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Metal complexes of poly(iminoethylene) modified with dithiocarbamate and poly(iminoethylene) compounded with montmorillonite as — flame retardant systems for polypropylene

Summary — This study is focused on the assessment of metal complexes of poly(iminoethylene) modified by dithiocarbamate compounded with montmorillonite and poly(iminoethylene) interchelated with montmorillonite as flame retardant materials for polypropylene. The assessment process is based on a comparative study of the results obtained using cone calorimeter at 35 kW/m^2 and thermogravimetric analysis (TGA). The comparative study revealed that the fire performance index (FPI) increased in the order: POZ8 > POZ2 > POZ3 > POZ1 > POZ4 as it is abbreviated in the text. Good agreement with these results was obtained from the char yield results using thermogravimetric analysis.

Key words: fire retardants, polymer-metal complexes, polymer/montmorillonite blends, polypropylene, cone calorimeter, thermogravimetry.

Thermogravimetric analysis is widely used to assess the thermal stability of polymers and additives, where an increase in thermal degradation temperature indicates thermally stable polymer and an increase in char yield indicates a good flame retardant additive [1]. The rate of heat release is one of the most important parameters for identifying fire hazard, since it is used as a measure of intensity of fire [2]. Cone calorimeter testing is also a very useful small-scale test as it can measure the heat release rate (*HRR*) associated with a variety of other parameters, which can provide a very important data in fire assessment [3, 4].

It is well known that montmorillonite clay (MMT) has very good intercalation and retention properties [5], which are best in the case of a metal-exchanged clay mineral, particularly substances that can form coordination compounds with those exchanged metal ions. So, high thermal stability of the intercalated compounds can be useful in industrial applications [6].

The present work concentrates on the preparation of dithiocarbamate polymer/metal chelate complexes compounded with montmorillonite and poly(iminoethylene) interchelated with montmorillonite compounds as flame retardants, in which dithiocarbamates usually form ring structured complexes, because of their characteristic bidentate coordination structure [7, 8]. From the objectives reported by G. Gallina *et. al* [9], I planned to study the fire behavior of polypropylene mixed with metal complexes of poly(iminoethylene) modified by dithiocarbamate (COMX) compounded with montmorillonite and poly(iminoethylene) interchelated with montmorillonite (PIEMMT) using cone calorimeter and thermogravimetry to establish whether the application of cone calorimeter and the comparison of the results with thermogravimetric ones is useful for definition of fire risk properties. These flame retardants were:

— COMX compounded with montmorillonite (COMX + MMT), where X = Co, Cu, Ni and Fe;

— PIEMMT.

Detailed description of mixtures of COMX + MMT and PIEMMT samples studies in my work is presented in Table 1.

Table 1. Characterization of COMX + MMT mixtures and PIEMMT samples

Sample type and content	Symbol
MMT 4% + COMCo 5%	POZ1
MMT 2% + COMCo 8%	POZ2
MMT 4% + COMCu 5%	POZ3
MMT 4% + COMNi 5%	POZ4
MMT 4% + COMFe 5%	POZ5
MMT 2% + COMFe 7%	POZ6
PIEMMT 3%	POZ7
PIEMMT 7%	POZ8

EXPERIMENTAL

Materials

K-Montmorillonite (MMT), poly(iminoethylene), carbon disulphide, ethanol, $CuSO_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ were obtained from Fluka, $FeSO_4 \cdot 7H_2O$ was delivered by Merck and polypropylene (PP, trade name "Malen PS-202") was produced by ORLEN SA.

Preparation of poly(iminoethylene) modified by dithiocarbamate (COM)

Carbon disulphide (10.20 g) in ethanol (50 cm^3) was added to a stirred solution of poly(iminoethylene) (30 g) in ethanol (75 cm^3) at 20°C. The white precipitate, which formed immediately in quantities yield, was filtered, washed with ethanol and dried in vacuum [7].

Preparation of COM/metal complexes (COMX)

COM (1 g), insoluble in water, was stirred with aq. solution (100 cm^3) of adequate amounts of $FeSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ or $CuSO_4 \cdot 5H_2O$ under air or nitrogen at 20°C for 0.5—1 h. COMX obtained was filtered, washed with water and dried in vacuum [7].

Samples preparation

PP was compounded with each COMX in the presence of MMT in Brabender (plasti-corder) extruder at weight ratio of 90 PP: 9—10 flame retardants at temperature 180—190°C for 15—18 min and then compression molded at 180°C under pressure 30—40 MPa to give the disks with 10.00 cm of diameter and 0.20 cm thick. These disks were then used for cone calorimeter testing. The same procedure was used to prepare the control samples (pure PP).

PIEMMT (3 wt.% or 7 wt.%) was mixed with PP (according to [10]) at 190°C for 15—18 min in Brabender extruder and compression molded at 170°C under pressure 30—40 MPa; 9.90 cm of diameter and 0.20 cm thick disks were obtained. These disks as well as the control samples (pure PP) were tested in cone calorimeter.

Methods

Cone calorimeter

Test was carried at 35 kW/m^2 heat flux using the cone calorimeter (made by ATLAS) according to ASTM 1345. The fire performance index (*FPI*) was calculated as the ratio between the ignition time (t_{ign}) and the peak of heat release rate (HRR_{peak}):

$$FPI = t_{ign}/HRR_{peak} \tag{1}$$

This *FPI* value gives useful information about the all flame retardants used in this study in reference to the degree of fire hazard [11].

Thermogravimetry

Analyses samples 5—15 mg were carried out with using TA-50 Shimadzu Thermogravimetric Analyzer at 10°C/min in nitrogen.

RESULTS AND DISCUSSION

Cone calorimeter studies

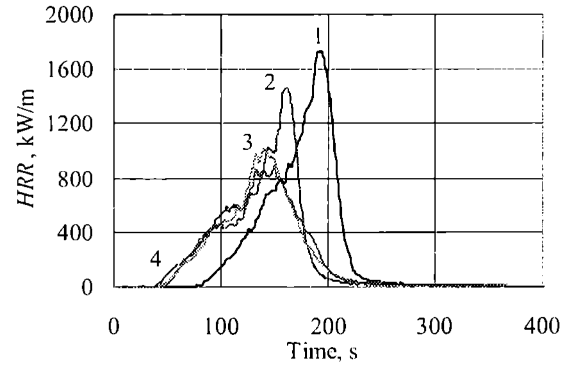

Fig. 1. Dependence of HRR on time for: 1 — pure PP, 2 — PP + POZ5, 3 — PP + POZ1, 4 — PP + POZ3 (for symbols see Table 1)

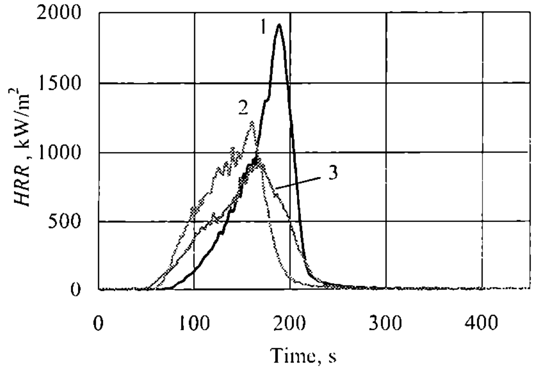

Fig. 2. Dependence of HRR on time for: 1 — pure PP, 2 — PP + POZ7, 3 — PP + POZ8 (for symbols see Table 1)

Figures 1 and 2 shows the decrease in *HRR* values of the samples containing both flame retardants in comparison with pure PP. Better results were obtained for Co and Cu used as a metal, not for Fe (Fig. 1). Also an increase in PIEMMT content in a composition decreases *HRR* value (Fig. 2). Low values of *HRR* are desired in fire hazard assessment. The reduction of t_{ign} of the samples containing flame retardant systems in comparison with pure PP may be due to the initial combustion of the flame retardants before they play their own role in sample [9] (table 2). Also in this case the advantageous highest *FPI* values have been obtained for Co or Cu containing systems.

Table 2. Results of cone calorimeter measurements

Sample*)	t_{ign}, s	t_{tot}**), s	HRR_{peak} kW/m^2	Final mass wt. %	*FPI* sm^2/kW
POZ1	28.39	351	1011.79	2.53	0.0280
POZ2	27.73	285	815.44	2.73	0.0340
POZ3	24.83	461	744.35	1.19	0.0333
POZ4	29.64	271	1180.54	1.13	0.0251
POZ5	31.55	253	1465.90	0.72	0.0215
POZ6	29.03	259	1375.35	0.69	0.0211
POZ7	42.28	269	1217.45	0.93	0.0347
POZ8	33.13	303	956.62	1.11	0.0346
PP	40.40	399	1827.90	0.30	0.0221

*) For symbols see Table 1.

**) t_{tot} = total burn time.

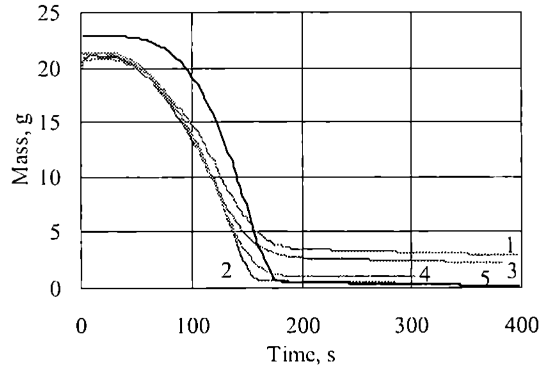

Fig. 3. Dependence of mass loss on time during cone calorimeter combustion for: 1 — PP + POZ3, 2 — PP + POZ5, 3 — PP + POZ1, 4 — PP + POZ4, 5 — pure PP (for symbols see Table 1)

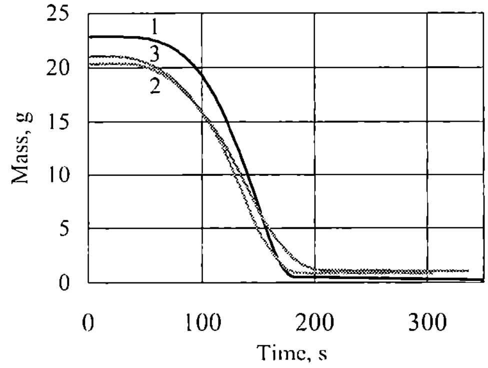

Fig. 4. Dependence of mass loss on time during cone calorimeter combustion for: 1 — pure PP, 2 — PP + POZ7, 3 — PP + POZ8 (for symbols see Table 1)

Figure 3 and 4 shows the mass loss values as a function of time. The longer the combustion, the lower mass loss rate and larger amount of char formed at the end of combustion. Table 2 contains the data concerning final masses of the samples investigated. So the biggest final masses correspond to the compositions showing the highest *FPI* values, it means from POZ1 to POZ4 and POZ7 and POZ8. Fe containing compositions (POZ5 and POZ6) are completely ineffective.

Thermogravimetric analysis

The thermogravimetric curves in Figs. 5—9 shows that samples of PP containing flame retardant systems degraded at higher temperatures than pure PP did (except of POZ1). They all produced in addition significant amounts of char.

More results of TGA analysis are shown in Table 3. As a rule, the higher the temperature for 5%, 10%, 15% and 20% mass loss, the lower the char yields at chosen temperature of 650°C.

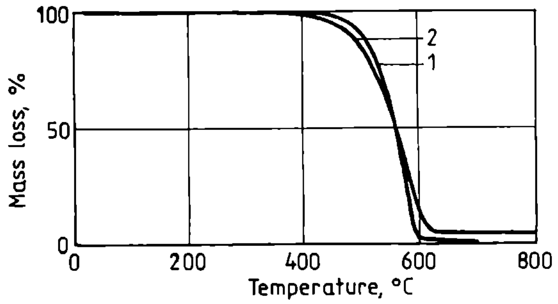

Fig. 5. TGA curves for pure PP (1) and PP + POZ1 (2)

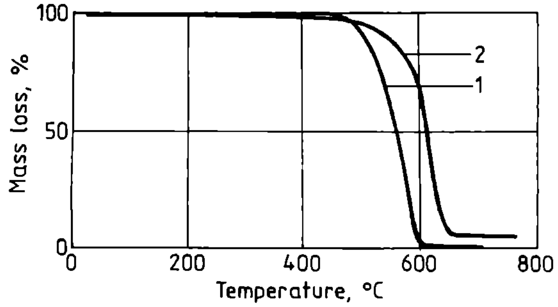

Fig. 6. TGA curves for pure PP (1) and PP + POZ2 (2)

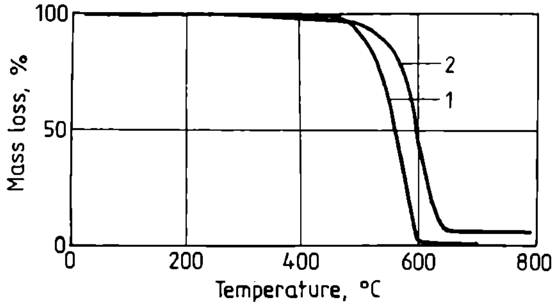

Fig. 7. TGA curves for pure PP (1) and PP + POZ3 (2)

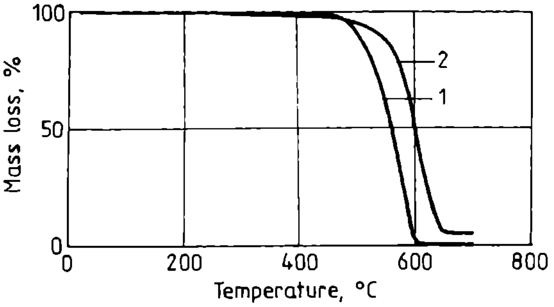

Fig. 8. TGA curves for pure PP (1) and PP + POZ4 (2)

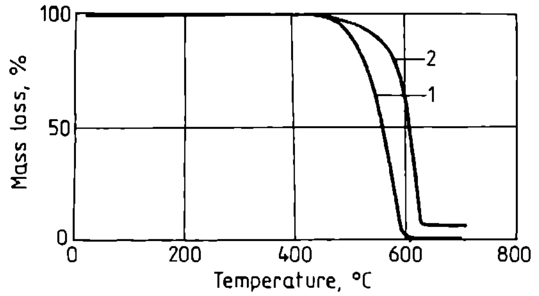

Fig. 9. TGA curves for pure PP (1) and PP + POZ8 (2)

T a b l e 3. Some results of TGA

Sample*)	Temperature (°C) at which mass loss is:				Char yield at 650°C, %
	5%	10%	15%	20%	
PP	485.21	502.39	514.01	522.91	0.298
POZ1	451.39	478.67	495.93	509.54	4.279
POZ4	508.33	540.15	556.16	566.01	5.389
POZ3	503.87	536.63	533.83	564.99	5.491
POZ2	502.14	536.97	599.92	576.43	5.832
PP + POZ8	510.78	545.32	564.07	576.16	6.017

*) For symbols see Table 1.

CONCLUSIONS

The cone calorimeter is very important and convenient intermediate-scale, test which can provide with important data in fire hazard assessment. Some of our compositions in this study seem to improve the flame retardancy of PP at heat flux 35 kW/m^2 and its thermal stability. Cone calorimetry and thermogravimetric results presented shows that char yield is a significant measure of an effectiveness of the systems investigated as the flame retardants for polypropylene.

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