The Effect of Adjuvant on the Halogen-Free Intumescent Flame Retardant ABS/PA6/SMA/APP Blend

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ABSTRACT: The adjuvant of organic bentonite (OBT), zinc oxide (ZnO), zeolite 4A (4A), aluminum phosphinate (AlPi), terephthaloyl-biscaprolactam (TBC), 2,2′-bis(2-oxazoline) (BOZ), and manganese dioxide (MnO_2) on flame retardant enhancement of acrylonitrile-butadiene-styrene copolymer (ABS)/polyamide 6 (PA6)/styrene-maleic anhydride (SMA)/ammonium polyphosphate (APP) blends were investigated by using the limiting oxygen index (LOI), the UL-94 (vertical flame) test, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The LOI datas and vertical flame tests showed that the synergistic flame retardant effect of OBT, ZnO, 4A, AlPi, BOZ, and MnO_2 on the ABS/PA6/SMA/APP blend was good, and the LOI value of ABS/PA6/SMA/APP/MnO_2 (55/15/5/25/2) system was 33% and class V-0 of UL-94 test was passed. The TGA data demonstrated that the incorporation of adjuvant was known to improve the fire properties essentially accompanied by only minor changes in thermal decomposition. The strong influence of oxygen on the thermal degradation of the ABS/PA6/SMA/APP system, and the oxygen could modify the carbonaceous structure. The microstructures observed by SEM indicated that the adjuvant can promote formation of compact intumescent inorganic-carbonaceous char layers in ABS/PA6/SMA/APP blends. Furthermore, the effects of adjuvant on the mechanical properties of ABS/PA6/SMA/APP blends were also investigated. The Izod impact strength of the ABS/PA6/SMA/APP/Adj composite showed a little depressing. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1552–1560, 2010

Key words: adjuvant; synergistic; intumescent flame retardant; ABS/PA6/SMA/APP blend

INTRODUCTION

Flammable materials were protected from fire through an intumescence process that has been known for several years. Intumescent technology, as a method to provide flame retardancy for polymeric materials, has found a place in polymer science.[1,2] During heating, the fire retardant intumescent materials form a foamed cellular charred layer on their surfaces, which protects the underlying materials from the action of heat flux and flame. The proposed mechanism is based on the fact that the charred layer acts as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phase.[3] Many investigations have been focused on the intumescent flame retardants (IFR) not only because they are more environment friendly than the traditional halogen-containing flame retardants but also more efficient than inorganic flame retardants, such as metal hydroxides.[4,5] Generally, intumescent flame retardants contain three ingredients[6]: an acid source (phosphate, borate), a carbonization agent (polyols), and a blowing agent (melamine, isocyanurate). The common carbonization agents in intumescent flame retardants system are polyols, such as pentaerythritol, mannitol or sorbitol.[7,8] However, these additives are confronted with the problems of exudation and water solubility. Furthermore, they are not compatible with the polymeric matrix, which weakens the mechanical properties of the material. Using oxygen-containing polymers as the carbonization agents, not only can avoid the problems of exudation and water solubility but also improve mechanical properties of the material. It was shown that incorporating ammonium polyphosphate (APP) in polyamide 6 (PA6) enables fire properties of materials to be obtained.[9,10] What's more, studies have focused on intumescent flame retardant for polyolefins by using charring polymers polyamide6 (PA6) as the carbonization agent.[11–16] In this work, various adjuvants were employed to investigate the synergistic effect of adjuvant on the thermal stability and flame retardancy of ABS/PA6/SMA/APP blend.
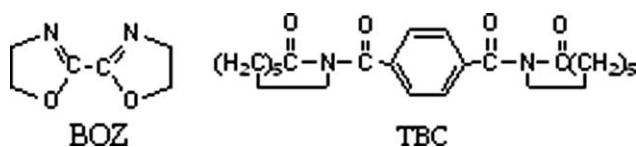
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EXPERIMENTAL

Materials

Acrylonitrile-butadiene-styrene copolymer (ABS) (0215A) was provided by Jilin Petrochemical

Scheme 1 The chemical structure of BOZ and TBC.

Corporation, the A : B : S ratio was 28.4 : 16 : 55.6, People's Republic of China. Polyamide 6 (PA6) was obtained from Yueyang Petrochemical Corporation (China); ammonium polyphosphate (APP) $[(NH_4PO_3)_n n = 1500]$ was supplied by Zhejiang Longyou Gede Chemical Factory (China); organic bentonite (OBT) (DK-1) was prepared from sodium montmorillonite by ion exchange reaction using hexadecyl trimethyl ammonium bromide (C16) in water, zinc oxide, zeolite 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and manganese dioxide were supplied by Chengdu Kelong Co., China; aluminum phosphinate {$Al(H_2PO_2)_3$} was supplied by Qingzhou Yichao Co., China; terephthaloylbiscaprolactam and 2,2'-bis(2-oxazoline) were prepared by our library, the chemical structure are reported in Scheme 1; styrene-maleic anhydride (SMA) (M14) was supplied by Shanghai Speed Petrochemical Hi-Tech Corporation (China), the molar concentration of MA is $9 \pm 2\%$.

Measurement M_n of PA6

The viscosity measurement of PA6 was conducted at $25.0 \pm 0.1°C$ in an Ubbelhode-type viscometer, PA6 was dissolved in m-cresol at the concentration of 0.005 g/mL (C). The intrinsic viscosity was calculated by using the Solomon–Ciuta[17] equation for a single-point measurement:

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{0.5}/C \qquad (1)$$

where η_{sp} is the relative viscosity increment and η_r is relative viscosity.

The number-average molecular weight (M_n) of the PA6 was calculated from the $[\eta]$ values using the Mark–Houwink equation:

$$[\eta] = K(M_n)^a \qquad (2)$$

where M_n is the number-average molecular weight and K and a are empirical constants which is 18×10^{-4} and 0.654 for PA6 at 25°C, respectively.[18] The intrinsic viscosity of PA6 was 1.632 dL/g which was calculated from the above eq. (1). Then from the above intrinsic viscosity value, we can estimate the M_n of the PA6 was 33,270.

Chain extension of polyamide 6 in a Haake mixer

Fifty grams of well-dried PA6 pellets and antioxidant were added into the mixing chamber of a Haake Rheocord mixer. The rotor speed was set as 50 rpm, and the temperature was set at 240°C. When the melting temperature reached 240°C, the chain extender was added to the PA6 melt. The melt torque was recorded during mixing to measure the extent of the reaction.

Preparation of flame-retarded ABS/PA6/SMA/APP/Adj alloys

Extrusion of the alloy was performed on a corotating twin-screw extruder with the screw having a diameter of 25 mm and L/D ratio of 33. A mixture of ABS, PA6, SMA, APP, adjuvant (ratio 55/15/5/25/2), and antioxidant were fed to the twin-screw extruder with screw speed of 110 rpm and barrel temperatures of 170, 190, 230, 230, 230, and 225°C. The extrudate was cooled by water and pelletized. The flame-retarded ABS/PA6/SMA/APP/Adj pellets were dried at 90°C for 16 h and injection molded into sheets of suitable thickness in an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co), sheet size and thickness were dependent on the testing methods used. The compositions of the different compounds are listed in Table I.

Limit oxygen index (LOI) and UL-94 test

The LOI value was measured using a XYC-75 instrument (Chengde, China) on sheets $120 \times 6 \times 3$ mm^3

TABLE I
Components of Flame-Retardant Systems Employed in this Work

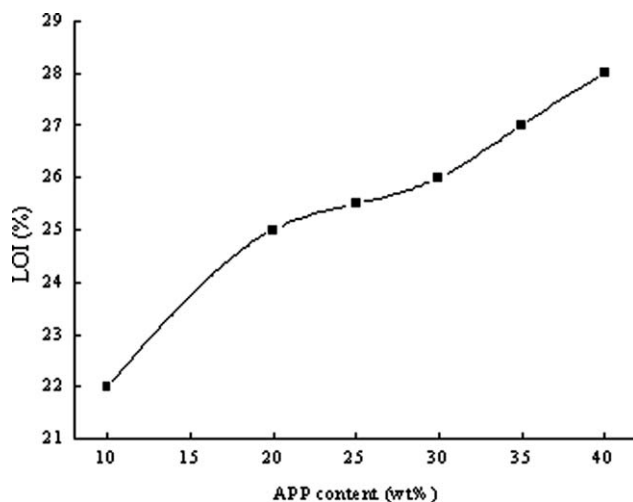| | ABS/PA6/SMA/APP | Composition (%) | | | | | | |
		OBT	ZnO	Ze 4A	AlPi	TBC	BOZ	MnO$_2$
1#	55/15/5/25	–	–	–	–	–	–	–
2#	55/15/5/25	2						
3#	55/15/5/25		2					
4#	55/15/5/25			2				
5#	55/15/5/25				2			
6#	55/15/5/25					2		
7#	55/15/5/25						2	
8#	55/15/5/25							2

Figure 1 Effect of APP content on flame retardance of ABS.

according to the standard oxygen index test ASTM D2863-77. The vertical test was measured on sheets $127 \times 12.7 \times 3$ mm^3 according to the UL-94 test ASTM D635-77.

Thermogravimetry (TG) analysis

Sample (about 8 mg) was examined under air and nitrogen flow on a Netzsch STA 449C thermobalance with Al$_2$O$_3$ sample holders, at a heating rate of 10°C/min from 100 to 800°C, and the flow rate was 50 mL/min.

Scanning electron microscope (SEM) analysis

The morphology of the char obtained after the LOI test was observed by using a HITACHI X-650 scanning electron microscope (SEM) at ×300 magnification. The specimens were previously coated with a conductive gold layer.

Mechanical properties analysis

Tensile and flexural tests were carried out according to the GB/T1040-92 and GB/T9341-88 methods by using an AG-10TA Universal Testing Machine. Izod impact strength tests were performed by UJ-40 impact-testing machine based on GB/T1843-1996 method.

RESULTS AND DISCUSSION

Evaluation of flammability

In this article, ABS resin compounded with different amounts of ammonium polyphosphate (APP) was studied. For all the composites, the LOI values and the classes of UL-94 tests were measured; the results are shown in Figure 1. As can be seem from Figure 1, the LOI values of composites became larger as the increase of the amount of APP. When the APP content reached 40 wt %, the LOI value of ABS/APP mixture was 28%. The above results indicated that the APP plays an important role in flame retardant system. However, the ABS/APP mixture with 40 wt % APP had no V-classification in the UL-94 tests. Although the LOI value of ABS/PA6/SMA/APP (ratio 55/15/5/25) was 28.5%, it was much better than that of ABS/APP (ratio 75/25) mixture. This is because the charring of Polyamide (PA6) acts as a physical barrier during the burning process, which slows down heat and mass transfer between the gas and the condensed phase. The mixture still has no V-classification in the UL-94 tests.

For obtaining better flame retardancy of the flame-retarded ABS/PA6/SMA/APP alloys, organic bentonite (OBT), zinc oxide (ZnO), zeolite 4A (4A), aluminum phosphinate (AlPi), terephthaloyl-biscaprolactam (TBC), 2,2′-bis(2-oxazoline) (BOZ) and manganese dioxide (MnO$_2$) were added as adjuvant into this system. The LOI values and UL-94 classes of flame-retarded ABS/PA6/SMA/APP alloys with different adjuvant are listed in Table II. As can be seen from Table II, the flame retardancy of ABS/PA6/SMA/APP blend was greatly improved after the incorporation of adjuvant, except TBC. When the content of adjuvant was 2 wt %, the adjuvant, such as OBT, AlPi, BOZ, and MnO$_2$ were incorporated into ABS/PA6/SMA/APP alloy, there was a significant increase for the flame retardancy. They were all identified as V-0 in the UL-94 test, and the LOI values were found to be 32, 31, 30, and 33, respectively. The UL-94 tests for ABS/PA6/SMA/APP/ZnO or ABS/PA6/SMA/APP/4A flame-retardant mixtures were identified as V-1, and the LOI value could both reach 31%. However, when 2 wt % TBC was added to the ABS/PA6/SMA/APP alloys, the flame retardancy of the system did not improve significantly, the LOI value only reached 29% and the mixture had no V-classification in the UL-94 tests.

TABLE II
Flame Retardant of Different Systems

	1#	2#	3#	4#	5#	6#	7#	8#
LO I (%)	28.5	32	31	31	31	29	30	33
UL-94	no V-classification	V-0	V-1	V-1	V-0	no V-classification	V-0	V-0

TABLE III
TGA Data for Different Systems

Sample	$T_{onset}/°C$	$CT_p/°C$	$R_{max}\,\%/°C$
ABS	387.3	440.3	20.3
1#	335.5	432.6	12.9
2#	345.4	430.1	15.2
3#	348.0	437.3	13.6
4#	341.2	427.5	13.4
5#	329.8	434.7	13.4
6#	333.4	432.6	14.8
7#	340.2	438.2	14.1
8#	331.9	443.9	13.2

T_{onset} represents the temperature at which mass loss is 5 wt %; T_p represents the temperature at the peak in DTG curve; R_{max} represents the loss rate at the peak in DTG curve.

Thermal behavior of ABS/PA6/SMA/APP/Adj alloys

According to the mechanism of intumescent flame retardance, flame-retardant intumescent materials will swell and form a dense and swollen char layer on the surface of the materials during the burning process, which slows down the heat and mass transfer between the gas and the condensed phase and protects the underlying materials from heat flux or flame. Therefore, the flame retardant effect of IFR was directly affected by the formation of charred layers and charred residues. For this reason, TGA was adopted to study the behavior of mass loss and char formed in different composites during heating.[19] To investigate whether there was any synergistic effect on the thermal stability of ABS/PA6/SMA/APP alloys under air condition, adjuvant was incorporated into ABS/PA6/SMA/APP alloys. The results are given in Table III and Figures 2 to 8. The adjuvant was used to improve the fire properties essentially accompanied by only minor changes in thermal decomposition. The addition of additional 2
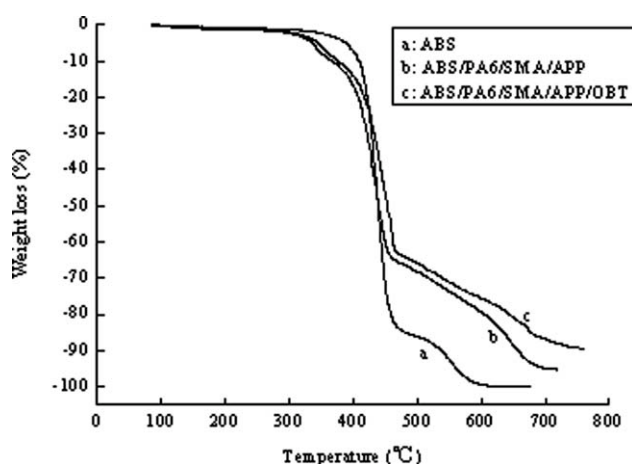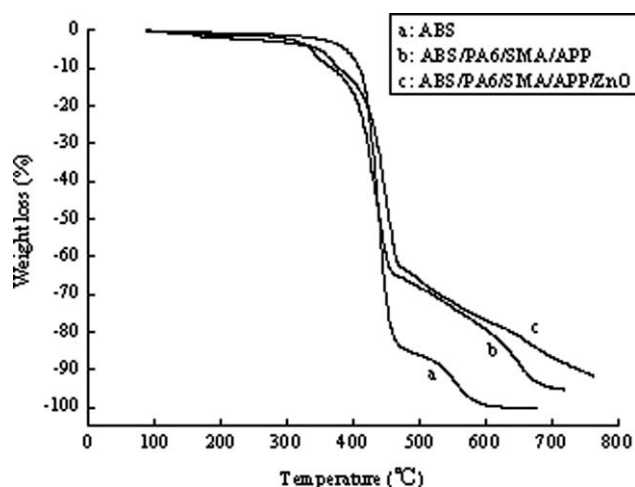

Figure 3 TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/ZnO mixture under air condition.

wt % adjuvant resulted in tiny changes in residue. Above 500°C, the amount of carbonaceous residue of ABS/PA6/SMA/APP/Adj was also a little more than that of ABS/PA6/SMA/APP system. This implies that there are interactions and reactions between adjuvant and ABS/PA6/SMA/APP. They may form a structure which can block their degradation products within the coating, and therefore, decrease the degradation rate of the system. As shown in Table III, the onset temperature of thermal degradation (T_{onset}) of ABS/PA6/SMA/APP composite was greatly decreased compared with pure ABS, which was because APP could catalyze the PA6 decompose. Furthermore, from Table III, one can see that when 2 wt % AlPi was added to ABS/PA6/SMA/APP system, compared with that of ABS/PA6/SMA/APP, the T_{onset} decreased by 5.7°C, however, when 2 wt % ZnO was added to ABS/PA6/SMA/APP blend, the T_{onset} increased by 12.5°C. The R_{max} of ABS/PA6/SMA/APP/Adj was
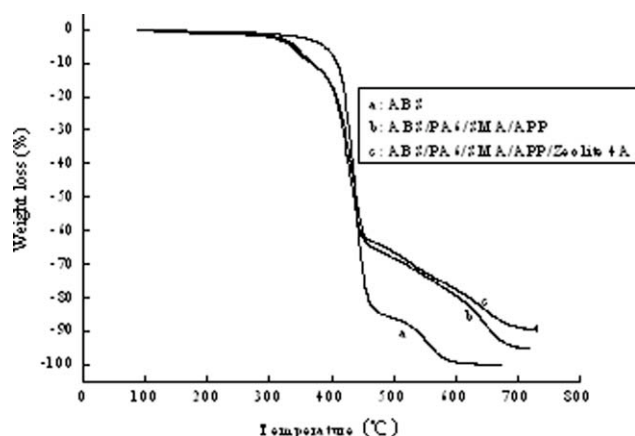

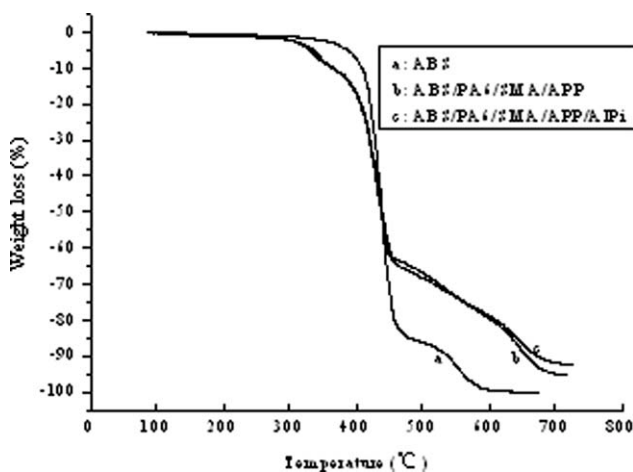**Figure 2** TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/OBT mixture under air condition.

Figure 4 TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/Zeolite 4A mixture under air condition.

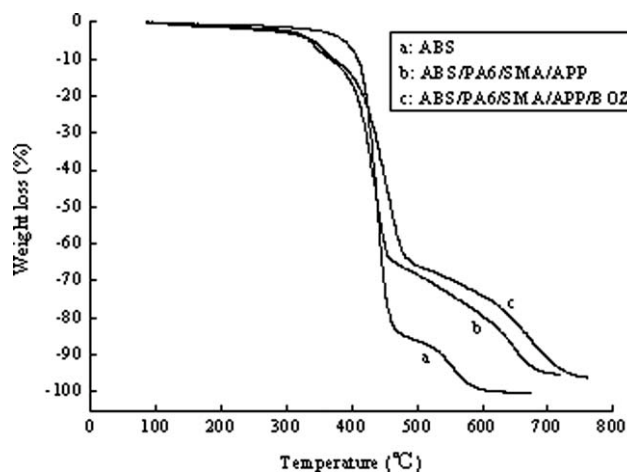**Figure 5** TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/AlPi mixture under air condition.

a little higher than that of ABS/PA6/SMA/APP mixture. As can be seen from Figure 9 (cure a), the inorganic-carbonaceous char of ABS/PA6/SMA/APP composite reached 5.2% when the temperature was 700°C under air condition. Previous studies showed that the carbonization process of the APP/PA6 system occurs via four steps,[20] and it may be adopted to explain our system. After 230°C, the APP can react with PA6 and form phosphate esters. The development of intumescence occurs between 280 and 350°C and the intumescent coating degrades between 350 and 430°C. At higher temperatures, there were structural changes leading to the formation of a new carbonaceous species (established in the temperature range of $430°C < T < 560°C$) up to 430°C, which may be interpreted as above. Then a plateau is observed between 430–560°C. This plateau may be assigned to a particular protective "carbon". Finally, the curve decreases at higher temperature. There is modification of the carbonaceous structure

which is no longer protective and the formation of a "high temperature" residue (about 5.2 wt % at 700°C), which can be seem from Figure 9 (cure a). However, under nitrogen, the beginning T_{onset} of ABS/PA6/SMA/APP was higher (about 369.8°C), and the degradation process of ABS/PA6/SMA/APP was quite different. The degradation was quite fast between 350 and 500°C, above 500°C, the degradation was almost completed. This showed the strong influence of oxygen on the thermal degradation of the ABS/PA6/SMA/APP system, and the oxygen could modify the carbonaceous structure. Furthermore, under nitrogen, above 500°C, the amount of carbonaceous residue of ABS/PA6/SMA/APP/Adj was also a little more than that of ABS/PA6/SMA/APP blend.

It had been reported that the layer silicate can form a barrier layer hindering the diffusion of gasses during the burn process.[21] Furthermore, the acidic proton resulted from the thermal decomposition of
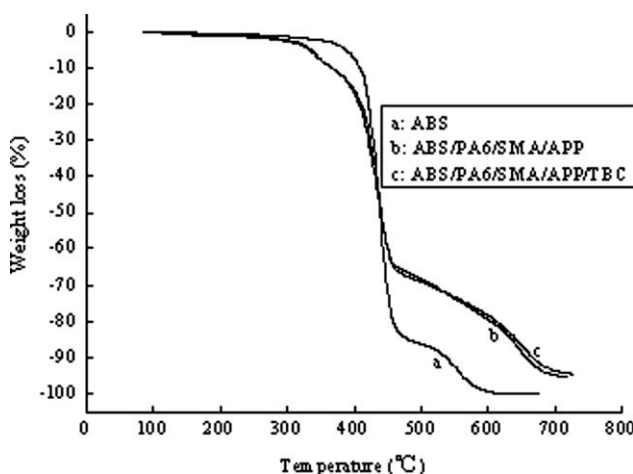

Figure 7 TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/BOZ mixture under air condition.

Figure 6 TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/TBC mixture under air condition.
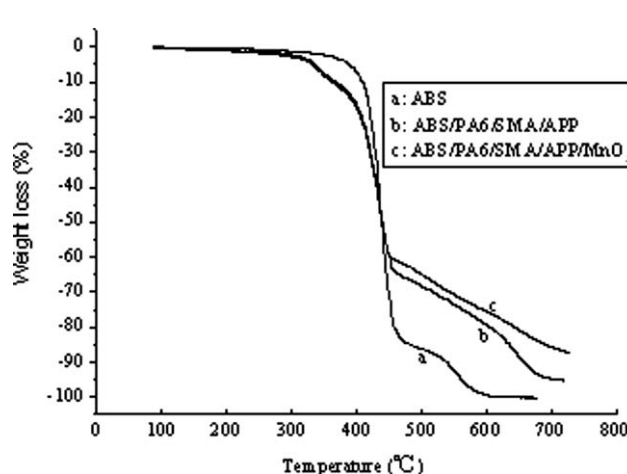

Figure 8 TGA curves of ABS, ABS/PA6/SMA/APP, and ABS/PA6/SMA/APP/MnO mixture under air condition.
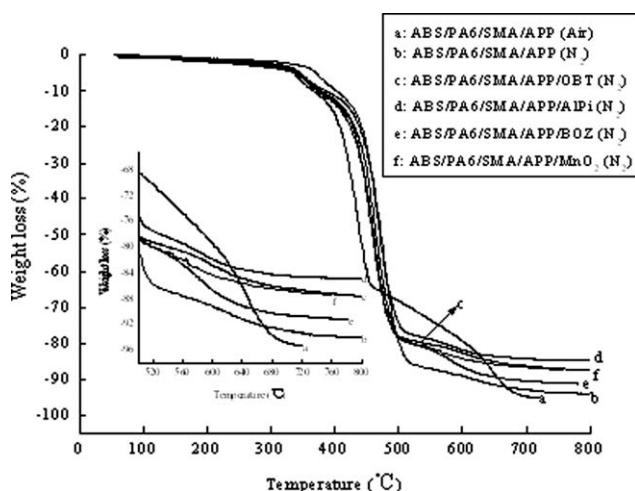
Figure 9 TGA curves of ABS/PA6/SMA/APP and ABS/PA6/SMA/APP/Adj mixture under air and nitrogen condition.

the OBT,[22] could promote condensed phosphoric acid which produced by the elimination of NH_3 from APP reacting with PA6 to form phosphoric ester, and finally to form the carbon–carbon unsaturations, leading to the enhancement in thermal stabilization.

It was reported by Lewin[23] that the divalent metal ions (Mn or Zn) can be generated in the intermolecular crosslink of APP. Based on this, the zinc ion may react with two monomeric phosphate groups, releasing two ammonia and two water molecules and producing a bridge between APP chains, which can be seem in Scheme 2. The formation of a small number of such bridges will bring about the stabilization of the APP and the decrease in the volatility of the phosphorus, and thus more will be available for phosphorylation and char formation. The crosslinks will, in effect, increase the degree of polymerization of the APP, which will nevertheless remain reactive. The increase of the molecular weight will increase the viscosity of the melt during pyrolysis and combustion and thus decrease its rate of flow to combustion surface and improve the barrier effect of the char.[24]

Zeolites are a class of important inorganic materials with a framework of $[SiO_4]$ and $[AlO_4]$ tetrahedral linked to each other at the corners by sharing
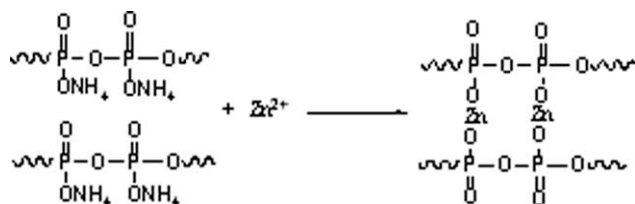
Scheme 2 Possible reaction of zinc with hydroxyl.

their oxygen atoms. The zeolite 4A promote the catalytic esterification of flame-retarded ABS/PA6/SMA/APP alloys, improve the "quality" of intumescent coating by "trapping" polymer links (via the formation of stable aluminosilicophosphate esters) into the structure and make flame-retarded ABS/PA6/SMA/APP alloys possess higher flame-retardant performance.[25]

It can be seen from Table III that the T_{onset} of ABS/PA6/SMA/APP/AlPi was lower than that of ABS/PA6/SMA/APP system, which indicated that the AlPi could promote the degradation of PA6, for the possible reason that AlPi could react with the carboxyl terminal of PA6, forming phosphoric acid, aluminum phosphate and phosphine. The phosphoric acid could dehydrate the nylon molecular and form the char easily. Aluminum phosphate can act as an inorganic glass, which improves the thermal shielding effect and creates proper protection of the char from thermo-oxidation at higher temperature. In our extrusion experimental, we could see combustion phenomenon take place in the extruder, and we suppose the gas is phosphine.

It is easy for oxazoline group to react with carboxylic acid, phenols, amines, amides and so on. Hence, it is widely used in the modification of the polymer. Akkapeddi and Gervasi[26] have suggested that the terephthaloyl-biscaprolactam (TBC) can be reacted with amine end-groups of PA6 through two possible mechanisms, that were, ring opening and elimination of caprolactam. The oxazoline groups can react with carboxyl terminal groups through addition reactions. These reactions led first to monesteramide and then to diesteramide. To compare our chain extension results, first, a blank run (control) was performed with PA6 alone and the initial melt torque of PA6 was recorded. Figure 10 showed an abrupt increase in the value of the melt torque of PA6 for
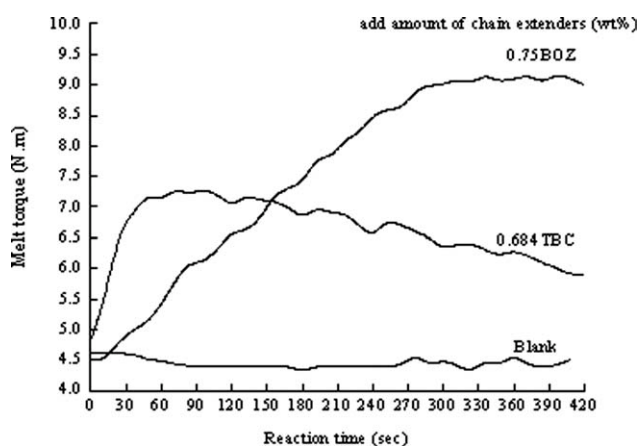

Figure 10 Effect of different amounts of chain extenders on meltorque of PA6 after mixing at 240°C and 50 c/min, for 420 sec.
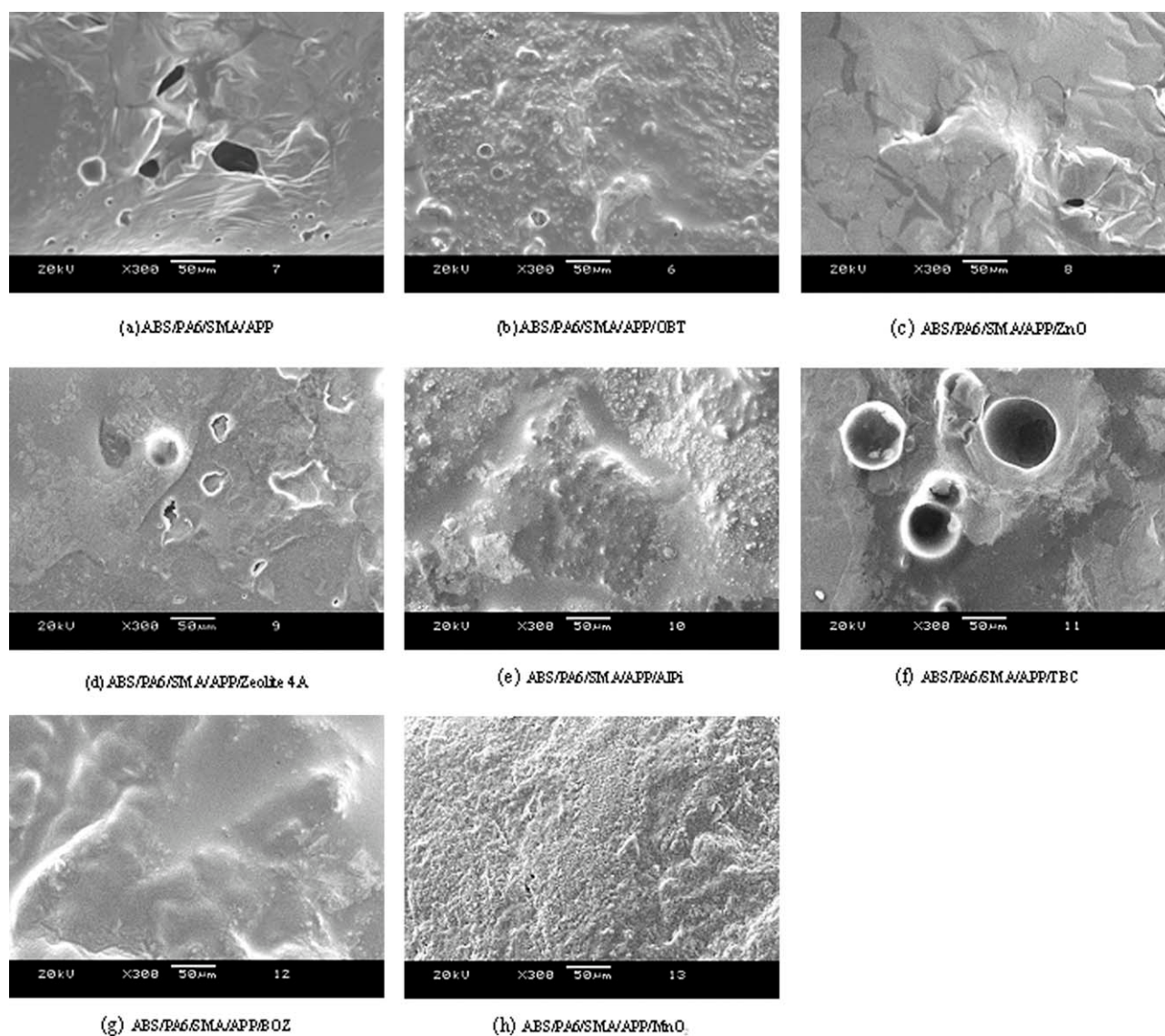
Figure 11 SEM pictures of surface structure of char.

various amounts of added chain extender. This was caused by the chain extension reaction. The reaction of BOZ with carboxyl group led to the increase of the molecular weight of PA6 during combustion. The higher the molecular weight of PA6, the higher the melt strength of PA6. Thus, the formed char layer of the system could be better foamed under pyrolytic gas during the burn process, leading to the formation of a thicker char structure, which decreased its rate of flow to combustion surface and improved the barrier effect of the char. At the same time, the BOZ could function as electron donor to absorb the active free radical and terminate the free radical reaction. Although the TBC could also react with the amine groups of PA6 to increase the melt strength of PA6, the flame results did not improve obviously. This was due to the reaction between TBC and amine groups of PA6 was reversible, which

can be seen in Figure 10, and the degree of reverse reaction may depend on the temperature. Although the melt strength of PA6 increased because of the reaction between TBC and amine groups of PA6, the dissociating reaction can be in a dominant position during the burn process. Hence, the quality of charred layer did not improve significantly.

The interaction between MnO_2 and APP starts at 270–280°C which corresponds to the beginning of thermal decomposition of APP. Pure $Mn(IV)O_2$ loses O_2 into $Mn(II)O$ at 470–530°C, whereas APP or phosphorus acid species catalyze $Mn(IV)O_2$ reduction, since at 350°C Mn(IV) already completely transforms to managanese(II)-ammonium polyphosphate $Mn(NH_4)_2(PO_3)_4$ and managanese(II)-ammonium cyclotriphosphate $MnNH_4P_3O_9$. On further heating, $Mn(NH_4)_2(PO_3)_4$ completely transforms to the $MnNH_4P_3O_9$ which was more thermostable, whereas

TABLE IV
Mechanical Properties of ABS/PA6/SMA/APP and ABS/PA6/SMA/APP/Adj Alloys

Sample	Izod impact strength (KJ/m^2)	Flexural strength (MPa)	Flexural module (MPa)	Tensile strength (MPa)
1#	2.7	60.8	2570.3	42.2
2#	1.9	63.7	3295.7	41.3
5#	1.9	61.9	2720.6	43.9
7#	1.9	56.0	2422.6	39.9
8#	2.3	59.6	2539.5	41.2

above 570°C managanese phosphate (inorganic) glass was formed. The inorganic glass improved the morphology of the char and its thermal shielding effect, and created proper protection of the char from thermo-oxidation at higher temperature.[27]

Scanning electron microscopy (SEM)

The SEM photographs of the morphological structures of the inorganic-carbonaceous char of the above system also prove the better charring performance of ABS/PA6/SMA/APP/Adj blends compared with that of the ABS/PA6/SMA/APP mixture. The scanning electron micrographs of chars from the various fire samples are given in Figure 11. It can be seen obviously that the ABS/PA6/SMA/APP system was porous because the inorganic-carbonaceous char layer could be easily broken by the pyrolytic gas during the burn process. Hence, it could not prevent heat and mass transferring between the gas and the condensed phase effectively. When compared with ABS/PA6/SMA/APP/ZnO, or Zeolite 4A, the number of cavities and holes decreases, and the sizes of holes shrink. Furthermore, it can be seen that the ABS/PA6/SMA/APP/OBT, AlPi, BOZ and MnO$_2$ systems had a good, foamed, coherent and dense, char structure, to some degree, which can serve as a barrier to O$_2$ supply and the pyrolytic gas, protecting the underlying material from the action of the heat flux or the flame during the burn process. On the contrary, the inorganic-carbonaceous char layer of the ABS/PA6/SMA/APP/TBC system was porous, which may explain why the flame retardancy of ABS/PA6/SMA/APP/TBC system was weak. Hence, the inorganic-carbonaceous char was a stable, coherent and dense char structure that played an important role in improving the flame retardancy of ABS/PA6/SMA/APP/Adj blends.

Mechanical properties

Poor mechanical property is a common problem for current flame retardant materials. Hence, how to increase and improve the mechanical properties,

which are made worse largely by adding flame retardant to polymer matrix, is becoming an unavoidable research topic. The influences of adjuvant on the mechanical properties of ABS/PA6/SMA/APP composite are summarized in Table IV. The Izod impact strength of the ABS/PA6/SMA/APP/Adj blends showed a little depressing due to the weak surface polarity of adjuvant and poor compatibility between adjuvant and ABS resin. However, the flexural strength, flexural module and tensile strength of ABS/PA6/SMA/APP/Adj were almost keep constant, or showed a little increment.

CONCLUSIONS

In this work the flame retardancy of ABS/PA6/SMA/APP blend was greatly improved after the incorporation of adjuvant, when 2 wt % adjuvant, such as OBT, AlPi, BOZ, and MnO$_2$ were incorporated into ABS/PA6/SMA/APP alloys, they were all identified as V-0 in the UL-94 test, and the LOI values were found to be 32, 31, 30, and 33, respectively. The addition of additional 2 wt % adjuvant resulted in tiny changes in residue. The strong influence of oxygen on the thermal degradation of the ABS/PA6/SMA/APP system, and the oxygen could modify the carbonaceous structure. The adjuvant can act as a very efficient catalyzer and promote formation of compact intumescent charred layers in ABS/PA6/SMA/APP blends. The expanded, coherent and dense inorganic-carbonaceous char layer formed after burning was observed by scanning electron microscopy (SEM).

References

1. Montaudo, G.; Scamporino, E.; Vitalini, D. J. J Polym Sci Polym Chem 1983, 21, 3361.
2. Wang, J. Q. Basis and Application of Halogen-Free Flame Retardant Polymers [M]; Chemical Industrial Press: Beijing, 2005; pp 49–93.
3. Bourbigot, S.; Le Bras, M.; Delobel, R. J Fire Sci 1995, 13, 3.
4. Velasco, J. I.; Morhain, C.; Martinez, A. B.; Rodriguez-Perez, M. A.; Saja, J. A. Polymer 2002, 43, 6813.
5. Li, Z. Z.; Qu, B. J. Polym Degrad Stab 2003, 81, 401.
6. Le Bras, M.; Bourbigot, S. J Mater Sci 1999, 34, 5777.
7. Le Bras, M.; Bourbigot, S.; Delporte, C.; Siat, C.; Tallec, Y. L. Fire Mater 1996, 20, 191.
8. Le Bras, M.; Bourbigot, S.; Tallec, Y. L.; Laureyns, J. Polym Degrad Stab 1997, 56, 11.
9. Levchik, S. V.; Costa, L.; Camino, G. Polym Degrad Stab 1992, 36, 229.
10. Riva, A.; Camino, G.; Fomperie, L.; Amigouet, P. Polym Degrad Stab 2003, 82, 341.
11. Bourbigot, S.; Le Bras, M.; Dabrowski, F.; Cilman, J. W.; Kashiwagi., T. Fire Mater 2000, 24, 201.
12. L, K. R.; Lu, Z. J. J Polym Mater Sci Eng 1999, 15, 59.
13. Lu, X. D.; Zhang, J.; Gu, H. M.; Wang, C. C. Plastics 2006, 35, 18.
14. Almeras, X.; Le Bras, M.; Poutch, F.; Bourbigot, S.; Marosi, G.; Anna, P. Macromol Symp 2003, 198, 435.

15. Almeras, X.; Renaut, N.; Jama, C.; Le Bras, M.; Tóth, A.; Bourbigot, S.; Marosi, G.y; Poutch, F. J Appl Polym Sci 2004, 93, 402.
16. Almeras, X.; Dabrowski, F.; Le Bras, M.; Delobel, M.; Bourbigot, S.; Marosi, G.y; Anna, P. Polym Degrad Stab 2002, 77, 315.
17. Karayannidis, G. P.; Psalida, E. A. J Appl Polym Sci 2000, 77, 2206.
18. Fukunmoto, M. Polyamide Resin Handbook; China Petrochemistry Publishing Co.: Beijing, China, 1994.
19. Almeras, X.; Le, Bras, M.; Hornsby, P.; Bourbigot, S. Polym Degrad Stab 2003, 82, 325.
20. Delobel, R.; Le Bras, M.; Ouassou, N.; Alistiqsa, F. Polym Degrad Stab 1990, 30, 41.
21. Xia, Y.; Jian, X.; Li, J. F.; Wang, X. H. Polym Plast Technol 2007, 46, 227.
22. Xie, W.; Gao, Z. M.; Pan, W. P.; Hunter, D.; Singh, A.; Vaia, R. Chem Mater 2001, 13, 2979.
23. Lewin, M.; Le Bras, M.; Camino, G. In Fire Retardancy of Polymeric Materials; 1999; pp 1–32.
24. Lewin, M.; Endo, M. Polym Advan Technol 2003, 14, 3.
25. Xia, Y.; Liu, S.; Wang, X.; Han, Y.; Li, J.; Jian, X. Polym Plast Technol 2008, 47, 613.
26. Akkapeddi, M. K.; Gervasi, J. Polym Prep 1988, 29, 567.
27. Levchik, S. V.; Levchik, G. F.; Camino, G.; Costa, L.; Lesnikovich, A. L. Fire Mater 1996, 20, 183.