

Fire Performance of Poly Propylene Treated with Ammonium Polyphosphate and Kaolin

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AMMONIUM polyphosphate was prepared and used as flame retardant materials for polypropylene nanocomposites. Then, kaolin was incorporated with ammonium polyphosphate nanoparticles as synergistic flame retardant system for polypropylene. This is in addition to modification of kaolin with sulfuric acid then incorporated with polyphosphate nanoparticles as good flame retardant materials for polypropylene. Flammability properties of polymer and developed polymer nanocomposites were improved achieving 26.4 and 10.2 % reduction in peak heat release rate (PHRR) compared to virgin polymer and polymer composite with ammonium polyphosphate nanoparticles alone. The synergistic effect of modified kaolin and nanoparticles was evaluated. The dispersion of ammonium polyphosphate and kaolin in polymer matrix were studied using microscopic techniques.

Keywords: Ammonium polyphosphate nanoparticles, Kaolin, Cone calorimeter, Flame retardant, Polypropylene.

Introduction

Polypropylene (PP) is one of the popular members of thermoplastic polymers which are widely used in various applications due to their interesting mechanical properties. However, its low thermal stability and high flammability hazard attributed to restriction in its use in other industrial applications [1]. Hence, flame retardant additives have to incorporate in polymer matrix improving their flame retardancy and enhancing their thermal stability such as phosphate–nitrogen materials and aluminosilicates based materials [2-3]. On the other hand, ammonium polyphosphate (APP) have been used as flame retardant materials for polypropylene either in nanoscale or microscale form [1,4]. Also, it is previously reported that optimum mass loading of APP achieving good flame retardancy is 10 wt. %[5]. Interestingly, addition of kaolin to APP as flame retardant system has been reported [6-7]. Recently, the APP incorporated with zeolite has been used as flame retardant filler for polywood coating [8].

In this study APP nanoparticles have used as flame retardant for PP. Also, APP nanoparticles

have been used in conjunction with kaolin layers. Moreover kaolin layers have been modified using sulfuric acid and then incorporated with APP nanoparticles as potential flame retardant system for PP. Flammability properties of the various polymer composites were evaluated and their synergistic effect was investigated.

Materials and Methods

Materials

Polypropylene (PP) has a chemical formula $(\text{CH}_2-\text{CH}-\text{CH}_3)_n$ according to IUPAC nomenclature. It has molecular formula $(\text{C}_3\text{H}_6)_n$, its density in the range of 0.855 to 0.946 gm.cm^{-3} for the amorphous or the crystalline form. It melts at about 130-171°C. The kaolin in this study was supplied from Wadi El Hamadiya region, Egypt.

Synthesis of Ammonium polyphosphate (APP)

APP was prepared by mixing certain amount of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) with urea $(\text{NH}_2)_2\text{CO}$ solution at ratio 1/2 and heated at 280°C. The ammonia solution (25%) were added slightly (2ml/2min) with continuous heating for 45 min, a white precipitate was formed

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DOI : 10.21608/EJCHEM.2017.1509.1110

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separated and dried in air as reported [4].

Modification of Kaolin

The chemical modification of kaolin ore was carried out by adding 50 g of the kaolin ore to 500 ml of sulfuric acid solution (10M) and refluxing at 110°C under the atmospheric pressure in a round bottom 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 polymer nanocomposites

Polypropylene and polypropylene containing 10% APP samples were prepared. Also, five samples of polypropylene containing APP and kaolin were prepared having number K2 to K10. Moreover five samples containing PP and APP with treated kaolin were prepared having number K2m to K10m. The samples codes and preparation conditions are listed in Table. 1.

Characterization

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

Cone calorimeter test

Cone calorimeter test was performed using fire testing technology LDT equipment according to ASTM 1354-95. Samples, with dimensions of 7.5 x 7.5 x 0.4 mm³, were tested horizontally under an incident flux of 35 kW/m².

Results and Discussion

Characterization of Polypropylene Nanocomposites

The IR spectra of PP and their nanocomposite with APP 10wt.% were depicted in Fig. 1. The Absorption bands observed at 3087, 2922, 1457, 1378 and 890 cm⁻¹ were corresponding to the C-H bond of the saturated and unsaturated part of the PP chain [9, 10]. Moreover, the characteristic absorption band related to the P-O and P=O attached with APP appeared at 1117, 1081 and 1079 cm⁻¹ [11]. Furthermore, the absorption bands located at 1158, 1000, 927 and 492 cm⁻¹ were attributed to the P-O and P-O-P indicated the interaction between the PP and APP [12]. On the other hand, the FTIR characterization of the unmodified and modified kaolin (K2, K4, K6, K8 and K10) and (K2, K4, K6, K8 and K10) are shown in Fig. 2&3. The absorption band situated at 1165, 990, 931, cm⁻¹ are assigned to (Si-O-P), (Si-O-C) and (SiOH) bonds respectively, which

TABLE 1. The samples codes and preparation conditions for all samples.

Sample code	PP %	APP %	kaolin(K) %	Modified kaolin(Km) %
PP	100	0	0	0
APP10%	90	10	0	0
K2	90	8	2	0
K4	90	6	4	0
K6	90	4	6	0
K8	90	2	8	0
K10	90	0	10	0
K2m	90	8	0	2
K4m	90	6	0	4
K6m	90	4	0	6
K8m	90	2	0	8
K10m	90	0	0	10

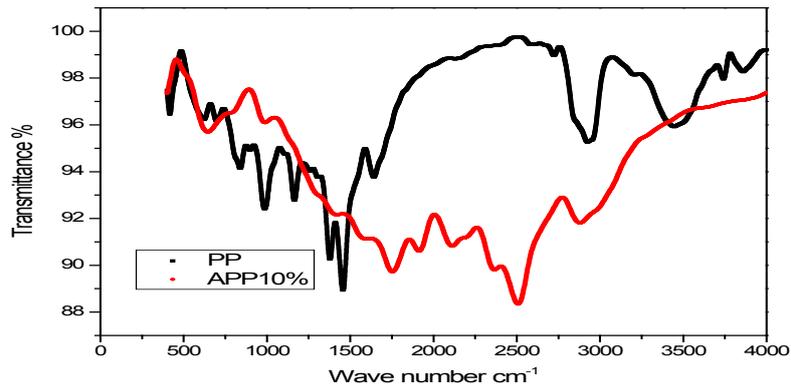


Fig. 1. FTIR spectra of polypropylene and their nanocomposite with APP-10.

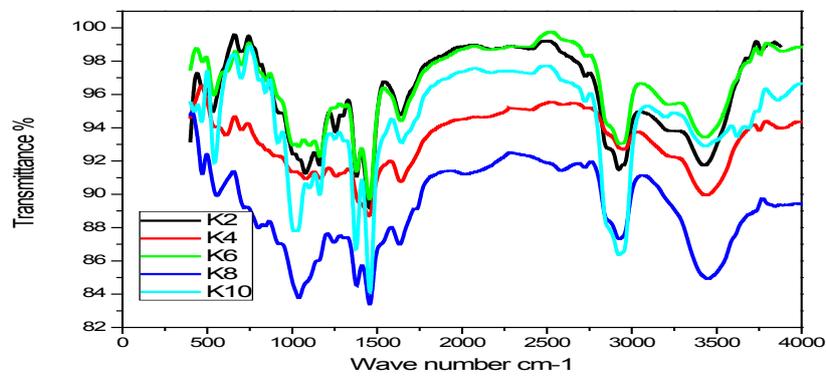


Fig. 2. FTIR spectra of polymer nanocomposite K2, K4, K6, K8 and K10.

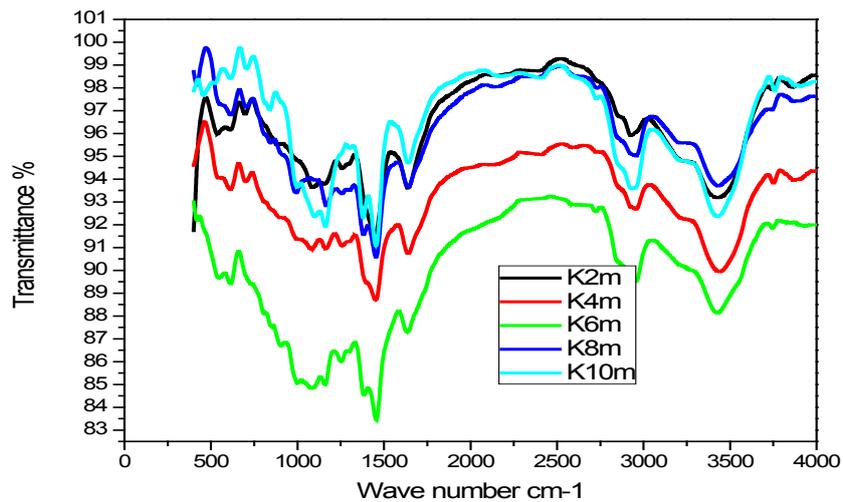


Fig. 3. FTIR spectra of polymer nanocomposite K2m, K4m, K6m, K8m and K10m.

indicated that there is an interaction between the kaolin (modified or unmodified) with PP and APP (Fig. 2&3).

On the other hand, the morphology of PP, PP/APP, PP/APP+kaolin or modified kaolin was studied using microscopic techniques. Figure 4a represents SEM image of PP blank which shows smooth surface of polymer matrix. However, the dispersion of APP was indicated in SEM image indicated in Figure 4b. Interestingly, when kaolin was incorporated with APP in PP nanocomposites, the surface became much rough and kaolin layers were dispersed in polymer matrix as indicated in Fig. 5a-e.

Flammability properties

The flammability of blank PP and their various nanocomposites with APP, APP-Kaolin unmodified and modified were evaluated using cone calorimeter instrument. The cone calorimetric

data of the nanocomposites were tabulated in Table 2 and Fig. 6&7. The virgin PP was ignited after 14 s and recording peak heat release rate (PHRR) of 1104 kW/m², however, when 10 wt.% of APP was dispersed the PHRR was reduced to 925 kW/m² achieved 16.2 % reduction. This flame retardancy was stemmed from decomposition APP during heating of PP nanocomposites releasing phosphoric acid which catalyze the formation char layer on PP nanocomposites surface. On the other hand, when kaolin layers were involved in conjunction APP in PP matrix, the PHRR was gradually reduced achieving 19.1% reduction as seen in Table 2 and Fig. 6. However, when kaolin was used alone the reduction in PHRR was less than one. This indicated the synergistic effect when kaolin and APP used together. This might be due to the incorporation kaolin strengthen the formed char layer. Interesting, the inclusion of modified kaolin with APP achieve better flame

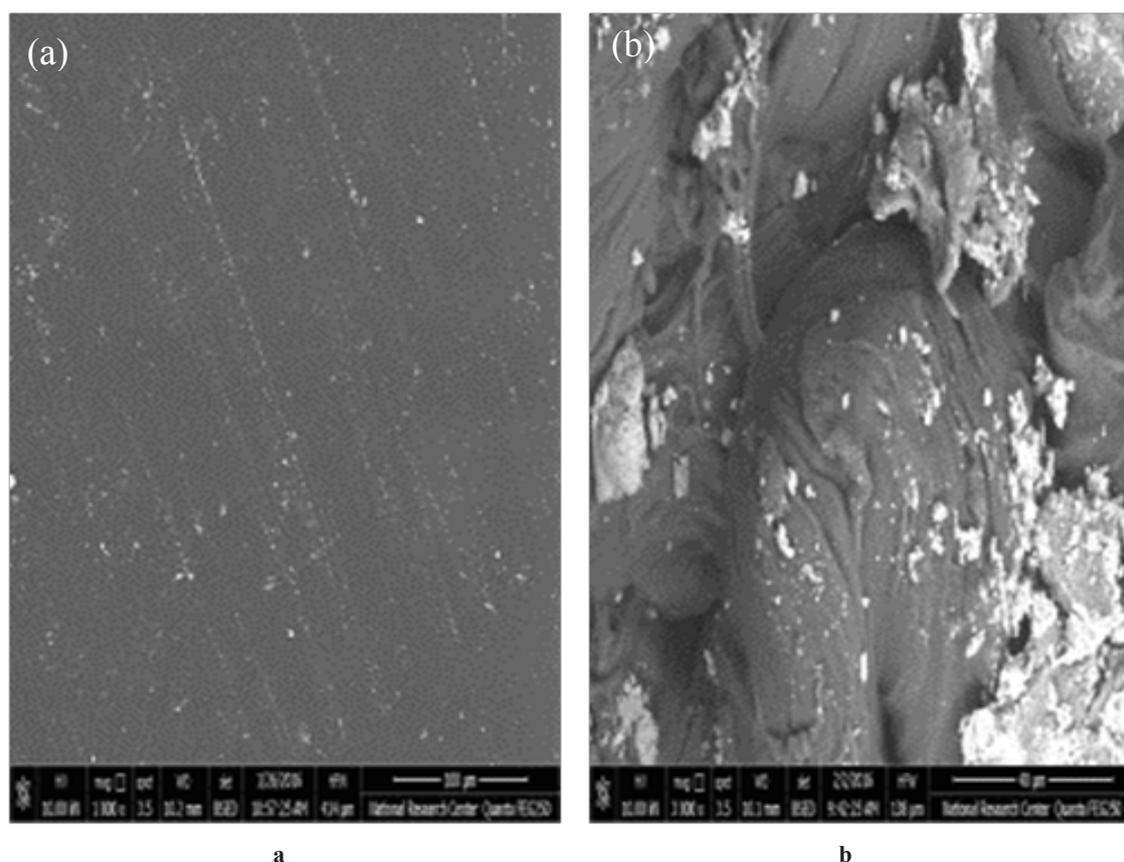


Fig. 4. SEM images of a) PP and b) PP/10%APP.

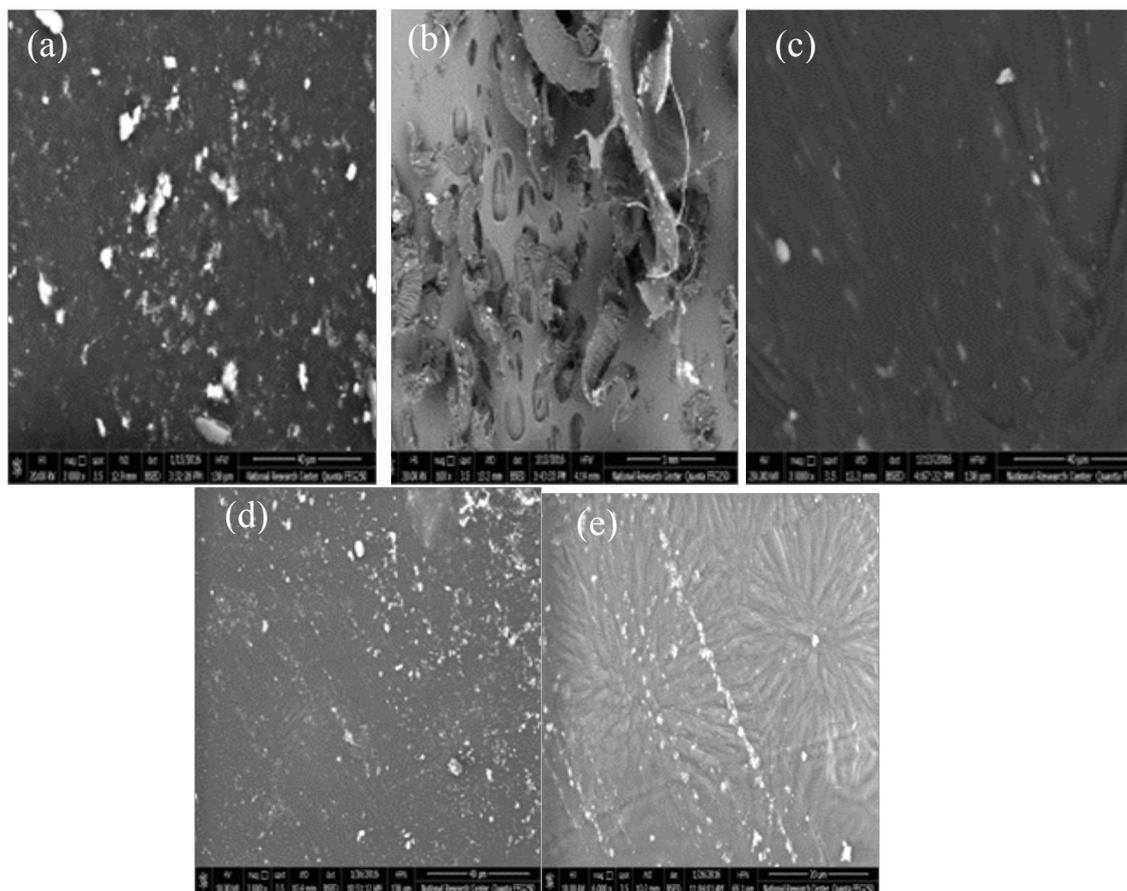


Fig. 5. SEM images of a)K2, b) K4, c)K6, d)K8 and e)K10.

TABLE 2. Main cone calorimeter parameters evaluated for all samples .

Samples	TTI (S)	PHRR (KW/m ²)	AV. HRR (KW/m ²)	FIGRA (kW/m ² s)	THR (MJ/m ²)	Time to end (S)	FPI (sm ² /kW)
PP	14	1104	447	13.8	106	143	0.01268
APP10%	24	925 (16.2%)	334	8.8	92	164	0.02595
K2	25	924 (16.3%)	319	8.03	90	176	0.02706
K4	27	911 (17.5%)	312	7.92	89	188	0.02964
K6	28	906 (17.9%)	300	7.88	85	189	0.03091
K8	29	893 (19.1%)	296	7.77	76	190	0.03247
K10	18	1102 (0.18%)	409	13.78	105	164	0.01633
K2m	29	889 (19.5%)	283	7.73	71	195	0.03262
K4m	30	827 (25.1%)	277	6.54	70	200	0.03628
K6m	30	817 (26%)	266	6.67	68	202	0.03672
K8m	31	813 (26.4%)	230	6.78	68	203	0.03814
K10m	19	1070 (3.1%)	404	12.59	103	164	0.01776

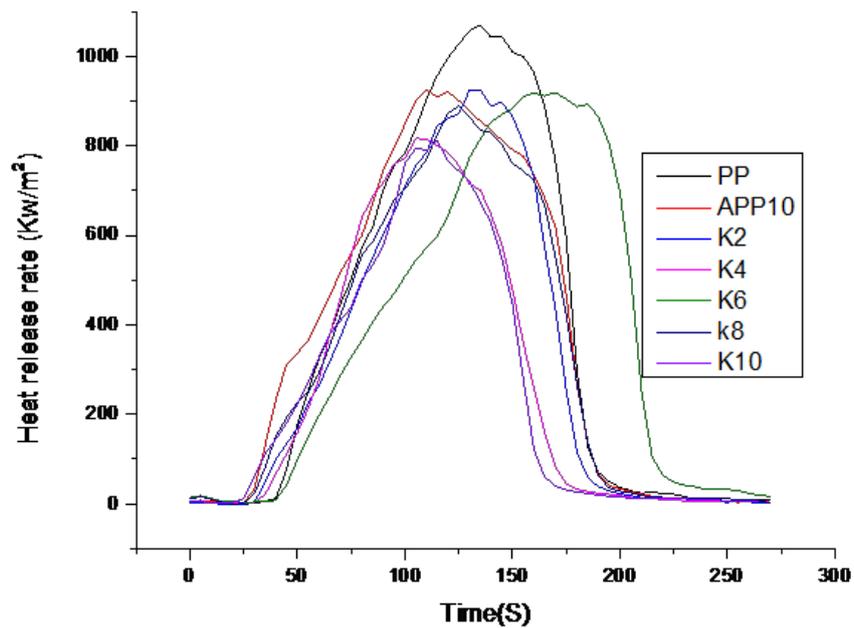


Fig. 6. HRR curves of PP, APP10%, K2, K4, K6, K8 and K10.

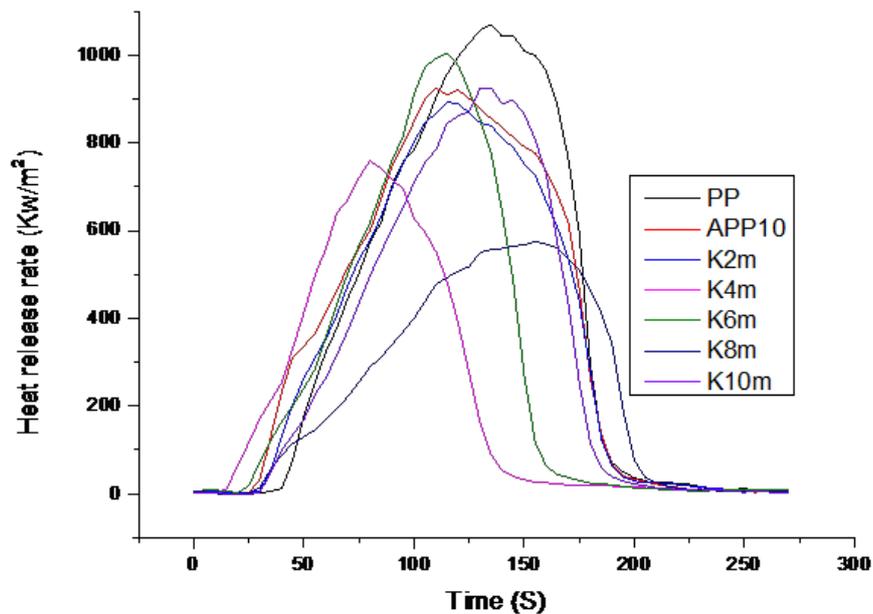


Fig. 7. HRR curves of PP, APP10%, K2m, K4m, K6m, K8m and K10m.

retardancy as indicated from Fig. 7 and Table 2. As, the PHRR was reduced in K8m achieved 26.4% reduction compared pure PP and 10.2% compared APP 10% and 9 compared to K8.

The fire growth rate (FIGRA), defined as PHRR/time to PHRR which provides the basis for estimation of both the predicted fire spread rate and the size of fire and is a good indicator of the contribution to fire growth of materials. The FIGRA for all samples is shown in Table.2. The values of FIGRA were decreased from 13.8 for PP without an addition to become 8.8 for the sample containing 10%APP only, while it decreased to become 8.03 for the samples k2. This decrease continues as the amount of kaolin increases recording value equals to 7.77 for the sample k8. For comparison, the sample 10 recorded value 13.3, this means that the mixture of APP and kaolin is the more effective as flame retardant. In all cases the samples which contain modified kaolin (K2m, k4m, k6m, k8m, k10m), the values of FIGRA is less than that for untreated kaolin. The results also, indicate that the treatment of kaolin improves the action of APP when used as flame retardant material for PP. Furthermore, another critical parameter was evaluated which is the fire performance index (FPI) was calculated as the ratio between the time to ignition (TTI) and peak of heat release (PHRR): $FPI = TTI/PHRR$

This FPI value gives useful information about the degree of fire hazard [13 - 16]. The calculated values of FPI for all samples as shown in table.2 are increased by adding APP or APP+ kaolin or modified kaolin. This means that the presence of kaolin increases the efficiency of APP when used as flame retardant for PP, and this efficiency increased by treatment of kaolin.

Conclusion

The flammability properties of the resulting nanocomposites (PP/APP+kaolin) were evaluated and reduced. The modification of kaolin layers played an important role on the flammability properties of the polymer nanocomposites. The PHRR of used polymer nanocomposites was reduced achieved 26.4 % compared with blank polymer and 10.2 compared to ammonium polyphosphate alone based polymer composites.

The evaluation of the synergistic effect of ammonium polyphosphate and kaolin layers indicated that the APP/kaolin improves the flammability of PP.

References

1. Duan, L., Yang, H., Song, Y., Hou, Y., Wang, W., Gui, Z. and Hu Y., Hyperbranched phosphorus/nitrogen-containing polymer in combination with ammonium polyphosphate as a novel flame retardant system for polypropylene. *Polymer Degradation and Stability* **134**, 179-185 (2016).
2. Attia, N., Hassan, M., Nour, M. and Geckeler, K., Flame retardant materials: synergistic effect of halloysite nanotubes on the flammability properties of acrylonitrile-butadiene-styrene composites. *Polymer International* **63**, 1168 (2014).
3. Attia N., Goda E., Nour M., Sabaa M. and Hassan M.: Novel synthesis of magnesium hydroxide nanoparticles modified with organic phosphate and their effect on the flammability of acrylonitrile-butadiene styrene nanocomposites. *Materials Chemistry and Physics* **168**, 147 (2015).
4. Marwa A., Adly A. and Alaa A., Synthesis and characterization of nanosized ammonium polyphosphate. *Canadian Journal of Applied Science*, **4**, 94.(2014).
5. Marwa A., Adly A., Abo-Elfotouh I. and Alaa. A.: The flammability of polypropylene nanosized ammonium polyphosphate system. *Canadian Journal of Applied Science* **5**, 39 (2015).
6. Marwa A., Adly A. and Alaa A.: Studies on the effect of diatomite on the flammability of ammonium polyphosphate / polypropylene. *International Journal of ChemTech Research* **9**, 822 (2016).
7. Adly A., Eglal S., Marwa A. and Alaa A., Studies on The Effects of Kaolin and Modified Kaolin on the Flammability of APP/PP system. *Egyptian Journal of Chemistry* **60**, 205 (2017).
8. Ayirilims. N., Candan Z. and White R., Physical, mechanical and fire properties of oriented standboard with fire retardant treated veneers. *Holz als Rohund Werkstoff*, **65**, 449 (2007).
9. Shahavazian M. and Seyedmir M.: Effects of MWNTs on flame retardation and thermal stabilization performance of phosphorus containing flame retardants in polypropylene. *Oriental Journal Of Chemistry* **28**, 1631 (2012).
10. Sun C., Luo J., Su X.: Determination of crystalline forms of APP with IR spectra. *Journal of Northeast Forestry University* **32**, 94 (2004).
11. Qu H, Hao J. and Wu W, Zhao X, Jiang S, *Egypt.J.Chem.* **60** , No.5 (2017)

- Optimization of sol gel coatings on the surface of ammonium polyphosphate and its application in epoxy resin. *Journal Of Fire Science.*, **30**, 357 (2012).
12. Lizheng S. and kefu C., Preparation and characterization of ammonium polyphosphate/Diatomite composite filler and assessment of their flame retardant effects on paper. *Journal of Bioresources.*, **9**, 3104 (2014).
13. Su S., Jiang D. and Wilkie C.: Novel polymerically - modified clays permit the preparation of intercalated and exfoliated nanocomposites of styrene and its copolymers by melt blending. *Polymer. Degradation and Stability.*, **83**, 333 (2004).
14. Hirschler M.: How to measure smoke obscuration in manner relevant to fire hazard assessment: Use of heat release calorimetry test equipment. *Journal of Fire Science.*, **9**, 183 (1991).
15. Nour M.: Metal complexes of poly(iminoethylene) modified with flame retardant system for PP, *Polimery Journal.*, **48**, 439 (2003).
16. Hassan E., Helal M., Nour M. and Shokry K., Characterization of physical mechanical and fire properties of fiber glass composite due weight fraction. *Key Engineering Materials* **600**, 547. (2014).

(Received 17 /8/ 2017;

accepted 12 /9/ 2017)

التطور الاشتعالي للبولى بروبيلين المضاف اليه بولى فوسفات الامونيوم والكاولين

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تم تحضير بولى فوسفات الامونيوم لاستخدامها كمثبط للحريق فى مادة بولى بروبيلين منفردة ثم تم ادخال الكاولين فى بولى فوسفات الامونيوم النانوميترية الحجم لدراسة تأثير اضافة الكاولين على فاعلية بولى فوسفات الامونيوم بالاضافة لمعالجة الكاولين بحمض الكبريتيك قبل اضافته لدراسة تأثير عملية المعالجة الحمضية على حبيبات بولى فوسفات الامونيوم عند استخدامها كمثبط للحريق.

وقد استخدم جهاز المسعر الحرارى المخروطى لمتبع تقدم الاشتعال فى البولى بروبيلين وقد دلت قياس معدل انطلاق الحرارة عند الاشتعال انخفاضاً فى قيمة القمم الدالة على ذلك بنسبة ١٠٪ مما يعطى دلالة على فاعلية استخدام بولى فوسفات الامونيوم والكاولين بصورة افضل من استخدام بولى فوسفات الامونيوم منفردة كما لوحظ ازدياد تلك الفاعلية بمعالجة الكاولين بحمض الكبريتيك.

ولقد استخدم الميكروسكوب الاليكترونى الماسح فى تتبع انتشار الكاولين خلال حبيبات بولى فوسفات الامونيوم وانتشارهما فى البولى بروبيلين.