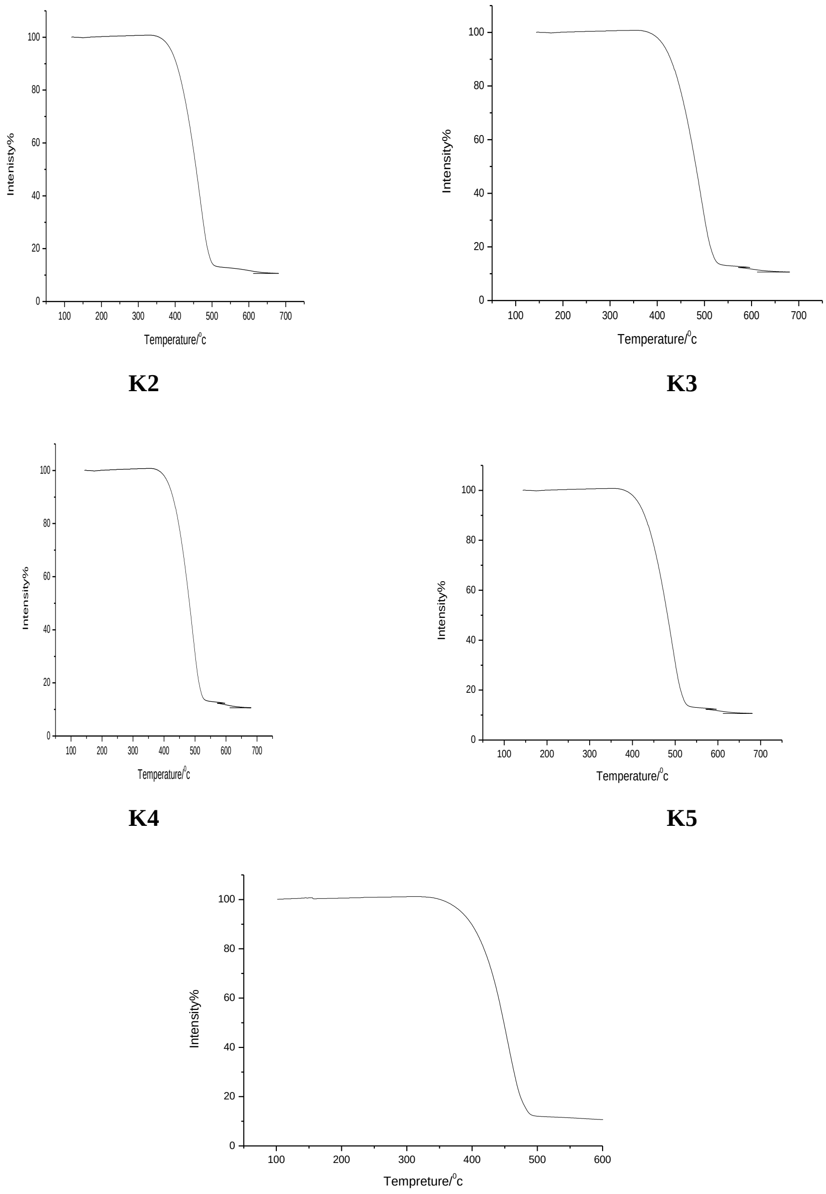


PP **PP/APP**

Fig.6. TGA of PP and APP(10%).

For sample K2 which contain (8% APP/2% kaolin), the TG curve shows that there is an observation change in both T_{onset} and T_{outset} to become equals 400 and 472 ^{o}C respectively. These behaviors extend to the samples K3 which contain 6% APP and 4% kaolin. As the percentage of kaolin increases to become 8% for sample K5, the values of the T_{onset} and T_{outset} change, where the T_{onset} decreased to record 4750C and T_{outset} become equal 405 with time of degradation equals 7 minutes as shown in Table 4. It may conclude that :

i) By adding only 10% APP to PP, the time of degradation equals 5.5 min.
ii) By adding 8%APPand 2%kaolin for sample K2 the time of degradation increases to become 7.2 min with increasing in the time of degradation equals 1.7 min.
iii) By increasing the percentage of kaolin to become 4%, the time of degradation increases to equals 11 min.
iv) As the percentage of kaolin increases to become equals 8%, the time of degradation reduced to become 7 min.



K2

K3

K4

K5

K6

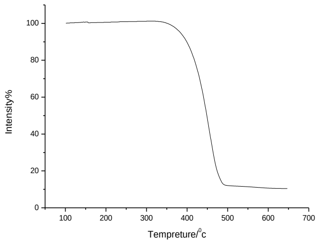
Fig. 7. TGA of PP/APP/ kaolin ore.

Hence the main effective sample when used as flame retardant for PP is that contain 4% App and 6% kaolin. This observations may lead to conclude that the presence of kaolin with 6% and 4% APP accelerating the thermal decomposition of PP where APP decomposed to form ammonia and water. On other hand kaolin delay the ending of degradation. From this finding, it is clear that the presence of the mixture of APP/kaolin increases the time of degradation.

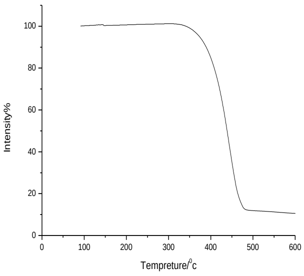
To increase the efficiency of this system, the chemical modification was made to improve the properties of the natural kaolin [18,19]. In this respect the preferable methods is the acid treatment. Kaolin is the typical structure of the family of the layered silicates similar to the other clays. It built in tetrahedral sheet, where SiO_4 is bonded with $AlO_2(OH)_4$ by forming a hydrogen bonds, sharing the oxygen atoms in the formula Al-O-H…..O…..Si [6]. It is a fine particles converted to a plasticity state when mixed with water and converted to a hard dried material when exposed to fire. It has a high surface area lead to give it a high adorability. For it elasticity it could penetrate through the APP particle and also could coated the particles. These behaviors enhance the working of the APP as flame retardant for PP. To benefit the use of kaolin particle in this work an acid treatment was carried to purification and increase the surface area. Different studies have been reported on the acid treatment for the clay materials and have been used to increase the surface area and number of acidic centers, modify the surface functional group and to obtain solids with high porosity.

Among the acid treatment of kaolin, H_2SO_4 and HCl are the most wide used in acid activation due to their effects in removing the impurities and having a considerable effects on the structure of kaolin [7].

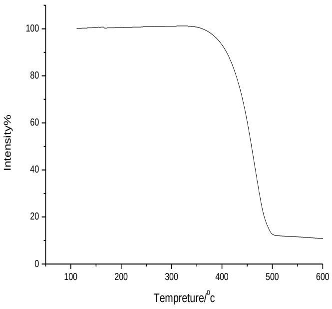
In this work, Fig. 8 represents the TG curves of (the modified kaolin/APP)/PP. Different samples have the same composition as that followed for the unmodified kaolin were followed for comparisons. From the obtained data for the T_{onset} and T_{outset}, it is observed that the modification of kaolin increases the time of degradation from 5.5 to 7.5 minutes for the sample Km2 and this increase continue in the same manner as that observed for untreated kaolin. By comparison between the kaolin ore and modified kaolin, it is observed that while the time of degradation equals to 11 min. for untreated sample K4 and it is equals to 12 min. for the modified sample Km4. It is may conclude from the analysis of data that modification of kaolin is more effective due to removal of the impurities such as Fe and Mg by leaching with acid, increasing the surface area and decreasing the particle size which enhance the penetrating of kaolin particles in the APP units.



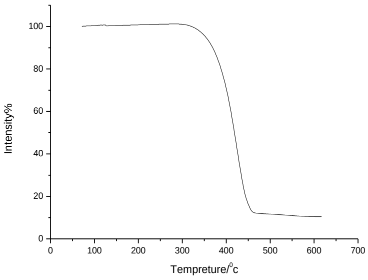
Km2



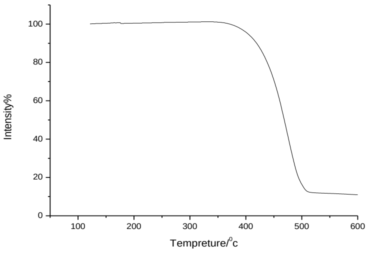
Km3



Km4



Km5



Km6

Fig. 8. TGA of PP/APP/ treated kaolin.

Conclusion

From the analysis of the obtained data it may concluded that :-

1. For using APP / Kaolin, the sample contains 6%kaolin/4% APP is the most preferable to inhibit the flame spread through the bulk of PP.
2. The acid treatment of kaolin leads to disaggregation of the kaolin particle and dissolution the outer layers which leading to change both the structure and the chemical composition of kaolin.
3. The modification of kaolin by H_2SO_4 leads to increase the SiO_2 content and the surface area, while the Al_2O_3 decreased. The percentages of the other constituted change slightly.
4. The using of APP/ Modified kaolin increases the effect of the samples on the flammability of the PP.

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دراسات عن تأثير الكاولين والكاولين المعالج على قابلية الاشتعال لنظام بولى فوسفات الامونيوم/ بولى بروبيلين

عدلى عبدالله حنا[1]، اجلال مريم ريمون صوايا[2]، مروه عادل شريف[1]، علاء صلاح عبد المعطى[1]
قسم الكيمياء غير العضويه- المركز القومى للبحوث- الدقى و[2]كلية العلوم- جامعة عين شمس – القاهرة – مصر.

هذا البحث امتدادا لابحاث سابقه قام بها المؤلفون لزيادة كفاءة بولى فوسفات الامونيوم على قابلية الاشتعال لمادة البولى بروبيلين حيث استخدم الباحثون كلا من خام الكاولين والمعالج بحامض الكبريتيك. وقد استخدم كل من طيف الاشعة السينية، طيف امتصاص تحت الحمراء والميكروسكوب الاليكترونى النافذ ودراسة كل من المساحة السطحية وحجم الحبيبات . بينما استخدم التحليل الحرارى الوزنى لتقييم التأثير الحرارى لخليط بولى فوسفات الامونيوم مع مادة البولى بروبيلين حيث تم تحضير خمس عينات فى كل من الكاولين الخام والكاولين المعالج ودلت نتائج التحاليل على ان معالجة الكاولين بالاحماض تزيد من نسبة ثانى اكسيد السيليكون الذى بدوره يرفع المساحة السطحية وفى نفس الوقت يحدث بعض التغيرات فى التركيب البللورى والطيفى للكاولين ودلت دراسات التحليل الحرارى الوزنى للمخاليط ان الكاولين المعالج وغير المعالج يزيد من زمن التحلل الحرارى مع ملاحظة ان الكاولين المعالج اكثر فعالية