eXPRESS Polymer Letters Vol.3, No.6 (2009) 359–365
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2009.45

Synergistic effects of iron powder on intumescent flame retardant polypropylene system

X. L. Chen[*], *C. M Jiao, Y. Wang*

College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, P R China

Received 14 February 2009; accepted in revised form 30 March 2009

Abstract. The effects of iron powder as a synergistic agent on the flame retardancy of intumescent flame retardant polypropylene composites (IFR-PP) were studied. The thermogravimetric analysis (TGA) and cone calorimeter (CONE) were used to evaluate the synergistic effects of iron powder (Fe). The TGA data showed that Fe could enhance the thermal stability of the IFR-PP systems at high temperature and effectively increase the char residue formation. The CONE results revealed that Fe and IFR could clearly change the decomposition behavior of PP and form a char layer on the surface of the composites, consequently resulting in efficient reduction of the flammability parameters, such as heat release rate (HRR), mass loss (ML), Mass loss rate (MLR), total heat release (THR), carbon monoxide and so on. Thus, a suitable amount of Fe plays a synergistic effect in the flame retardancy of IFR composites.

Keywords: *polymer composites, flame retardant, combustion, polypropylene*

1. Introduction

Polypropylene (PP) is used in many fields, such as automobiles, furniture, electronic casings, interior decoration, and architectural material. However, due to its chemical constitution, the polymer is easily flammable and so flame retardancy becomes an important requirement for PP. Traditionally, halogen containing compounds, alone or in conjunction with antimony trioxide, are the main flame retardants for PP. However, the use of these flame retardants has been limited for the consideration of life safety and environmental problems [1]. Therefore, it is worthwhile to investigate the halogen-free flame retardation of PP. The compounds used as halogen-free flame retardants in PP include metal hydroxides, phosphorus-containing compounds, phosphorus and nitrogen-containing compounds, etc. Furthermore, metal hydroxides are widely used as flame retardant additives in polypropylene, but the high loading destroys the mechanical properties of polymeric materials [2–5].

In recent years, intumescent flame retardant (IFR) approach [6–12] was well known as a new generation of flame retardants in polypropylene and other polyolefins for some of their merits, such as very low smoke and toxic gases produced during burning, and antidripping property, which conform to the tendency of flame retardants' development. However, it has also some drawbacks compared with bromine-containing flame retardants [13], such as low thermal stability. In order to enhance the flame retardancy, new intumescent flame retardant systems have been found [14–17], which has high flame retardant efficiency and good water resistance ability; and synergistic agents have been used in IFR systems, such as zeolites [18, 19], montmorillonite [20, 21], organoboron siloxane [22, 23], and some transitional metal oxides and

---

[*]Corresponding author, e-mail: xlchen@qust.edu.cn

metal compounds [24–27]. Many researches have shown that synergistic agents can effectively increase the strength and stability of char layer [18, 28], and promote catalyzing the reactions among IFR components in IFR-PP systems.

Iron compounds can be used as flame retardant synergists [29–31]. Carty and co-workers have studied the effects of antimony(III) oxide and basic iron(III) oxide on the flammability and thermal stability of a tertiary polymer blend [29]. Cai and co-workers have studied the catalyzing carbonization function of ferric chloride based on acrylonitrile-butadiene-styrene copolymer/organophilic montmorillonite nanocomposites [30]. Zhang and co-workers have studied the influence of Fe-MMT on the fire retarding behavior and mechanical property of (ethylene-vinyl acetate copolymer/magnesium hydroxide) composite [31]. Up to now, iron powder has not been reported to improve the flame retardance of plastics.

In this work, iron powder is selected to investigate the synergistic effect in PP-IFR composites, it is used in an IFR system consisting of ammonium polyphosphate (APP) and pentaerythritol (PER). Thermogravimetric analysis (TGA) and cone calorimeter (CONE) are used to evaluate the synergistic effect of Fe in PP-IFR systems.

2. Experimental results

2.1. Materials

Polypropylene (F401) was provided by Yangzi Petroleum Chemical Company. APP and PER was supplied by Hefei Keyan Institute of Chemical Engineering; the intumescent flame retardant (IFR) was obtained with the mass ratio of APP and PER is 3:1. Iron powder (Fe), with the particle size of 80~150 nm, supplied from the First Reagent Co. of Shanghai, was used as received. The formulations are given in Table 1.

Table 1. Formulations of flame retarded PP composites

Sample code	PP [%]	IFR [%]	Fe [%]	LOI	UL 94
PP0	100.0	–	–	18.0	No rating
PP1	70.0	30.0	–	31.0	V-0
PP2	70.0	29.0	1.0	32.5	V-0
PP3	70.0	28.0	2.0	32.0	V-0
PP4	70.0	27.0	3.0	32.0	V-0
PP5	70.0	25.0	5.0	31.8	V-0

2.2. Preparation of samples

All samples were prepared on a two-roll mill at a temperature range of 170–175°C for 15 min. After mixing, the samples were hot-pressed under 10 MPa for 5 min at about 175°C into sheets of suitable thickness and size for analysis.

2.3. Measurements

2.3.1. Limiting oxygen index (LOI)

Limiting oxygen index (LOI) was measured according to ASTM D 2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100×6.5×3 mm^3.

2.3.2. UL 94 testing

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The specimens used were of dimensions 130×13×3 mm^3.

2.3.3. Cone calorimeter

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions 100×100×3 mm^3 was wrapped in aluminium foil and exposed horizontally to an external heat flux of 35 kW/m^2.

2.3.4. Thermogravimetry (TG)

Each sample (approx. 10 mg) in powder form was examined in open vitreous silica pans under nitrogen flow on a STA 409C TGA apparatus (Netzsch Company, Germany) with crucible sample holders, at a heating rate of 10°C/min.

3. Results and discussion

3.1. LOI and UL 94 rating

The LOI and UL 94 tests are widely used to evaluate flame retardant properties of materials and to screen flame retardant formulations. Table 1 lists the related LOI and UL 94 data obtained from different loadings of iron powder. It can be seen from

Table 1 that the LOI value of PP1 containing 30.0 wt% IFR increases rapidly to 31.0 from 18.0 of original PP without any additive. The LOI values of samples (PP1 to PP2) increase to 32.5 with 1.0 wt% loading of Fe powder in the formulation. Then, the LOI decreases with the addition of iron powder. And, the LOI value of PP5 decreases to 31.8 when the loading of iron powder reaches to 5.0 wt%. This above result also gives the evidence that the 1.0 wt% iron powder has the best synergist effect with IFR in the PP blends. The results obtained from the UL 94 tests show that all the samples pass the UL 94 test.

3.2. Cone calorimeter study

The cone calorimeter is one of the most effective bench scale methods for studying the flammability properties of materials. The heat release rate (HRR), particularly the peak HRR, has been found to be the most important parameter for evaluating fire safety [29, 32–35]. The flammability properties of flame retardant PP composites have been studied using cone calorimeter. Although intumescent flame retardant is commonly used for PP for fire safety materials, sometimes the high loading can deteriorate the mechanical properties of materials. It is necessary, therefore, to develop novel synergistic flame-retardant systems with high efficiency and acceptable environmental impact.

In this study, Fe is added into PP/IFR composites as synergist. The flammability properties were evaluated with cone calorimeter experiments. In the flame retardant PP/IFR/Fe composites, the mass fraction of IFR and Fe was 30 wt%. The HRR curves are shown in Figure 1. A synergistic effect can be seen between IFR and Fe. Figure 1 shows that when 30 wt% IFR was added to pure PP, the peak HRR was 650 kW/m^2. When the 1 wt% IFR was substituted with Fe (PP2), the curves show that the peak HRR of the sample was 591 kW/m^2. It should be noted that the time for peak HRR moves from 304 s (PP0) to 353 s (PP1). When the Fe loading is raised to 2 wt%, the peak HRR of PP3 can further reduced to 461 kW/m^2. Also, the time for peak HRR delays to 368 s. It is very interesting that there is peak HRR when the burning time is about 124 s. This phenomenon can be explained that proper Fe can promote the formation of good carbon char residue, which can isolate heat and oxygen from flame zone to the substrate and barrier combustible gas degraded from the substrate from flame. With the addition of Fe, the peak HRR can be further decreased, but the decline rates have been not obvious. And, the time for peak HRR shortens with the loading of Fe from PP3 to PP5. Furthermore, the first peak HRR increases with the addition of Fe from PP2 to PP5. This can be explained that high loading of Fe on the surface can be oxidized, giving off a lot of heat, which leads the first peak HRR increases. Another reason may be that the iron powder in the bottom of the sample can catalyze PP depolymerisation, which results in many combustible gases.

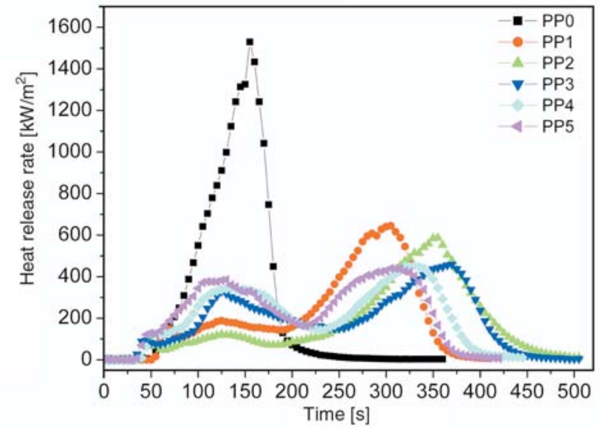

Figure 1. Heat release rate curves of flame retardant PP at a flux of 35 kW/m^2

The primary parameter which was responsible for HRR of the samples filled with IFR is the mass loss rate (MLR) during combustion, which was significantly reduced compared with those values observed for the pure polymer. Figure 2 shows that the MLR decreased in the order of PP2>PP1>PP3>PP4>

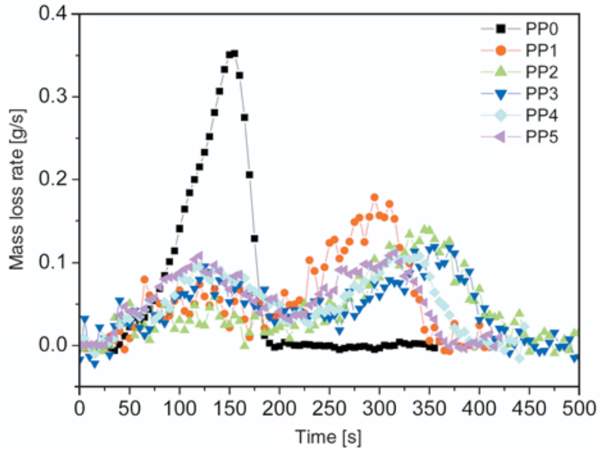

Figure 2. Mass loss rate curves of flame retardant PP at a flux of 35 kW/m^2

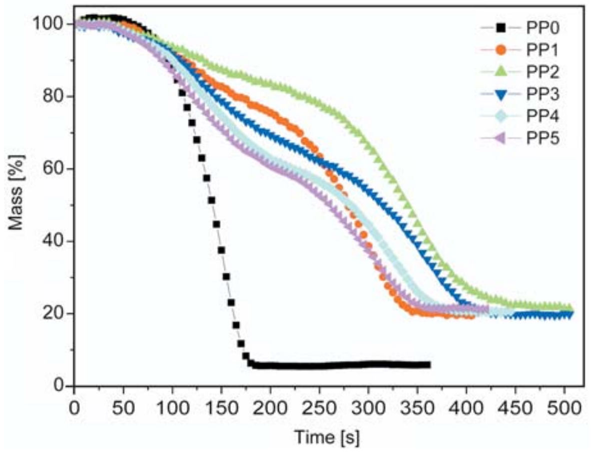

Figure 3. Mass curves of flame retardant PP at a flux of 35 kW/m^2

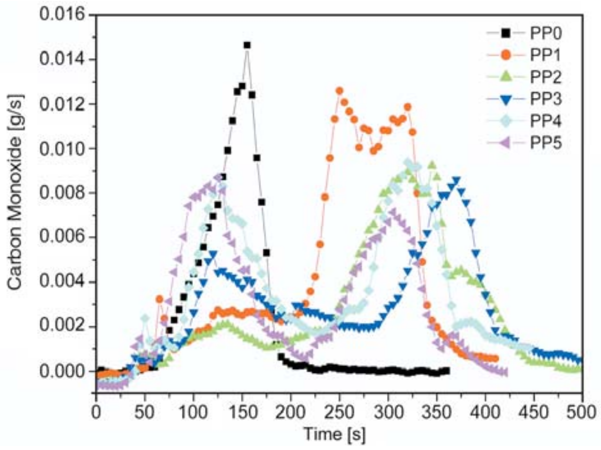

Figure 4. Carbon monoxide curves of flame retardant PP at a flux of 35 kW/m^2

PP5>PP0 between 0 and 200 s, and the MLR decreased in the order of PP5>PP4>PP3>PP2>PP1 between 200 and 450 s. This trend is the same as those of the HRR in the cone calorimeter (Figure 1). These similarities indicate that the mechanism of the observed reduction in HRR and also in MLR depends mainly on the condensed phase process instead of the gas phase process.

Figure 3 shows the weight of the char residues. During combustion, proper Fe may promote the IFR to carbonization on the surface of the burning composite creating a physical protective barrier on the surface of material. From Figure 3, it can be seen that the mass loss of PP2 is much less than that of the other sample, which can be showed that a dense protective barrier formed on the sample. It can explain the fact that the heat release rate of PP2 is the lowest one among all the samples. The physical process of the layers reassembling would act as a protective barrier in addition to the intumescent shield and can thus limit the oxygen diffusion to the substrate or give a less disturbing low volatilization rate.

Figure 4 and Figure 5 show the CO and CO_2 produced from PP and flame retardant PP under a heat flux of 35 kW/m^2. The incomplete combustion of flame retardant composite systems can be seen in the CO production rate. From Figure 4, it can be seen that the CO production rate of PP2 is the lowest one among all the flame retardant samples. Furthermore, the first peak of the CO production rate increases and the second peak of the CO production rate decreases with the addition of Fe. This phenomenon can be explained by that metallic Fe can promote the formation of carbon char residue, which can block heat. So the combustible gases on the surface of the sample can complete combustion. With the addition of Fe, the first peak of the CO production rate increases. This phenomenon may be that iron promotes a depolymerisation process. Many combustible gases cause incomplete combustion. However, the second peak of the CO production rate decreases with the addition of Fe. This can be illustrated that more iron powder is added, more iron oxides will be formed, which can oxidize CO into CO_2.

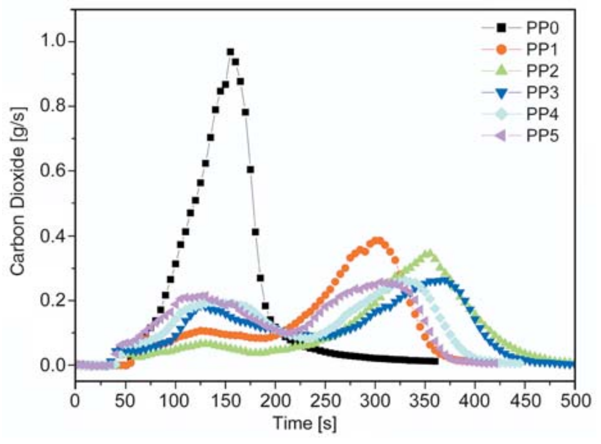

Figure 5. Carbon dioxide curves of flame retardant PP at a flux of 35 kW/m^2

The CO_2 production rates of the flame retardant systems significantly decrease at the time between 220 and 470 s, because the dense and compact char structure formed on the surface of the sample. However, in the time between 0 and 200 s, only the CO_2 production rate of PP2 is lower than PP1. Furthermore, the CO_2 production rate increases with the addition of Fe from PP2 to PP5. It can be explained that higher loading of Fe can lead more heat release (Figure 1). So a large number of combustible gases released, and reacted with oxygen to form carbon dioxide.

3.3. Thermogravimetric (TG) analysis

Figure 6 shows the TG curves of the pure PP and its flame retardant composites. It is clearly seen that all flame retardant PP composites decompose early in comparison with PP, which begins to decompose at about 399°C. However, at a temperature higher than 419°C, the FR PP composites are more thermally stable than PP. For example, PP almost decomposes completely at 500°C, whereas the undecomposed parts at the same temperature for PP1, PP2, PP3, PP4 and PP5 are 14.4, 15.4, 17.6, 18.6 and 19.5%, respectively. The above results showed that IFR has very good carbonization performance. The phenomenon that the char residue increases with the addition of iron powder can be illustrated that the quality of iron powder will only increase rather than decrease during combustion. The amount of residue of the FR PP composites at 600°C is still higher than 12.7%. The char residue increases with the addition of Fe. The reason may be that the reaction between Fe and oxygen can lead the mass increased, and Fe or Fe oxide can catalyze PP or intumescent flame retardant to form char residue. Fe oxide on the surface of the char residue can protect the underlying substrate from further decomposition.

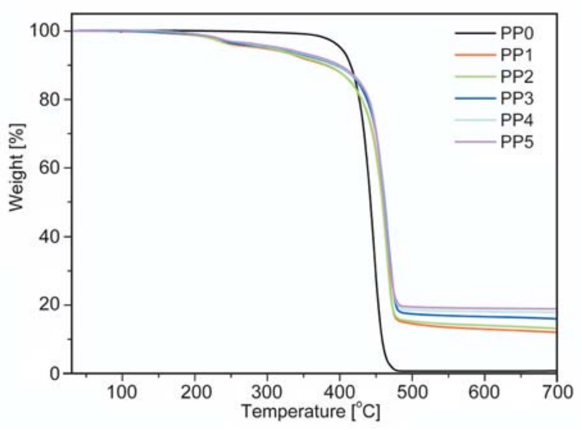

Figure 6. Thermal analysis curves of flame retardant PP

4. Conclusions

Flame retardant polypropylene composites were prepared by melt blending starting from APP, PER and Fe with the polymer matrix. The incorporation of Fe into IFR (APP+PER) leads to a remarkable influence on charring of PP formulations as revealed by TGA and CONE data. Cone data gives a measure of the size of the fire. It is confirmed that Fe acts as an effective additive functioning as flame retardant synergist. There is a synergistic effect occurred when Fe and IFR are both present in polypropylene composites.

Acknowledgements

The National Natural Science Foundation of China (No. 50876048) is gratefully acknowledged.

References

[1] Sen A. K., Mukherjee B., Bhattacharya A. S., Sanghi L., De K., P. P., Bhowmick A. K.: Preparation and characterization of low-halogen and nonhalgoen fire-resistant low-smoke (FRLS) cable sheathing compound from blends of functionalized polyolefins and PVC. Journal of Applied Polymer Science, **43**, 1673–1684 (1991).
DOI: 10.1002/app.1991.070430910

[2] Wittek T., Tanimoto T.: Mechanical properties and fire retardancy of bidirectional reinforced composite based on biodegradable starch resin and basalt fibres. Express Polymer Letters, **2**, 810–822 (2008).
DOI: 10.3144/expresspolymlett.2008.94

[3] Sanchez-Olivares G., Sanchez-Solis A., Camino G., Manero O.: Study on the combustion behavior of high impact polystyrene nanocomposites produced by different extrusion processes. Express Polymer Letters, **2**, 569–578 (2008).
DOI: 10.3144/expresspolymlett.2008.69

[4] Plentz R. S., Miotto M., Schneider E. E., Forte M. S. M. C., Mauler R. S., Nachtigall S. M. B.: Effect of a macromolecular coupling agent on the properties of aluminum hydroxide/PP composites. Journal of Applied Polymer Science, **101**, 1799–1805 (2006).
DOI: 10.1002/app.23558

[5] Hong C. H., Lee Y. B., Bae J. W., Jho J. Y., Nam B. U., Chang D-H., Yoon S. H., Lee K. J.: Tensile properties and stress whitening of polypropylene/polyolefin elastomer/magnesium hydroxide flame retardant composites for cable insulating application. Journal of Applied Polymer Science, **97**, 2311–2318 (2005).
DOI: 10.1002/app.21776

[6] Li B., Xu M. J.: Effect of a novel charring-foaming agent on flame retardancy and thermal degradation of intumescent flame retardant polypropylene. Polymer Degradation and Stability, **91**, 1380–1386 (2006).
DOI: 10.1016/j.polymdegradstab.2005.07.020

[7] Riva A., Camino G., Fomperie L., Amiqouët P.: Fire retardant mechanism in intumescent ethylene vinyl acetate compositions. Polymer Degradation and Stability, **82**, 341–346 (2003).
DOI: 10.1016/S0141-3910(03)00191-5

[8] Le Bras M., Bourbigot S., Christelle D., Siat C., Le Tallec Y.: New intumescent formulations of fire-retardant polypropylene-discussion of the free radical mechanism of the formation of carbonaceous protective material during the thermo-oxidative treatment of the additives. Fire and Materials, **20**, 191–203 (1996).
DOI: 10.1002/(SICI)1099-1018(199607)20:4<191::AID-FAM577>3.0.CO;2-S

[9] Almeras X., Le Bras M., Hornsby P., Bourbigot S., Marosi Gy., Keszei S., Poutch F.: Effect of fillers on the fire retardancy of intumescent polypropylene compounds. Polymer Degradation and Stability, **82**, 325–331 (2003).
DOI: 10.1016/S0141-3910(03)00187-3

[10] Almeras X., Le Bras M., Poutch F., Bourbigot S., Marosi G., Anna P.: Effect of fillers on fire retardancy of intumescent polypropylene blends. Macromolecular Symposia, **198**, 435–447 (2003).
DOI: 10.1002/masy.200350837

[11] Chen Y. H., Wang Q.: Preparation, properties and characterizations of halogen-free nitrogen-phosphorous flame-retarded glass fiber reinforced polyamide 6 composite. Polymer Degradation and Stability, **91**, 2003–2013 (2006).
DOI: 10.1016/j.polymdegradstab.2006.02.006

[12] Weil E. D., Levchik S.: Current practice and recent commercial developments in flame retardancy of polyamides. Journal of Fire Sciences, **22**, 251–264 (2004).
DOI: 10.1177/0734904104040546

[13] Camino G., Grassie N., McNeill I. C.: Influence of the fire retardant, ammonium polyphosphate on the thermal degradation of poly(methyl methacrylate). Journal of Polymer Science Part A: Polymer Chemistry, **16**, 95–106 (1978).
DOI: 10.1002/pol.1978.170160110

[14] Li B., Xu M. J.: Effect of a novel charringe-foaming agent on flame retardancy and thermal degradation of intumescent flame retardant. Polymer Degradation and Stability, **91**, 1380–1386 (2006).
DOI: 10.1016/j.polymdegradstab.2005.07.020

[15] Allen D. W., Edwyn C., Shiel L. E.: Structure-property relationships in intumescent fire retardant derivatives of 4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-1-oxide anderton. Polymer Degradation and Stability, **45**, 399–408 (1994).
DOI: 10.1016/0141-3910(94)90210-0

[16] Hu X-P., Li Y-L., Wang Y-Z.: Synergistic effect of the charring agent on the thermal and flame retardant properties of polyethylene. Macromolecular Materials and Engineering, **289**, 208–212 (2004).
DOI: 10.1002/mame.200300189

[17] Almeras X., Dabrowski F., Le Bras M., Delobel R., Bourbigot S., Marosi G., Anna P.: Using polyamide 6 as charring agent in intumescent polypropylene formulations. II. Thermal degradation. Polymer Degradation and Stability, **77**, 315–323 (2002).
DOI: 10.1016/S0141-3910(02)00066-6

[18] Demir H., Arkiş E., Balköse D., Ülkü S.: Synergistic effect of natural zeolites on flame retardant additives. Polymer Degradation and Stability, **89**, 478–483 (2005).
DOI: 10.1016/j.polymdegradstab.2005.01.028

[19] Bourbigot S., Le Bras M., Delobel R., Bréant P., Tremillon J. M.: 4A zeolite synergistic agent in new flame retardant intumescent formulations of polyethylenic polymers-study of the effect of the constituent monomers. Polymer Degradation and Stability, **54**, 275–287 (1996).
DOI: 10.1016/S0141-3910(96)00055-9

[20] Tang Y., Hu Y., Wang S. F., Gui Z., Chen Z. Y., Fan W. C.: Intumescent flame retardant-montmorillonite synergism in polypropylene-layered silicate nanocomposites. Polymer International, **52**, 1396–1400 (2003).
DOI: 10.1002/pi.1270

[21] Tang Y., Hu Y., Li B. G., Liu L., Wang Z. Z., Chen Z. Y., Fan W. C.: Polypropylene/montmorillonite nanocomposites and intumescent, flame-retardant montmorillonite synergism in polypropylene nanocomposites. Journal of Polymer Science Part A: Polymer Chemistry, **42**, 6163–6173 (2004).
DOI: 10.1002/pola.20432

[22] Ravadits I., Tóth A., Marosi G., Márton A., Szép A.: Organosilicon surface layer on polyolefins to achieve improved flame retardancy through an oxygen barrier effect. Polymer Degradation and Stability, **74**, 419–422 (2001).
DOI: 10.1016/S0141-3910(01)00179-3

[23] Marosi G., Márton A., Anna P., Bertalan G., Marosföi B., Szép A.: Ceramic precursor in flame retardant systems. Polymer Degradation and Stability, **77**, 259–265 (2002).
DOI: 10.1016/S0141-3910(02)00057-5

[24] Estevao L. R. M., Le Bras M., Delobel R., Nascimento R. S. V.: Spent refinery catalyst as a synergistic agent in intumescent formulations: Influence of the catalyst's particle size and constituents. Polymer Degradation and Stability, **88**, 444–455 (2005).
DOI: 10.1016/j.polymdegradstab.2004.11.016

[25] Wu Q., Qu B. J.: Synergistic effects of silicotungistic acid on intumescent flame-retardant polypropylene. Polymer Degradation and Stability, **74**, 255–261 (2001).
DOI: 10.1016/S0141-3910(01)00155-0

[26] Liu Y., Wang Q.: Catalytic action of phospho-tungstic acid in the synthesis of melamine salts of pentaerythritol phosphate and their synergistic effects in flame retarded polypropylene. Polymer Degradation and Stability, **91**, 2513–2519 (2006).
DOI: 10.1016/j.polymdegradstab.2006.03.009

[27] Li Y., Li B., Dai J., Jia H., Gao S..: Synergistic effects of lanthanum oxide on a novel intumescent flame retardant polypropylene system. Polymer Degradation and Stability, **93**, 9–16 (2008).
DOI: 10.1016/j.polymdegradstab.2007.11.002

[28] Li J. M., Wilkie C. A.: Improving the thermal stability of polystyrene by Friedel-Crafts chemistry. Polymer Degradation and Stability, **57**, 293–299 (1997).
DOI: 10.1016/S0141-3910(97)00013-X

[29] Zanetti M., Camino G., Thomann R., Mülhaupt R.: Synthesis and thermal behaviour of layered silicate-EVA nanocomposites. Polymer, **42**, 4501–4507 (2001).
DOI: 10.1016/S0032-3861(00)00775-8

[30] Cai Y. B., Hu Y., Song L., Xuan S. Y., Zhang Y., Chen Z. Y., Fan W. C.: Catalyzing carbonization function of ferric chloride based on acrylonitrile-butadiene-styrene copolymer/organophilic montmorillonite nanocomposites. Polymer Degradation and Stability, **92**, 490–496 (2007).
DOI: 10.1016/j.polymdegradstab.2006.08.029

[31] Zhang Y., Hu Y., Song L., Wu J., Fang S. L.: Influence of Fe-MMT on the fire retarding behavior and mechanical property of (ethylene-vinyl acetate copolymer/magnesium hydroxide) composite. Polymers for Advanced Technologies, **19**, 960–966 (2008).
DOI: 10.1002/pat.1059

[32] Zanetti M., Kashiwagi T., Falqui L., Camino G.: Cone calorimeter combustion and gasification studies of polymer layered silicate nanocomposites. Chemistry of Materials, **14**, 881–887 (2002).
DOI: 10.1021/cm011236k

[33] Gilman J. W., Jackson C. L., Morgan A. B., Harris R., Manias J. E., Giannelis E. P., Wuthenow M., Hilton D., Phillips S. H.: Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chemistry of Materials, **12**, 1866–1873 (2000).
DOI: 10.1021/cm0001760

[34] Chiu S-H., Wang W-K.: Dynamic flame retardancy of polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine additives. Polymer, **39**, 1951–1955 (1998).
DOI: 10.1016/S0032-3861(97)00492-8

[35] Dabrowski F., Le Bras M., Cartier L., Bourbigot S.: The use of clay in an EVA-based intumescent formulation. Comparison withthe intumescent formulation using polyamide-6 clay nanocomposite as carbonisation agent. Journal of Fire Sciences, **19**, 219–241 (2001).