MOHAMED A. NOUR[1)*], MOHAMED M. HASSANIEN[2)]

Effect of copper chelate of pyridineanilide modified montmorillonite on the flammability and thermal stability of polypropylene

Summary — Polypropylene (PP) compositions with montmorillonite (MMT) modified with either pyridineanilide (PyA) or its copper chelate (CuPyA) were the subjects of our study. The effects of PyA/MMT and CuPyA/MMT on the following properties of PP compositions were studied using cone calorimetry: time to ignition (*TTI*), combustion time, heat release rate (*HRR*), heat of combustion, CO and CO_2 evolution and specific smoke extinction area (*SEA*). It has been found that the composition PyA/MMT:PP (5:95, MH2) showed the best flame retardant properties. Thermal stability of the compositions investigated has been determined by thermogravimetric analysis. Introduction of PyA/MMT as well as of CuPyA/MMT significantly improves thermal stability of PP, although what concerns an increase in onset temperature slightly better effect has been observed in case of the samples containing copper.

Key words: polypropylene compositions, montmorillonite, modification, pyridineanilide, copper complexes of pyridineanilide, flame retardancy, thermal stability.

The most common approach to improve the flame retardancy of organic polymers is largely achieved currently *via* the incorporation of flame retardant additives. These additives must be easily processed with the polymer, must not be excessively deteriorating the other performance properties and must not create environmental problems in terms of recycling or disposal. Some of the commonly used flame retardants can reduce the thermal and mechanical properties of the polymer [1—3]. Use of metal compound or chelated metal compound with polymer is one of the more interesting areas in flame retardancy studies and not only for their potential as technological materials, but also for providing a convenient microscopic system to study the fundamental scientific issues concerning the polymers [4]. They are known to affect the initial stages of polymer degradation [5]. In some cases, they increase the amount of char formed from the polymer and this can produce a significant decrease in polymer flammability [6, 7]. In the last few years many researchers tried and found a new thermally stable flame retardant by some organic treatment of montmorillonite (MMT). Montmorillonite is a natural clay mineral having a myriad of applications due to its remarkable ion exchange [8], intercalation and swelling properties [9, 10]. Modified MMT can act as a good host for several compounds and has a wide range of applications as flame retardant for different types of polymers [11—16]. In this work, studies have been made on the effects of either pyridineanilide modified montmorillonite (PyA/MMT) or its copper chelate (CuPyA/MMT) on the flammability and thermal stability of polypropylene.

EXPERIMENTAL

Materials

Montmorillonite was supplied by Fluka, Switzerland. Ethanol, xylene, ethylacetoacetate and copper acetate were supplied by Edwic, Egypt.

Table 1. Specification of polypropylene

Property, unit	Value
Melt flow rate, g/10 min	12.00
Density, g/cm^3	0.900
Tensile strength at yield, MPa	27.00
Elongation at yield, %	5.000
Flexural modulus, MPa	1450

2-Aminopyridine was supplied by WINLAB. Polypropylene (PP) was supplied by HMC polymers company limited, Thailand. Its specification is shown in Table 1.

[1)] National Institute of Standards, Tersa str., El-Ahram, El-Giza, P.O.Box: 136 Giza, Code No. 12211 Giza, EGYPT; e-mail: m_a_nour@hotmail.com
[2)] Chemistry Department, Industrial Education College, Beni Suef, e-mail: mmhassanien2002@yahoo.com
[*)] Author, to whom all correspondence should be addressed.

Synthesis

Pyridineanilide

In a round flask a molar ratio of 2-aminopyridine and ethylacetoacetate, was refluxed in xylene for 4—6 h. The precipitate was collected, washed and dried.

Pyridineanilide modified montmorillonite (PyA/MMT)

The aqueous suspension of MMT was added to the ethanol solution of pyridineanilide. The mixture was refluxed at 60—70 °C for 25 h. The precipitate was collected by filtration, washed by ethyl alcohol and dried in oven for 24 h.

Copper chelate of pyridineanilide modified montmorillonite (CuPyA/MMT)

Ten grams of the prepared PyA/MMT were added to the aqueous solution of copper acetate under stirring at room temperature for 5 h. The formed complex was filtered and dried.

Preparation of the samples for cone calorimetry

The polypropylene compositions were prepared by compounding PP with CuPyA/MMT or PyA/MMT. The samples were then compressed at 200 °C for 10 min under (1 MPa) pressure.

The polypropylene compositions are shown in Table 2:

T a b l e 2. PP compositions prepared

Sample	PP	PyA/MMT	CuPyA/MMT
MH1	100	—	—
MH2	95	5	—
MH3	95	—	5
MH4	93	—	7

Methods

Cone calorimetry tests were carried out at heat flux 35 kW/m^2. Time to ignition (*TTI*), heat release rate (*HRR*) maximum, average and total, average specific smoke extinction area (*SEA*), average heat of combustion, weight lass, burning time, average evolved CO and CO_2 gases were measured.

Thermogravimetric analyses (TGA) were carried out at heating rate 10 °C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Flammability

Cone calorimetery results for the different samples of PP compositions are presented in Table 3.

T a b l e 3. Cone calorimetry results for PP compositions

Property, unit	Sample			
	MH1	MH2	MH3	MH4
TTI, s	91	132	51	32
Burning time, s	93	149	214	148
Weight loss, residue %	0.0	13.56	13.2	10.00
Maximal *HRR*, kW/m^2	2771.8	2083.22	1619.998	1836.8
Average *HRR*, kW/m^2	1838.23	867.697	1128.35	938.2
Total *HRR*, kJ/m^2	306.7	161.77	476.10	258.4
Heat of combustion, MJ/kg	46.663	40.817	38.663	39.9
SEA, m^2/kg	3795.00	1149.063	1270.61	1209.8
CO, kg/kg	0.011	0.010	0.009	0.0088
CO_2, kg/kg	2.55	1.740	1.676	1.74

It was noticed that the sample MH2 showed the most clear reduction in average *HRR*. It showed 52.797 % reduction in average *HRR* compared to pure PP sample (MH1). Samples MH3 and MH4 showed 36.61 % and 48.96 % reduction in the average *HRR*, respectively.

The sample MH2, showed 47.25 % reduction in total HRR compared to MH1, while sample MH4 has 15.74 % reduction in total HRR compared to MH1. The only exception in the value of total *HRR* is that of MH3, where it showed 55.23 % increase in the total HRR in comparison to MH1. It was also noticed that the sample MH2 showed prolonged *TTI* and extinguished early. Burning time of sample MH1 is only 93 seconds, while burning times of the other polypropylene compositions were 149, 214, and 148 for MH2, MH3 and MH4, respectively. *SEA* value of pure propylene (MH1) is equal 3795.00 m^2/kg, and it is reduced in modified PP compositions. It can be noticed that the values of CO emitted from different PP compositions are generally reduced in comparison to the value of MH1. The values of CO evolved from different PP composition are arranged in the following order MH1 > MH2 > MH3 > MH4. The decrease in the value of CO_2 emitted during combustion was clearly seen after the incorporation of PyA/MMT or CuPyA/MMT into polypropylene. Quantities of CO_2 emitted from the samples MH2 and MH4 are equal. The biggest amount of emitted CO_2 concerns MH1 sample while the smallest — MH3 one.

It was clear from the different data collected from cone calorimeter, that sample MH2 showed better flammability properties than the samples MH3 and MH4. Simultaneously MH2 sample showed also a good environmental effect when compared with the other samples.

Thermal stability

The TGA results of PP compositions are collected in Table 4 and were shown in Fig. 1. The results indicate that the total weight loss of pure PP (MH1) sample which occurred at 600 °C is 98.074 %, while the total weight loss of the other PP compositions: MH2, MH3

T a b l e 4. Decomposition temperature of PP compositions

Sample	Onset temperature, °C	Peak temperature, °C	Char Yield at 700 °C, %
MH1	462.15	591.35	1.338
MH2	525.08	606.57	5.126
MH3	571.02	634.75	2.714
MH4	541.71	627.59	5.008

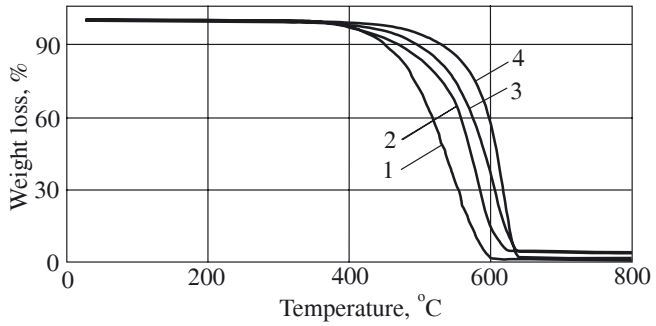

Fig. 1. TGA curves of PP compositions: 1 — MH1, 2 — MH2, 3 — MH3, 4 — MH4

and MH4 are nearly 94.52 %, 97.151 %, and 94.781 % and occurred at 626.49 °C, 640 °C and 640 °C, respectively. This indicates that the thermal stability of modified polypropylene compositions have been increased in comparison with the pure PP. The increase in the thermal stability of polypropylene composition is apparent from the onset and peak temperature. A greatest shift of onset temperature towards its increase was observed in the case of sample MH3, a bit smaller for MH4 and the smallest for MH2. Also there is a good improvement in the peak temperature of the samples MH2, MH3 and MH4 in comparison with that of MH1 (591.35 °C). It was noticed that the incorporation of PyA/MMT or CuPyA/MMT into PP samples showed a good effect on enhancement of char formation.

CONCLUSION

The PyA/MMT shows a better effect on flame retardancy of polypropylene than its copper complex. Introduction of either PyA/MMT or CuPyA/MMT significantly improves thermal stability of PP although what concerns an increase in onset temperature a bit better effect has been observed in case samples containing copper.

REFERENCES

1. Nelson G. L.: "Fire and polymer II", ACS Symposium Series 599 (Ed. G. L. Nielson), American Chemical Society, Washington (DC) 1995, p. 1—28.
2. Levchik S., Camino G., Costa L.: *Fire Mater.* 1995, **19**, 1.
3. Hochberg A.: Proceedings of the fall FRCA meeting, Naples (FL) 1996, p. 159.
4. Giannelis E. P., Krishnamoorti R., Manias E.: *Adv. Polym. Sci.* 1998, **138**, 107.
5. Cullis C. F., Gad M. M., Hirschler M. M.: *Eur. Polym. J.* 1990, **26**, 919.
6. Cuennadi E. Z., Sergei M. L.: *J. Appl. Polym. Sci.* 1998, **68**, 715.
7. Nour M. A.: *Polimery* 2003, **48**, 439.
8. Vaia R. A., Teukolsky R. K., Giannelies E. P.: *Chem. Mater*. 1994, **6**, 1017.
9. Labhsetwar N. K., Shrivastava O. P.: *Can. J. Chem.* 1992, **70**, 1927.
10. Labhsetwar N. K., Shrivastava O. P.: *J. Chinese Chem. Soc.* 1995, **42**, 67.
11. Gilman J. W.: *Appl. Clay Sci.* 1993, **15**, 31.
12. Gilman J. W., Kashiwagi T., Lichtenhan J. D.: *Sampe J.* 1997, **33**, 40.
13. Gilman J. W., Jackson C. L., Morgan A. B., Harris R. H., Manias E., Giannelis E. P., Wuthenow M., Hilton D., Philips S. H.: *Chem. Mater.* 2000, **12**, 1866.
14. Zanetti M., Camino G., Thomann R., Mulhaupt R.: *Polymer* 2001, **42**, 5401.
15. Gilman J. W., Awad W. H., Davis R. D., Shields J., Harris Jr. R. H., Davis C., Morgan A. B., Sutto T. E., Callahan J., Truelove P. C., Delong H. C.: *Chem. Mater.* 2002, **14**, 3776.
16. Nour M. A.: *Polimery* 2002, **47**, 25.

Received 13 IV 2004.