

Polyamide 6에서 Cyclic Diphosphonate Ester와 Melamine의 난연 효과

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Flame Retardant Synergistic Performance between Cyclic Diphosphonate Ester and Melamine in Polyamide 6

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Abstract : A commercial cyclic diphosphonate ester (TPMP) and melamine (MA) was combined and added to polyamide 6 (PA6) to prepare the fire retardant PA6. An increase of the oxygen index to 28.6 as well as an improvement of the UL-94 classification to V-0 rating was observed. Cone measurements explained the rate of heat release (RHR) decreased and TGA showed the early decomposition and high solid residue due to co-addition of TPMP and MA, suggesting the occurrence of synergistic effect of TPMP and MA on fire resistance of PA6. The morphology of the char developed during combustion showed the appearance of thick, intumescent cells on the surface of retardant PA6, which protects the underlying material from the action of the heat flux or flame and limits the diffusion of combustible volatile products towards the flame and oxygen.

Keywords : polyamide 6, melamine, cyclic diphosphonate ester, flame retardancy.

Introduction

Polyamide has been widely used in electric and electronic industries and automotive production, where fire retardant properties of polymer are required, but neat polyamide is combustible. Addition of flame retardant agents to polymers could make them more difficult to ignite and suppress the propagation of flame.¹ Halogenated compounds have been approved to be effective for fire resistance. For example, decabromodiphenyl ether (DBE) was employed as a halogenated flame retardant to add into poly(propylene-graft-maleic anhydride) (PP-g-MA) and polyamide 6 (PA6) to impart flame resistance of these polymers.^{2,3} However, halogenated compounds are harmful to the environment and human health as decomposition. There is a tendency to use halogen free flame retardant in polymers. Among the non-halogenated flame retardants currently in use, one of the most commonly used classes for polymers is the phosphorus based flame retardants. In

polyamide and polyester, bisphenol A bis(diphenyl phosphate) showed moderate flame retardant efficiency.^{4,5} Phosphorus-nitrogen containing fire retardants were used to prepare flame retardant poly(butylene terephthalate).⁶ Mostly, these phosphorus-containing additives are usually combined with other compounds, such as melamine (MA) to generate the intumescent flame retardant system.^{7,8} For instance, a cyclic diphosphonate ester (TPMP) and melamine provided excellent fire retardant performance in poly(butylene terephthalate) (PBT).⁹

In this work, a commercial cyclic diphosphonate ester (TPMP) and melamine (MA) was added into polyamide 6 to prepare the fire resistant PA6. The combustion performance and decomposition characteristics of them was investigated.

Experimental

Materials. All the starting materials are commercially available. The cyclic diphosphonate ester (TPMP) was a commercial product under trade name Antiblaze 1045, with the chemical structure shown in Figure 1 polyamide 6 used with a melting

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flow index of 2.7 g/10 min was supplied by BASF kindly. The melamine (MA) was obtained from Shenzhen Meijie plastic additives company.

Preparation of Fire Retardant PA6 and Samples. The fire retardant PA6 was prepared by melt mixing of PA6 with TPMP and MA using a twin-screw extruder ($2 \times \Phi 25$ mm) at the temperature from 230~245 °C. The samples used for vertical burning rates and cone measurements were molded in an extruder machine.

Characterization and Measurements. The combustion performance of the formulations was studied by both the oxygen index test (limiting oxygen index, LOI) following the ASTM D 2863 standard and the vertical burning rates on a CZF-2 instrument according to UL-94 standard. Samples ($100 \times 100 \times 10$ mm³) were exposed to a Stanton Redcroft Cone Calorimeter according to 1194 ASTM 1356-90 under a heat flux of 50 kW/m². The solid residues of samples after burning at 400 °C for different time were investigated by FT-IR on Nicolet 20 sx B equipment. Scanning electron microscopy (Hitachi model JSM-5600LV) was employed to observe the residues of the formulations after burning. TGA was performed on Netzsch TG-209 from TA Company at the heating rate of 10 °C/min in a steady flow of 20 mL/min nitrogen.

Py-GC/MS analyses were carried out with GCMS-QP2010 produced by Shimadzu of Japan. The samples were pyrolyzed at 400 °C for 10 s. The carrier gas was helium at flow rate of 3.0 mL/min. The GC column temperature was initially held at 40 °C for 3 min; then at a rate of 10.0 °C/min, it was raised to 260 °C and held for 25 min. The GC-MS interface was set at 280 °C. Mass spectra were recorded under an electron impact ionization energy of 70 eV. The total flow was split at a ratio of 100 : 1. The mass of each sample was about 0.5 mg. The mass range was 20-600 amu.

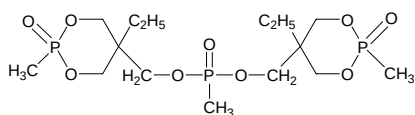


Figure 1. Chemical structure of TPMP.

Results and Discussion

The Dispersion of TPMP and MA in PA6. The preparation of fire retardant PA6 was performed by melt mixing through a twin-screw extruder. The dispersion of TPMP and MA in PA6 matrix was observed by SEM, as shown in Figure 2. The additives are generally dispersed well in PA6 matrix; the size of the dispersed particles is smaller than 0.5 micron.

The Flame Retardant Performance. From the Table 1, it is obvious that PA6 with a low LOI value (21.7) is easy to burn accompanied by heavy melt dripping. MA addition to PA6 decreases the burning time and slightly increase LOI to 24.1, the melt dripping could still secondly ignite. At the same time, it is noticed that the combination of TPMP and MA to PA6 is more efficient to prevent PA6 from burning than MA addition. Not only the burning time greatly reduced, but also the LOI value reaches 28.6. Furthermore the melt dripping does not secondly ignite, which leads to the flame retardance to v-0 rating. Therefore, it could be concluded that the co-addition of MA and TPMP apparently provide a synergistic effect on flame retardance. As a matter of fact, a similar compound, *N,N'*-bis(neopentyl phosphate)-piperazine, has been blend with PA6 to prepare the flame retardant products. However, the sole addition of this phosphorus and nitrogen contained flame retardant, even up to 20 wt%, could not improve the fire-resistance of PA6 to v-0 rating.¹⁰ Contrary, when the combination of TPMP and MA was added to PBT, the synergistic effect on flame retardance was found.⁹

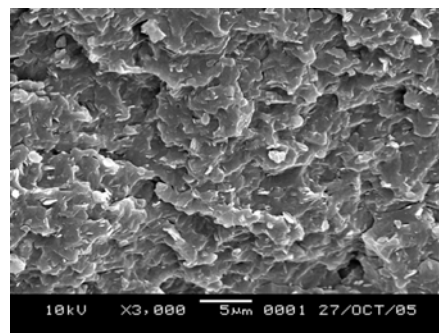


Figure 2. Dispersion of TPMP and MA in PA6.

Table 1. The Flame Retardant Behavior of the Blends

Formulations			UL 94						LOI
PA6 (wt%)	MA (wt%)	TPMP (wt%)	t_1 s	t_2 s	$t_1 + t_2$ s	Melt dripping	Secondly ignite	Flame-retardant rating	
100			11	6	17	+++	Yes	v-2	21.7
84	16		4	1	5	++	Yes	v-2	24.1
84	14	2	0	0	0	+	no	v-0	27.8
84	12	4	0	0	0	+	no	v-0	28.6

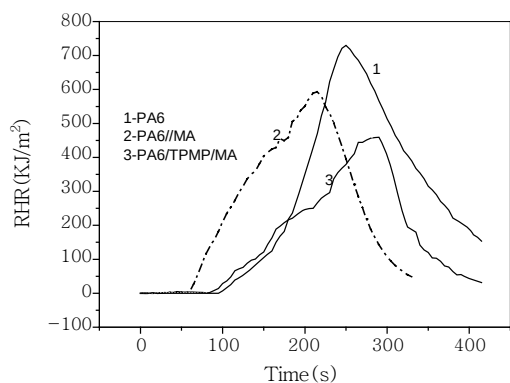


Figure 3. RHR values for different formulations.

Cone Measurements. The dependence of the rate of heat release (RHR) during burning on time is shown in Figure 3. It is found that the PA6/TPMP/MA exhibits the lowest RHR value while PA6 the highest RHR value, and the RHR of the PA6/MA locates in the middle position. But at the early stage of combustion the PA6/MA shows higher RHR, which may be ascribed to the early thermo-decomposition of MA. By comparison, the co-addition of TPMP and MA effectively reduces the increment of RHR value especially at the beginning of combustion. This is also an indication of synergistic action between TPMP and MA. This kind change of RHR shows a typical type of intumescent systems. That is, after ignition, there is an early and rapid additives degradation, and as a consequence an increase of RHR from thermo-degradation of additives; then the flame retardant products are produced and the expanded charred layer forms due to formation of intumescent cells, therefore decreases RHR. The RHR represents the evolution of energy flow versus time for a given sample combustion. The greater the peak RHR, the more heat the material could receive, and the quicker the material will decompose. Therefore, the reduction of RHR is equivalent to the resistance to fire.

Thermal Analysis. The TGA in Figure 4(a) shows that the TPMP compound is heat stable until 300 °C, which meets the need of melt mixing with thermoplastic polymers. Furthermore, the weight loss of TPMP becomes slower above 400 °C, which is the characteristic of self-resistance to fire due to the formation of flame retardant materials such as phosphoric acid salt etc.¹¹

The evolution of weight loss of different formulations on heating is given in Figure 4(b). Because of the early decomposition of TPMP and MA, both PA6/MA and PA6/TPMP/MA exhibit an earlier onset of heat decomposition and more weight loss before 400 °C. However, the PA6/TPMP/MA could almost keep weight constant above 400 °C and at last the remained residue from PA6/TPMP/MA is much greater than

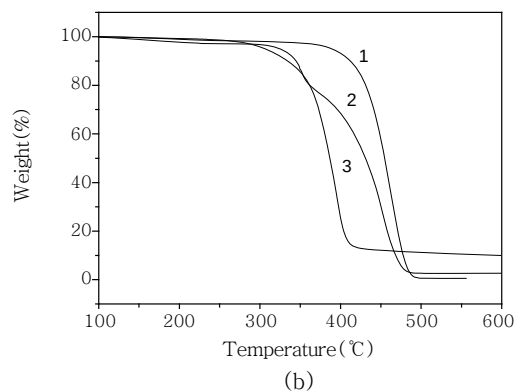
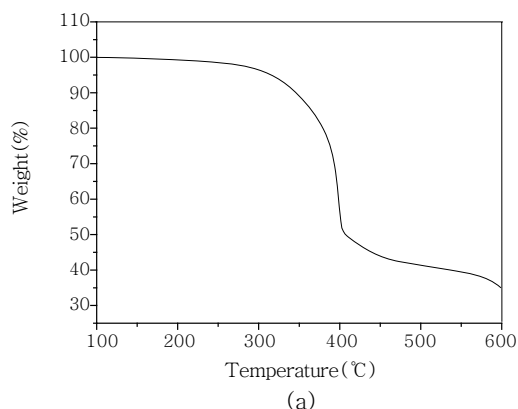


Figure 4. Thermal stability of different formulations. (a) TPMP and (b) 1 : PA6, 2 : PA6/MA, 3 : PA6/TPMP/MA.

that from both the PA6/MA and the neat PA6. For example, the solid residue from PA6/MA (the weight ratio of PA6 : MA=84 : 16) is about 2–3%, and that from the PA6/TPMP/MA is about 11–12%. In the formulation of PA6/TPMP/MA, the weight ratio of TPMP and MA is 4% and 12% respectively. This is an evidence of the interaction between TPMP and MA as well as between PA6 and additives.

Infrared Study during Combustion. The infrared spectrum of the initial formulation PA6/MA and PA6/TPMP/MA are shown in Figure 5. The typical absorptions of PA6 are 1640 cm^{-1} (C=O), 1262 cm^{-1} (C–NH), 3306 cm^{-1} , and 3082 cm^{-1} (NH), whereas the absorptions of MA are 3394, 1737, 1448 cm^{-1} (NH_2), the band at 814 cm^{-1} is the symmetric triazine ring. In the case of PA6/TPMP/MA, many bands of TPMP are covered by strong absorption of PA6 and MA. There have been extensive studies where the thermal decomposition products of PA6 were investigated. The formation of NH_3 , CO, CO_2 , and HCN has been reported,^{12,13} the presence of hexene nitrile and cyclopentanone was also found,¹¹ the mostly yielded product during the degradation of PA6 is ϵ -caprolactam which is a result of a cis-elimination of a six-membered intermediate of PA 6.¹⁴ The incorporation of TPMP

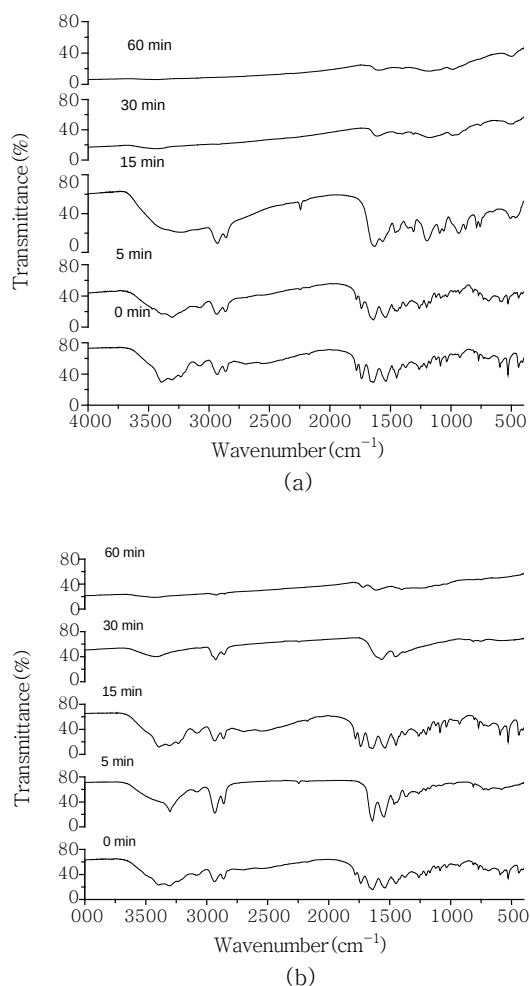


Figure 5. FT-IR spectra of residuals burned at 400 °C for varied time. (a) PA6/TPMP/MA and (b) PA6/MA.

could speed up the thermal decomposition, due to the production of methylphosphonic acid ($\text{CH}_3\text{H}_2\text{PO}_3$) from decomposition of TPMP.⁹ Hornung *et al.* studied the degradation of PA6 with H_3PO_4 as a catalyst. They found that acid catalysis with H_3PO_4 reduces the apparent activation energy by about 50 kJ mol^{-1} in comparison with the non-catalysis reaction and change the reaction order to a second order.¹⁴ In this way PA6 degradation takes place at lower temperature under phosphonic acid catalysis, as explained in Figure 6.

Actually, it is found from FT-IR spectra (Figure 5) that the formulation of PA6/TPMP/MA degrades more quickly than that of the PA6/MA. The band at 814 cm^{-1} in the PA6/TPMP/MA disappears on 15 min-degradation at 400 °C while vanished on 30 min in PA6/MA formulation. At the same time it is noticed that a new weak absorption at 782 cm^{-1} which is typical for melamine salts and their condensates appears instead in the PA6/TPMP/MA formulation as the band at 814 cm^{-1} disappears, and this band decreases

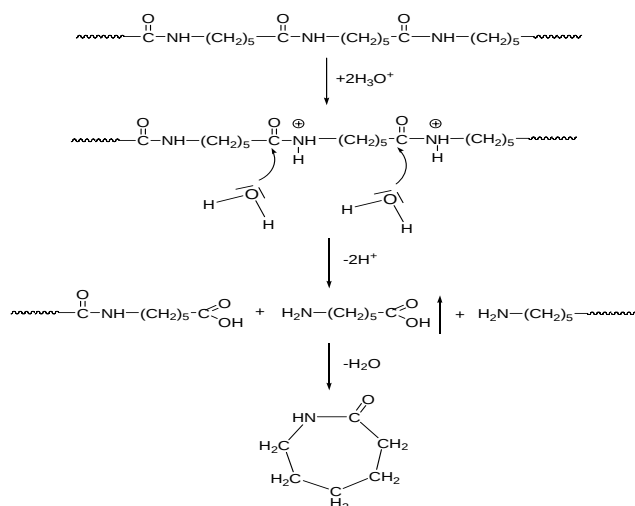


Figure 6. Schematic decomposition of PA6 in the presence of acid catalysis.

on further burning. There is almost no this absorption in the PA6/MA. This is the indication that methylphosphonic acid produced from TPMP reacts with MA, so melamine helps to increase the solid residue after the main step of weight loss. The similar result was also observed in the PBT/TPMP/MA formulation.⁹ A new absorption at 2232 cm^{-1} , which is typical of nitriles, appears on 5 min-burning for the PA6/TPMP/MA whereas on 15 min for the PA6/MA. Generally there are only some absorption patterns at $1300\text{--}900 \text{ cm}^{-1}$ which come from phosphoric/polyphosphoric acids and their ester after 30 min combustion at 400 °C in the PA6/TPMP/MA, while the bands at $2930, 2860, 1455 \text{ cm}^{-1}$, typical absorptions of CH_2 in caprolactam, still remain at that time in the case of PA6/MA. So the PA6/TPMP/MA decomposes more rapidly than the PA6/MA during burning.

GC/MS Analysis of Different Formulations. The gas chromatograms of the pyrolysis products of different formulations are given in Figure 7. After mass spectra analysis, the mostly yielded pyrolysis product with 15–16 min retention time is ϵ -caprolactam. By comparison, there are more varieties of products produced from the PA6/MA than that from the PA6/TPMP/MA during the combustion; on the other hand, the amount of ϵ -caprolactam released during burning from the PA6/TPMP/MA is much higher than that from the PA6/MA. This is coincidence with the observation from FT-IR, that is, TPMP could accelerate the thermal decomposition of PA6. At the same time, some gaseous NH_3 appeared from MA may combine with H_3PO_4 from the decomposition of TPMP to form salts, which may lead to less varieties of volatile products. Balabanovich *et al.* considered that formation of the phosphonic acid salts prevents volatilization of MA and promotes its

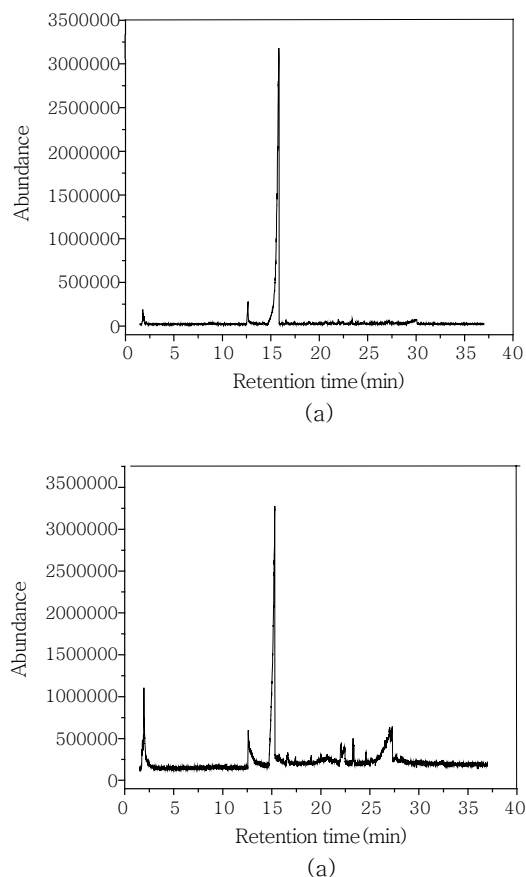


Figure 7. The gas chromatograms of the pyrolysis products for different formulations. (a) PA6/TPMP/MA and (b) PA6/MA.

condensation via amino groups.⁹ There is a strong absorption band appeared at 935 cm^{-1} on 15–30 min degradation of the PA6/TPMP/MA from the FT-IR in Figure 5, which matches the formation of phosphoric ammonium salts. The other possible products may be hexene nitrile, cyclopentanone, hexene acid amide, as well as dimers of PA6.¹¹

The Morphology of the Char Developed during Burning. SEM micrographs in Figure 8 show the morphologies of the residues of different formulations after combustion 30 min in air at $400\text{ }^{\circ}\text{C}$. The residue from the net PA6 is relatively smooth, no swelling and residual char is found (Figure 8(a)). While the residue from the blends shows different. The PA6/MA is very intumescent but very thin charred layer left after burning (Figure 8(b)). Thus, as it could be expected, both swelling and thick char is present in the residual of the PA6/TPMP/MA blend (Figure 8(c)), which may be ascribed to the synergistic of TPMP and MA. That is to say, MA not only acts as a gas resource producing inner gas NH_3 , but also helps to increase the solid residue through connection with TPMP; TPMP as a char-forming agent through rapid production of carbonaceous materials on the surface of PA6.⁶

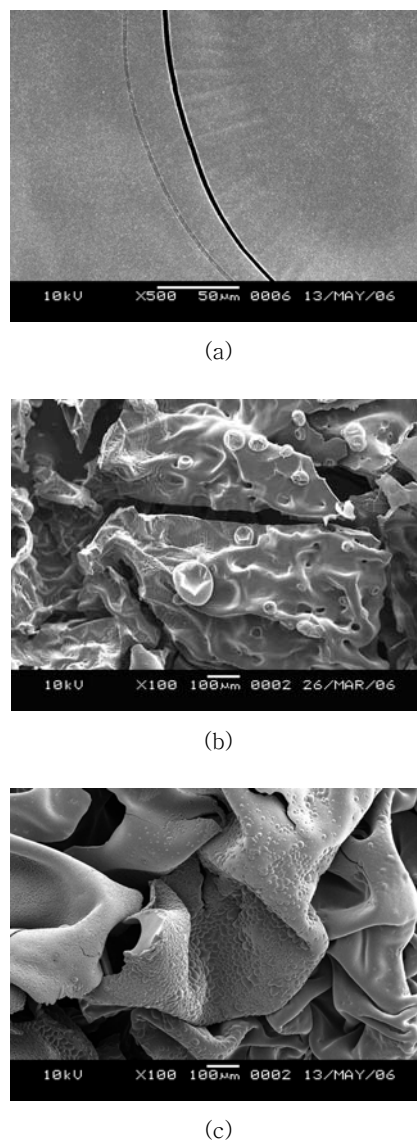


Figure 8. SEM micrographs of the solid residues from different formulations. (a) Neat PA6, (b) PA6/MA, and (c) PA6/TPMP/MA.

The Flame-Retardant Mechanism. It is likely that combination of TPMP and MA provides a dual mechanism of fire retardance action associated with the condensed and gas phases. In the condensed phase, interaction between TPMP and MA results in formation of phosphorus–nitrogen containing solid residue, even at relatively small yield can be very efficient to provide superior barrier between fire and the matrix polymer because of its glass-like performance.⁹ On the other hand, The inert gaseous NH_3 produced from the decomposition of MA and liberated water through the condensation of phosphoric acid to polyphosphoric acids could contribute to the fire retardant effect in the gas phase by diluting oxygen concentration. In addition, the produced phosphoric acid and liberated water could

speed the production of carbonaceous materials. These carbonaceous materials combined the yielded gas can quickly form swollen cells on the surface of PA6 material. In this way, the swollen char formed, which acts as an excellent thermal insulator between the underlying materials and heat, prevents the temperature of the substrate from rising under a fire situation.

Conclusions

Melamine could slightly improve the fire retardancy of PA6: LOI rises from 21.7 to 24.2 at 16% loading and V-2 rating is achieved in the UL94 test. Co-addition of MA and TPMP leads to a strong increase of the LOI to 28.6 and help to attain a v-0 rating in the UL94 test. The change of the rate of heat release (RHR) with burning time also shows the improved flame retardance while MA and TPMP was jointly added into PA 6. Through TGA and FT-IR analysis, it has been revealed that the synergistic performance of TPMP and MA should be owing to the combination which provides a dual mechanism of fire retardance action associated with the condensed and gas phases.

References

1. F. L. Fire, *Combustability of Plastics—Flame Retardant and Flame Retarded Plastics*, Van Nostrand Reinhold Publication, New York, 1991.
2. M. Zanetti, G. Camino, D. Canavese, A. B. Morgan, F. J. Lamelas, and C. A. Wilkie, *Chem. Mater.*, **14**, 189 (2002).
3. H. Wang, Z. Ling, Y. Zhuang, Z. Chen, and W. Fan, *Macromol. Mater. Eng.*, **288**, 272 (2003).
4. S. V. Levchik, G. F. Levchik, and E. A. Murashko, *et al.*, "Fire and Polymers, Materials and Solutions from Hazard Prevention", *ACS Symposium Series*, ACS, Washington, DC, Vol **797**, p 214 (2001).
5. A. I. Balabanovich, *J. Anal. Appl. Pyrol.*, **72**, 229 (2004).
6. G. F. Levchik, Grigoriev Yu V., A. I. Balabanovich, S. V. Levchik, and M. Klatt, *Polym. Int.*, **49**, 1095 (2000).
7. Y. Tang, Y. Hu, S. Wang, Z. Gui, Z. Chen, and W. Fan, *Polym. Int.*, **52**, 1396 (2003).
8. L. Songa and Y. Hu, *Polym. Degrad. Stabil.*, **86**, 535 (2004).
9. A. I. Balabanovich, G. F. Levchik, S. V. Levchik, and J. Engelmann, *J. Fire Sci.*, **20**, 71 (2002).
10. J. Jin, T. Lin, and J. Jiang, *Journal of Donghua University (Chinese Edition)*, **32**, 7 (2006).
11. M. Herrera, M. Wilhelm, G. Matuschek, and A. Kettrup, *J. Anal. Appl. Pyrol.*, **58**, 173 (2001).
12. M. Nielsen, P. Jurasek, J. Hayashi, and E. Furimsky, *J. Anal. Appl. Pyrol.*, **35**, 43 (1995).
13. S. V. Levchik, L. Costa, and G. Camino, *Polym. Degrad. Stabil.*, **36**, 229 (1992).
14. H. Bockhorn, S. Donner, M. Gernsbeck, A. Hornung, and U. Hornung, *J. Anal. Appl. Pyrol.*, **58**, 79 (2001).