



International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.9, No.05 pp 822-830, 2016

# Studies on the effect of diatomite on the flammability of ammonium polyphosphate/polypropylene

Marwa. A. Sherief, Adly. A. Hanna\*, Alaa S. Abdelmoaty

# Inorganic chemistry department, National Research Centre, 33 Elbohooth St.(Tahrir) Dokki,P.O.Box: 12622, Postal code: 11787, Giza, Egypt.

**Abstract:** The flammability of a mixture of (APP/DE)/PP was studied by using both the thermogravimetric analysis and the cone- calorimeter test. In this study the (APP/DG)/PP system was characterized by using the IR spectra, the X-ray diffraction and the morphology of their mixture. The IR spectra indicate that there are incorporate of DE into the APP structure, while X-ray patterns shows that when the percentage of DE equals to 0.4 the system converted to the amorphous state. The SEM of the samples show an interference of the DE particles through the APP units. The analyses of the obtained data from the thermogravimetric and the cone- calorimeter measurements indicate that when mixing DE with APP the flammability of PP was improved. Also, the obtained results indicate that mixing of DE with APP up to 0.6 ratio is the more preferable sample. The mechanisms of the retardant the flammability of PP in presence of APP and DE may due to the formation of phosphoric acid and nitrogen from decomposition of APP and formation of Al and Si oxides from the degradation of DE.

## **1-** Introduction:

In previous works(1,2), the authors synthesized nano particles of ammonium polyphosphate (APP) and used it as flame retardant for polypropylene (PP). They used both the thermogravimetric analyses (TG and DTA) and the cone calorimetric measurements to evaluate the addition of different percentage of APP to PP as flame retardant. The analyses of the obtained data indicate that APP can be used successively as flame retardant with 10 % wt. Ammonium Polyphosphate, NH4(PO<sub>4</sub>)n, is an inorganic flame retardant because it built mainly from phosphorous and nitrogen , it decomposed by heat to form phosphoric acid and ammonia. Phosphoric acid acts an acid catalyst in the dehydration of carbon bond of poly alcoholic materials, such as cellulose in wood or paper and the hydrocarbons chain in the polymeric materials and finally released  $CO_2$  gas which helps to dilute the oxygen and inhibit the spread of flame. While nitrogen is an inert gas works as inhibitor to spread the flame. Several trails (3-5) were done to improve the flammability of APP. In this field, for example Bertalan et al (4) modified the surface of APP by using reactive surfactant that contains boron- silicon segment. In general the modification of APP includes the methods of preparation to produce a high surface area particles or adding some modifier materials, organic or inorganic. Recently a system of ammonium polyphosphate / Diatomite composite fillers was used as flame retardant for paper by Sha et al (6).

On other hand the authors used Diatomite (DE) to remove some pollutants cations such as  $Cd^{+2}$ ,  $Cu^+$ ,  $pb^{+2}$ , and  $PO_4^{-3}$  from the waste water. They conclud that owing to the special properties of the diatomite (7, 8), it can be used to remove the impurities from the waste water. Diatomite is non- metallic mineral contains ~ 85% of SiO<sub>2</sub> with high porous structure, low density, high surface area, strong adsorption capacities and low

cost. For these advantages, several modifications (9-12) were carried to improve the own properties of DE. In 2015, Hanna et al (7,8) modified DE by treatment with FeCl<sub>3</sub> and by using micro emulsion solution. Also, they modified the kaolin rock to increase its efficiency for removing Pb(II) from its aqueous solution (13).Goren et al(10) increased the surface area of DE by using HCl and calcination. Khraisheh et al (11) modified diatomite by NaOH treatment and magnesium oxide to improve the adsorption capacity. Another modification was carried out by Wuj et al(14) using aluminum sulphate for using to remove the phosphate anions from the waste water. Micro emulsion process and magnesium oxides, also, used to increase the adsorption capacities of DE.

For using the clays as modifier of the APP, Zhang et al (15) used nano-clays as modifier to reduce the flammability of the polyamides material. Also, Reija et al (16) studied the effects of a mixture of APP and nano -clays on the rheological and flame retardant properties of epoxy. In 2009 Hapuarachchi (17) studied the effect of Al (OH)<sub>3</sub> when added to APP as flame retardant of polyester.

In the present work, a system of the prepared nano-particles of APP was modified by adding different amount of diatomite to be used as flame retardant for polypropylene. In this study different samples including APP and different percentage of diatomite were tested.

# 2- Experimental:-

## 2-1: Materials:-

The start materials of this work are:

- 1. Natural diatomite (DE) without purification except washing with distilled water. DE samples were exposed to chemical analysis and characterized with different techniques as described elsewhere (7). It contains ~ 83.6% SiO<sub>2</sub> and 4.24 Al<sub>2</sub>O<sub>3</sub>, 1.07 % Fe<sub>2</sub>O<sub>3</sub>, 6.17% CaO, and others oxides 4.86 % and it is free from TiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O and MgO(1).
- 2. Nano-particles of ammonium polyphosphates (APP) was prepared previously (2) by mixing certain amount of ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) with urea (NH<sub>2</sub>)<sub>3</sub>CO solution at ratio 1/2 and heated at 280 C. Then the ammonia solution (~25%) were added gradually (1ml/min) with continuous heating for 45 min, the white precipitate was formed, separated and dried.
- 3. Polypropylene (PP)(LG chem, LTD seetc, N 1600 Boo 1046M, Korea was used in the preparation of tested samples.

## 2-2: preparation of (APP/DE)/PP samples:-

Five samples were prepared contains APP-diatomite and PP with the following composition

Sample (0) APP (10% wt)/PP Sample (I) APP (8% wt) +DE (2%wt)/PP Sample (II) APP (6% wt) +DE (4%wt)/PP Sample (III) APP (4% wt) +DE (6%wt)/PP Sample (IV) APP (2% wt) +DE (8%wt)/PP

To furnish the prepared samples to become suitable for cone calorimetric test the following procedure was used. Before melt spinning the PP were compounded with (APP+DE) in twin screw co- rotator extruder where RPM of screw was 60-80 rpm. The temperatures setting of the extruder from the hopper to die were 175,185,195,210 and 220 °C for zone 1 to 5 respectively. The melt spinning of the PP pallets were blended with (APP+DE) in laboratory melt spinning machine extruder zones and maintained in 190,200 and 220°C for the three zones respectively. The extruder zones were provided with nitrogen gas to prevent the oxidation of PP. Then, the melt pallets after shaping was cooled down by cool air in 1.5m long quench dut( 2 ).

### 2-3: Characterization of the samples (2)

The prepared APP was characterized previously by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis, (TG/DTA) scanning electron microscope (SEM), Transmission electron microscope (TEM). The results of the characterization show that the prepared APP is crystalline in form I and have particle sizes equal to 5-65 nm.

The same techniques were used to characterize the APP/diatomite mixture after mixing with PP.

## 2-4: The flammability evaluation of (APP/DE)/PP system

There are different methods to investigate the flammability of the substances such as limiting oxygen index (LOI),underwrites laboratory (UL94), horizontal burning test (94HB),vertical burning test (94v), testing for gas and smoke, cone calorimeter test (ASTME 1354/ ISO-5660) and thermogravimetric analysis (TG and DTA).

Both the thermogravimetric analysis and the cone calorimetric methods were used in this work to study the flammability of [APP/DE]/PP system.

The thermal analyses were performed by USA Perkin-Elmer thermogravimeter with heating rate 10  $^{\circ}$ C/min.

The cone calorimeter measurements of the samples were carried according to the fire testing technology, 1LK at an incident heat flux of 35 kw/m<sup>2</sup> (ISO 5600). The cone calorimeter measurements were described in the previous work (2). Different parameters were obtained from the cone- calorimeter test such as heat release rate (HRR), time of ignition (TI) and so on. The experimental error of the obtained data was about 5%.

#### 3- The Results and discussion

#### 3.1. FTIR spectra

The IR chart of the prepared nano-sized APP is shown previously in the first part of this work (1). The IR curve for APP shows different absorption peaks at 760, 682, 597, 3200 and 1256 cm<sup>-1</sup>corrosponding to the formation of APP in form 1.

For the samples including (APP/DE)/PP system, the IR chart Fig 1., shows the appearance of different absorption bands at 3500, 1080 and 1740 cm<sup>-1</sup> which characterization the presence of SiO<sub>2</sub> as observed in the previous work(8) beside the specific peaks of the polyphosphate. The appearing of these peaks indicates the incorporate of DE into APP units.



Fig.1. IR spectra of the (APP/DE)/pp system (0-IV)

#### **3.2. X-ray diffraction**

To specify the crystalline form of the prepared ammonium polyphosphate, the x-ray patterns was performed. Also, to study the crystalline changes by adding diatomite or by mixing with polypropylene with different percentage, x-ray spectra were recorded in Fig 2. From the x-ray patterns of pure APP an appearance of a maximum intensity at  $2\Theta$ = 14-18 was recorded. The appearance of this peak indicates that the prepared APP is in form I. On other hand, the profile of the x-ray pattern when compared with other works is almost

identical and inagreement with the previous work obtained by other workers. When the mixtures of APP and diatomite (APP/DE) sample 1,2 added to the PP new peak on the x-ray patterns were appeared at  $2\Theta$ = 25, 38. The appearance of these peaks indicate that there is an interaction between APP and DE was happened before mixing with PP, where this peak corresponding the diatomite mineral



Fig.2. X-ray diffraction of the (APP/DE)/pp system (0- IV)

As 0.8 APP/0.2 DE sample I was mixed with PP, a sharp peaks on the x-ray chart were appeared at 2  $\Theta$  = 35 and 2  $\Theta$  = 38. The presence of these two peaks indicates that there are incorporate for DE into APP. For sample II (0.6APP/0.4DE) the x-ray chart indicates that there is a tendency for the mixture with PP to become amorphous and the crystalline phase disappeared Fig 2. As the percentage of APP decreases to become equals to 0.4 or 0.6 the system converted to the amorphous state

## 3.3. Scanning electron microscope



Fig.3. SEM of the (APP/DE)/pp system (0- IV)

#### Marwa A. Sherief A. Hanna et al /International Journal of ChemTech Research, 2016,9(5),pp 822-830. 826

Fig 3.represents the SEM photos of the various samples (0-IV). The photo of APP/PP without DE shows that the APP has rounded nano-particles with different size and some agglomerate units distributed randomly was appeared.

To study the effects of mixing APP and DE with different percentage to PP for explain their effects on the flammability of PP, the morphology of these mixtures were studied. Fig 3a.which represents the photo shows that the fine particles of APP were distributed randomly through the PP matrix. By adding a mixture of APP and DE (0.8 APP + 0.2 DE) to the PP, the shape of the SEM shows a sharp like flower with clear boundary. Fig 3b. This structure may due to the distribution of APP particles on the surface of the diatomite unit. When the percentage of DE increased to 0.4 DE, the photo shows homogeneity of the particles Fig 3 c. By increasing the % of the added DE, the photos show a well spread of the APP/DE mixture on the surface of the PP especially at (0.4 APP+0.6 DE). This changes in the morphology of the mixed particles may due to two mechanism, the first one happened at 0.2 and 0.4 represents the distribution of APP particles on the surface of DE, while the second was happened after saturation of the surface and then the APP particles penetrate to occupy the porous of the DE. From this study it may conclude that the mixture of APP/DE having 0.6 APP,

0.4 DE is the more preferable to be used as flame retardants for PP plates, where the APP on the surface is the more acceptable to decomposed than that in the porous of DE.

#### 4- The flammability of APP/DE/PP system

Both the thermogravimetric and the cone calorimetric measurements were used to evaluate the APP/DE as flame retardant for PP.

#### 4-1 :The thermogravemitry:-

The TG curves of the prepared samples with and without diatomite were recorded in Fig 4. The thermogravimeteric curves between 25 and 500 °C take place the same trends including three distinguished stages in sequence referring to the evaporation of moisture content and the other volatile materials the main degradation and the carbonization of the residual. In the previous publication, the TG curves show that for the PP materials the T<sub>onset</sub> equals to 385 and the T<sub>outset</sub>equals to 420 °C which represents the beginning and the ending of degradation respectively with time of degradation equal 1.7 sec. This time increased to become 4 sec by adding 1% APP and continue to increase equals 3.5 sec. as the percentage of APP becomes 10 %(2).



Fig.4. Thermal analysis of the (APP/DE)/pp system (0- IV)

The effects of diatomite on the flammability of the samples as shown from the TG curves indicate that:

- 1. The adding a mixtures of APP/diatomite to the polypropylene gives TG curves in similar behavior and similar to the TG curve obtained for APP/PP system (2).
- For the sample containing 0.8 APP/0.2 DE the time of thermal degradation, calculate from the T<sub>onset</sub> and T<sub>outset</sub>, increases from 1.7 to 3.5 sec. This increase may due to the presence of diatomite which resulting SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> by thermal degradation

- 3. For the sample containing 0.6 APP/0.4DE, the time of the thermal degradation increases dramatically to become equals to 12.5 sec. This increase in the time of degradation delate the spread of flame and hence gives the chance for the firemen to work.
- 4. As the percentage of DE increases from 0.4 to 0.8 the time of the thermal degradation increases gradually from 12 to 14.5 sec. This finding means that the using a high amount of DE causes a slight in the thermal degradation time.

In general, the addition of DE to APP as flame retardant increases the thermal degradation time than that observed for APP only (2). For comparison Table 1. Shows the values of  $T_{onset}$ ,  $T_{outset}$  and the time of the degradation for PP in presence of APP or a mixture of APP/DE for retardant the flame through the PP materials

Table 1: The T<sub>onset</sub>, T<sub>outset</sub> and the time of degradation of PP in presence of APP and APP/DE mixtures

Items to compare	(APP/DE)/PP %				
_	0	Ι	II	III	IV
T <sub>onset</sub>	382	275	250	230	235
T <sub>outset</sub>	420	400	400	350	380
Time of degradation	5.5	3.5	12.5	14	14.5

The comparison between the readability properties by using APP or APP/DE as flame retardant shows that using DE at 0.2 up to 0.4 is more effective in delate the spread of the flames.

#### 4-2. cone calorimeter test

By using the cone calorimeter test, the fire retardancy according to international organization for standardization (IOS 5660-1) was performed. Heat release rate (HRR), Total heat release (THR), CO and  $CO_2$  amounts, were obtained through the cone- colorimeter test.

#### 4-2-1: Total heat release (THR)

The useful parameter produced from the cone- calorimeter test is the total heat release (THR) which represents the flame spread through the balk of the polymer for the treated and untreated samples. For the samples containing APP/PP and (APP/DE)/PP, the variation of THR with time of ignition were shown Fig 5. The results indicate that for all samples, during the first 2 minutes, there is a dramatic increase in the values of THR then slightly increases forming a like- steady state after the first 3 min. This behavior means that the fire spread rapidly tell the thermal degradation of APP starts to be formed, hence it role as an agent to prevent the spread of flame. From the curves of THR-time, it may conclude that the more affective sample which contain about 0.6 DE



Fig.5. Total heat release rate of the (APP/DE)/pp system (0- IV)

#### 4-2-2: The heat release rate (HRR).

The heat release rate (HRR) is the main parameter produced from the cone- calorimeter test. The curves of the five samples are recorded in

Fig 6. The values of HRR for the samples are increased rapidly till the first 50 sec., and then it decreased slightly between 50-60 sec. and increased slightly again forming two peaks with small bottom. The first peak in HRR curves refers to the evolving of heat at the first time (18) while the bottom on the curve represents the thermal decomposition of APP or DE producing phosphoric acid, nitrogen and Al and Si oxides. The producing of these materials coated the PP particles and inhibited the spread of the flame through the polymer unit. Then the heat of the cone calorimeter is transformed to the polymer material from one side and then it burns gradually forming the second peak on the HRR curves. The last part of the curves (the descending part) represents the action of the APP/DC system on spreading the flame (19).



Fig.6. Heat release rate of the (APP/DE)/pp system (0- IV)

For HRR of (APP/DE)/PP system; it is observed that both the first and the second peaks shift to lower time than that observed for APP/PP system. The shift in the HRR curves were considerable for the samples 2 (0. 4 % DE and 0.6 APP), while it is slight for the samples containing more than 4% DE as shown in Fig 6. This finding may explained by forming polyphophoric acid which produced from the decomposition of APP and leads to dehydration and carbonization of the polymer. The carbonization of the polymer causes a char layer formation at lower temperature and coating the polymer by the diatomite and hence inhibits the spread of heat. It is noteworthy that the shifts of the peaks on the HRR curves for the samples containing more than 0.4% DE is in general less than that of APP only while it is slightly higher than the samples containing less than 0.4 %. This may attributed to the effects of DE on the thermal decomposition which coated the APP particles.

#### 4-2-3: The ignition time

The time of ignition as produced from the cone calorimeter test is recognized the time from the beginning to the start of sustained firing (20). It is a promoter measure the spread of the fire through the balk of materials, the longer ignition time is the more resistance of the fire to spread. The measurements of the ignition time by cone- colorimeter for the untreated sample (APP/PP) equals to 26sec. where it increase to become 34sec. for the simple containing (0.8 APP/0.2 DE)/PP and increased to 36sec for the sample (0.6APP/0.4 DE)/PP. By increase the percentage of DE, it decreases slightly to 32 and 31sec. for the samples containing 0.4 PP/0.6 DE and 0.2 APP/0.8 DE respectively. This means that the better sample for increase the ignition time is that containing 0.4 -0.6 DE.

#### 4-2-4: The CO and CO<sub>2</sub> masses

It is well known that, the ignition of the polypropylene  $(CH_2=CH-CH_2)n$  produces  $CO_2$ , CO gases and  $H_2O$  vapor, So that the percentage of CO and  $CO_2$  will be increased by burning PP. Fig 7a and Fig 7b represent the percentage of both CO and  $CO_2$  respectively as obtained from cone- calorimeter test. The curves

indicate that the percentage of  $CO_2$  or CO increased rapidly during the first two min. forming sharp peaks and then decreased rapidly. For the treated samples with APP or APP/DE, the intensity of the main peak was observed but increases gradually from sample (10% APP/0% DE) to the samples 4 (0.2% APP/0.8% DE) for CO production with time. This means that through the first two minutes the ignition of the polymer produces CO gas and the amount of gases increases by increasing the percentage of DE as show in Fig 7a. In the case of the CO<sub>2</sub> production Fig 7b, it is observed that for all treated samples the production of CO<sub>2</sub>increases by increasing the percentage of DE up to 0.4%. The appearance of these sharp and defined peaks indicates to the complete burning of the polymer by the time. The appearance of these peaks for CO or CO<sub>2</sub> products at lower time than that containing a high % of DE give an explanation to the producing of their gases at short time, then give a chance to the firemen doing their work.



Fig.7.a. CO yield of the (APP/DE)/pp system (0- IV)



Fig.7.b. CO<sub>2</sub> of the (APP/DE)/pp system (0- IV)

For comparison between the behavior of the CO and  $CO_2$  amounts with time, it may conclude that the sample which contains 0.6 APP/0.4 DE is the best one to be used

## 5- Conclusion

1. From the analysis of the IR, X-ray and SEM measurements, it may conclude that there is an incorporated of the APP on the surface and the porous of DE.

- 2. The thermogravimetric analysis and the cone calorimeter test, indicate that the adding of DE to APP improvement the action of APP as flame retardants for polypropylene.
- 3. The adding of DE to APP with percentage ranging from 40-60 % is sufficient to be used.

# 6- References

- 1. Sherief, M.A., Hanna, A.A, ,Abdelmoaty, A.S.,"synthesis and characterization of nanosized ammonium polyphosphate" Can.J.ApplSci. 2014, 3:94-99.
- 2. Sherief, M.A., Hanna, A.A., Abdelhakim, A.I., Abdelmoaty, A.S., "the flammability of polypropylene nanosized ammonium polyphosphate system" Can.J.APP.Sci, 2015,5:59-49.
- 3. Hongqiang, Q., Jianwei, H., Weihong, W., Xiaowei, Z. and Subin, Optimization of sol-gel coatings on the surface of ammonium polyphosphate and its application in epoxy resin"J., J.of Fire Sci 2012, 30:357-371.
- 4. Bertalan, G., Marosi, G. and Anna, P., "Role of interface modification in filled and flame- retarded polymer systems", J.Solid State Ionics, 2001, 1412.
- 5. Demir, H., Balko D. and Ulku, S., J.Polymer. Degrad and Stabi, Influence of surface modification of fillers and polymer on flammability and tensile behavior of polypropylene-composites", 2006, 91:1079.
- 6. Sha, L., Chen. K.," Preparation and Characterization of Ammonium Polyphosphate/Diatomite Composite Fillers and Assessment of their Flame- Retardant Effects on Paper" bioresources, 2014, 9(2): 3104-3116.
- 7. Hanna, A.A., Sherief, M.A. and Aboelenin, R.M.M., "Removal of Some Heavy Metals from Wastewater by Using Diatomaceous Earth." Res J.Phos.Biolog.and chem. 2014, 5:198-205.
- 8. Sherief, M.A., Hanna, A.A. and Aboelenin, R.M.M." Removal of Phosphate Ions from Aqueous Solutions by Using Modified Diatomaceous Earth." Res.J.Phos.Biolog. and Chem. 2015, 6, 583-588.
- 9. Wenhui, X, Jian, P. water Res." Development and characterization of ferrihydrite-modified diatomite as a phosphorus adsorbent 2008, 42: 4869-4877.
- 10. Goren, R., Baykara, T., Marsoglu, M., "Effects of purification and heat treatment on pore structure and composition of diatomite", Br. Ceram. Trans: 2002, 101:177-180.
- 11. Khraisheh, M., Gnouti, M.A.Al-, Allen, S.I..Ahmed, M.N. Effect of OH and silanol groups in the removal of dyes from aqueous solution using diatomite, water Res 2005,39:922-932.
- 12. Khraisheh, M., Al-degs, Y.S., Mominn, W.A.M., "Remediation of wastewater containing heavy metals using raw and modified diatomite" Chem.Eng.J. 2004,99:177-184.
- Drweesh, S.A., Fathy, N.A., Wahbe, M.A., Hanna, A. A., Akarish A.I.M., Eman.I.M., Elzahany, E.A.M., El.sherif, I.Y., Abou-Elsherbini, K.S., "Equilibrium, kinetic and thermodynamics studies of Pb (II) adsorption from aqueous solutions on HCl- treated Egyption kaolin" J.Envir.Chem.Eng. 2015,4: 1674-1684.
- 14. Wu, J., Yang, Y.S., Lin, J.J., "Advanced tertiary treatment of municipal wastewater using raw and modified diatomite" J.Hazard Mater. 2005, 127:196-203.
- 15. Zhang, S., Rhchard, A., Hull, R. and Baljinda, K., "Flammability, degradation and structural characterization of fibre-forming polypropylene containing nanoclay–flame retardant combinations", J.Polym.Degr. Stab. 2006, 91:719.
- 16. Reija, S., Katja, N., Jyrki, V., "The effect of ammonium polyphosphate and Nano clay on the rheological, thermal, and flame retardant properties of epoxy". Annual Trans. of Norel. 2009, 17:263.
- 17. Hapuarachchi, T.D, Peijs, T, "T.,"Aluminiumtrihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin", J.Express. Polymer let.2009 11:743.
- 18. Grexa, O, Horvathova, E., Besinova, O., and Lehocky, P.," Flame retardant treated plywood", Polym.Degr.andStabil., 1999,64(3), 529-533.
- 19. Grexa, O, Lubke, H," Flammability parameters of wood tested on a cone calorimeter" Poly.Deg. andstabil., 2001, 74(3):427-432.
- 20. Craft, S.T., Isgor, B., Hadji, G., and Mehaffey, J.R., "Predicting the thermal response of gypsum board subjected to a constant heat flux" Fire and Materials, 2008, 32: 335-355.