

# Flame-Retardant and Smoke-Suppressant Properties of Zinc Borate and Aluminum Trihydrate-Filled Rigid PVC

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**ABSTRACT:** The effects of zinc borate (ZB), aluminum trihydrate (ATH), and their mixture on the flame-retardant and smoke-suppressant properties of poly(vinyl chloride) (PVC) as well as their mechanism for flame retardancy and smoke suppression were studied through the limiting oxygen index (LOI) test, smoke density test, TGA, GC-MS, and SEM. The results show that incorporation of a small amount of ZB, ATH, and their mixture can greatly increase the LOI of PVC and reduce the smoke density of PVC during combustion. The mixture of ZB with ATH has a good synergistic effect on the flame retardance and smoke suppression of PVC. TGA and GC-MS analyses results show that incorporation of a small amount of ZB, ATH, and their mixture greatly promotes the char formation of PVC and decreases the amount of hazardous gases such as benzene and toluene released in PVC during combustion. Their mechanism is also proposed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3119–3127, 2000

**Key words:** PVC; aluminum trihydrate; zinc borate; smoke suppression; flame retardance

## INTRODUCTION

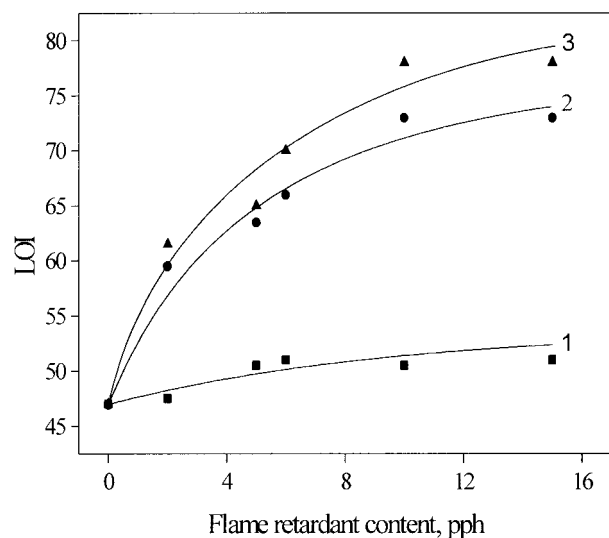
It is well known that poly(vinyl chloride) (PVC) has a high chlorine content, so it is an incombustible material. Because of its high level of combustion resistance, PVC has been widely applied as a covering insulation for electrical and communication cables and in domestic uses such as in gutters, window frames, doors, and house sidings. However, it is more and more recognized that PVC is not a safe material due to its production of much smoke and toxic gases (i.e., chlorine compounds, benzene, and other aromatic compounds) during burning. Smoke suppression during combustion of PVC is getting more and more atten-

tion. Additives used to reduce the flammability and smoke formation of PVC have been studied and reported.<sup>1–13</sup> The additives include compounds containing antimony, tin, zinc, copper, iron, and molybdenum, etc., while the most important commercial smoke suppressants are zinc and molybdenum compounds. Many of these investigations have been aimed at the effects of these compounds on the flame retardancy and smoke suppression of PVC as well as on the chemistry of PVC decomposition.<sup>14–16</sup> Zinc borate (ZB) has a unique function of being both a fire retardant and a smoke suppressant of PVC,<sup>17,18</sup> but there is little evidence on how ZB increases char residue and decreases smoke formation. To enhance the smoke-suppression efficiency of ZB and to improve the thermal stability of ZB-filled PVC, the synergistic effect of the combination of ZB and aluminum trihydrate on the flame retardancy, smoke suppression, and thermal degradation kinetics of PVC and its mechanism were studied in

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**Figure 1** Effects of ATH, ZB, and ZB-ATH contents on LOI of PVC.

this article. The toxic gases released during the burning of PVC were detected through GC-MS. The char formation and the morphology of the condensed phase after combustion of PVC were also investigated.

## EXPERIMENTAL

### Materials and Sample Preparation

The materials used were PVC-S700 (Shangdong Qilu Petrochemical Co., Zibo, Shangdong-China) with a number-average molecular weight of  $4.49 \times 10^4$ ; a mercaptide organotin heat-stabilizer thermolite 175 (Beijing Elf Autochem Polystab Co. Ltd., Beijing, China), ZB ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ), and aluminum trihydrate (ATH; Hebei Hongxing Chemicals Co., Cang Zhou City, China).

Samples were prepared by mixing PVC with ZB, ATH, and a certain amount of the mercaptide organotin heat stabilizer and lubricants, then blending them in a two-roller at  $170^\circ\text{C}$  for 10 min and compression molding them at  $180^\circ\text{C}$ . The test specimens were cut from the molded sheets.

### Measurements and Characterization

Limiting oxygen index (LOI) values were determined with an LOI1045 instrument (Atlas Electric Devices Co., USA) according to the ASTM D2863 method. Smoke-density measurements were made with an LOI1045 smoke-density

equipment by the ASTM E-662 method. Smoke density ( $D_s$ ) is calculated by the following equation:

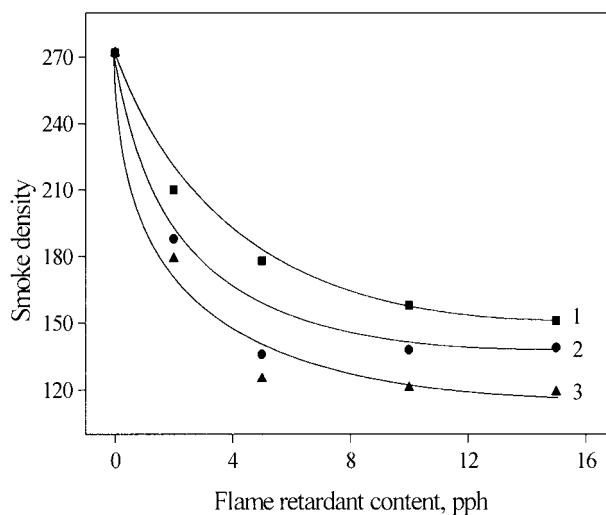
$$D_s = 132 \times \log(100/T_m)$$

where  $T_m$  is the percent transmittance at maximum smoke density.

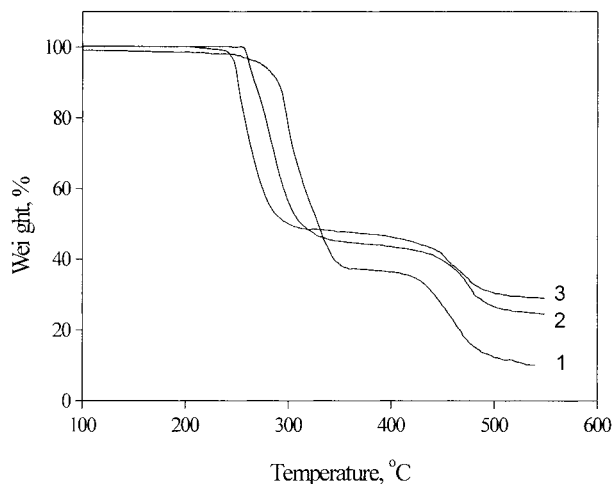
Thermal degradation behavior was measured with a DuPont 2000 TGA instrument under  $N_2$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Weight-loss curves of ZB- and ATH-filled PVC were recorded from room temperature to  $600^\circ\text{C}$ .

A certain amount of PVC and PVC/ZB-ATH (a mixture of ZB with ATH) was weighed and the weights based on PVC in the samples are equal. The samples were decomposed in air at  $600^\circ\text{C}$ . The toxic gases released under air pyrolysis of PVC at  $600^\circ\text{C}$  were dissolved in 100 mL of ethanol, then detected with an HP5890II gas chromatograph and an HP5972 mass spectrometer (Hewlett-Packard Co., USA). Nitrogen and helium were used as carrier gases in GC and MS, respectively. According to the relative intensity of the peaks, the relative content of toxic gases released from PVC and PVC/ZB-ATH could be measured so as to study the mechanism for smoke suppression of ZB-ATH.

PVC and PVC/ZB-ATH films were decomposed in air at  $250^\circ\text{C}$  for 5 min. The ultraviolet absorption spectra of the decomposed films were recorded with a ultraviolet-visible UV-240 spectrophotometer (Shimadzu Corp., Japan) so as to in-



**Figure 2** Effects of ATH, ZB, and ZB-ATH contents on smoke density of PVC.



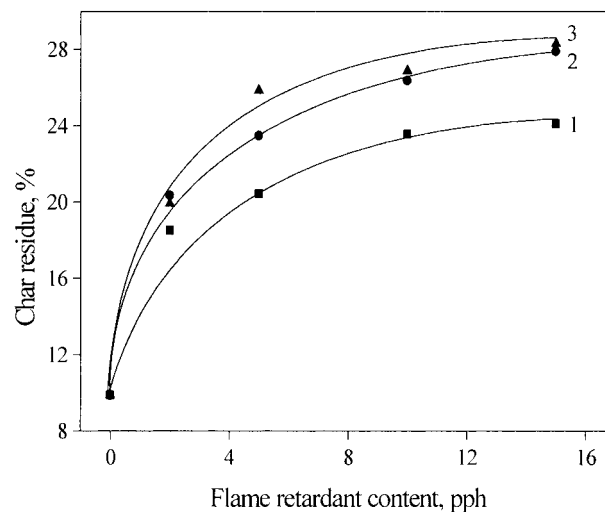
**Figure 3** TGA curves of PVC and PVC/ZB-ATH.

investigate the conjugated polyene structure formed during decomposition.

The morphology of char formed after combustion of PVC in a spirit lamp was observed through an SEM-X650 (Hitachi Co., Japan). Before observation, the surfaces of char were covered with silver. The char residue after combustion of PVC is calculated by following equation:

$$\text{Char residue} = w_2/w_1 \times 100\%$$

where  $w_1$  and  $w_2$  are the weights of PVC before combustion and the residue after combustion of PVC, respectively.



**Figure 4** Effects of ATH, ZB, and ZB-ATH contents on char residue of PVC.

## RESULTS AND DISCUSSION

### Flame Retardance and Smoke Suppression

As shown in Figures 1 and 2, the LOI of PVC increases and smoke density decreases with increase of the amount of ZB, ATH, and ZB-ATH. The LOI of PVC/ZB-ATH is much higher than that of PVC/ZB and PVC/ATH. The smoke density of PVC/ZB-ATH is much lower than that of PVC/ZB and PVC/ATH, which indicates that ZB and ATH have a good synergistic effect on the flame retardancy and smoke density of PVC.

**Table I** TGA Results of PVC and PVC/ZB-ATH

Stages	PVC	PVC/ZB (100/5)	PVC/ZB-ATH (100/5)	PVC/ZB-ATH (100/15)
First stage				
Onset (°C)	281	237	257	245
Inflection (°C)	300	246	286	254
Completion (°C)	340	294	310	290
Weight loss (%)	62.8	58.5 <sup>a</sup>	55.9 <sup>a</sup>	52.3 <sup>a</sup>
Max weight loss rate	14.2	11.4	11.5	15.0
Second stage				
Onset (°C)	421	437	450	433
Inflection (°C)	459	457	489	461
Completion (°C)	494	484	495	489
Weight loss (%)	26.7	18.0 <sup>a</sup>	20.4 <sup>a</sup>	19.1 <sup>a</sup>
Max weight loss rate	4.5	2.7	3.5	3.0
Char residue (%)	10.5	23.6 <sup>a</sup>	23.7 <sup>a</sup>	28.6 <sup>a</sup>

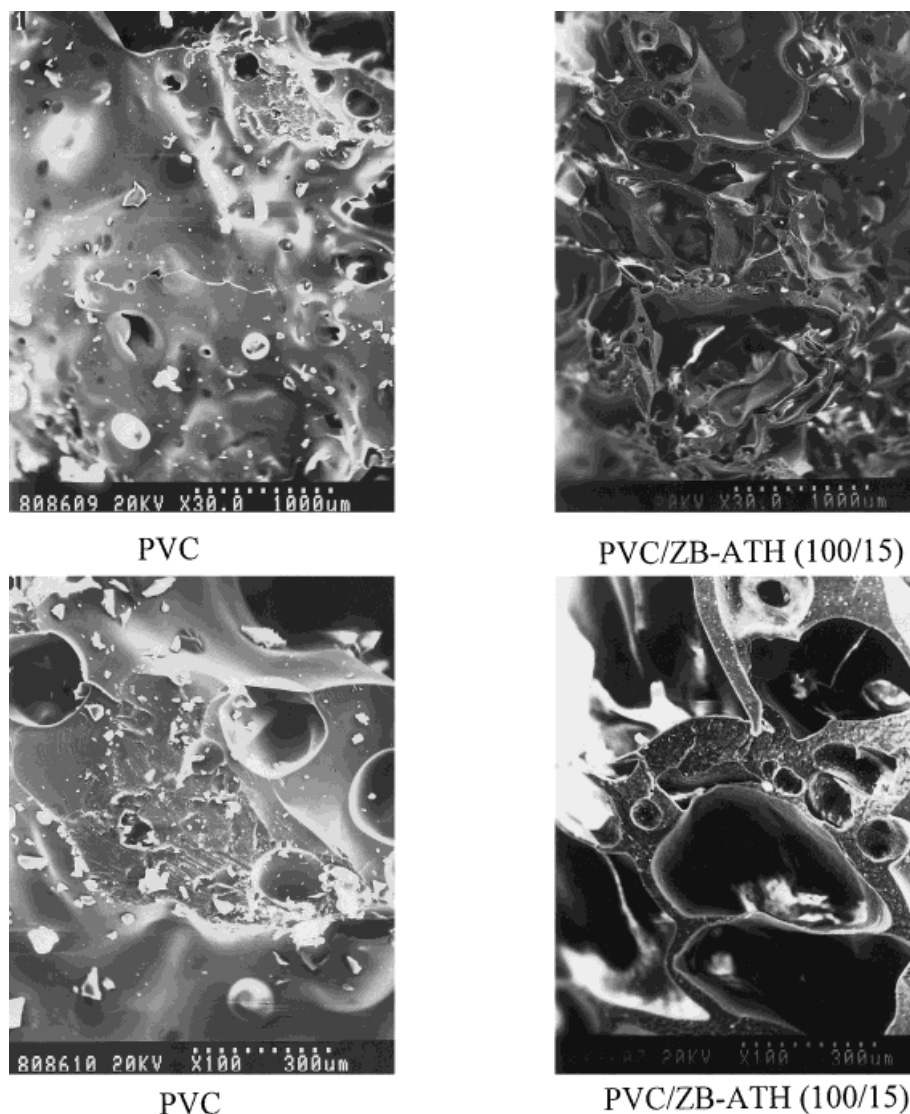
<sup>a</sup> The numbers are on the basis of the PVC involved.

**Table II TGA Linear Regression and Iterative Method Results of PVC and PVC/ZB-ATH**

Samples	Method					
	Linear Regression			Iterative Method		
	$E$ (kJ/mol)	$n$	Relative Coefficient	$E$ (kJ/mol)	$n$	Relative Coefficient
PVC	388.4	4.77	0.995	336.4	4.02	0.999
PVC/ZB (100/5)	169.1	1.84	0.997	154.1	1.54	0.999
PVC/ZB-ATH (100/5)	152.3	1.63	0.995	140.0	1.44	0.999
PVC/ZB-ATH (100/15)	130.0	1.48	0.999	110.0	1.49	0.999

As shown in Figure 3, the thermal decomposition of PVC is divided into two stages: The thermal decomposition in the first stage is mainly the

evolution of hydrogen chloride. The thermal decomposition in the second stage is mainly the cyclization of conjugated polyene sequences to

**Figure 5** SEM micrographs of PVC and PVC/ZB-ATH.

form aromatic compounds. Incorporation of small amounts of ZB and ZB-ATH reduces the thermal decomposition temperature in the first stage, while it increases the thermal decomposition temperature in the second stage. The data listed in Table I show that incorporation of a small amount of ZB and ZB-ATH greatly decreases the weight loss of the PVC thermal decomposition. The char residue of PVC increases by about 130% after incorporation of 5 pph of ZB and ZB-ATH, respectively, also indicating that ZB and ZB-ATH are good smoke suppressants for PVC. The data listed in Table I also indicate that the thermal degradation temperature of PVC/ZB-ATH (100/5) is much higher than that of PVC/ZB, revealing that the thermal stability of PVC/ZB becomes greatly improved in the presence of ATH.

PVC, PVC/ZB, PVC/ATH, and PVC/ZB-ATH samples were combusted in air in a spirit lamp and the char residue was calculated (Fig. 4). The char residue increases as the contents of ZB, ATH, and ZB-ATH increase. The char residue in PVC/ZB-ATH is higher than that in PVC/ZB and in PVC/ATH, indicating the good synergistic effect of ZB and ATH on the smoke suppression of PVC. The char residue of PVC/ZB-ATH (100/5) amounts to 25.9%, which is consistent with the TGA result (23.7%). From these results, it can be concluded that the increase in the char residue is consistent with the decrease in smoke formation.

The thermal degradation kinetics of PVC was studied using the TGA results. It obeys the following equation:

$$d\alpha/dt = k(1 - \alpha)^n$$

$$k = A \exp(-E/RT)$$

$$d\alpha/dt = A \exp(-E/RT)(1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the ratio of PVC thermodegradation at time  $t$ ;  $k$ , a kinetic constant;  $n$ , the reaction order; and  $E$ , the activation energy for thermal degradation.

Because the heating rate  $\beta$  is a constant and equals  $dT/dt$ ,  $dt$  equals  $dT/\beta$ . If  $dt$  in eq. (1) is replaced by  $dT/\beta$ , then eq. (1) converts to

$$d\alpha/dT = (A/\beta)\exp(-E/RT)(1 - \alpha)^n \quad (2)$$

$$\ln(d\alpha/dT) = \ln(A/\beta) - E/RT + n \ln(1 - \alpha) \quad (3)$$

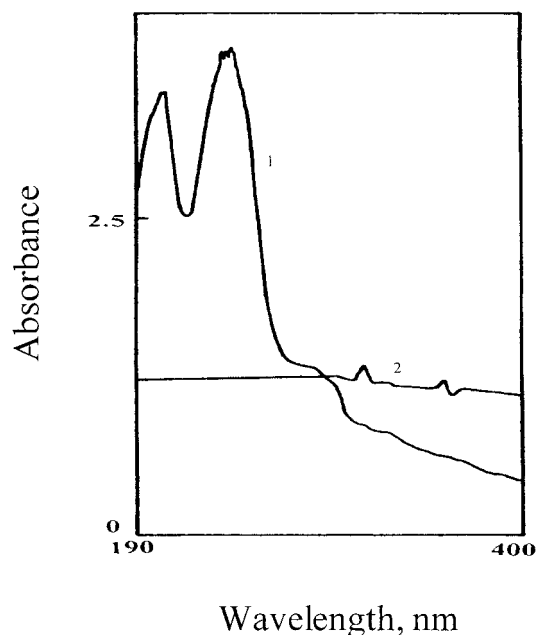
$$\Delta \ln(d\alpha/dT) = -E/R\Delta(1/T) + n\Delta \ln(1 - \alpha) \quad (4)$$

$$\Delta \ln(d\alpha/dT)/\Delta \ln(1 - \alpha)$$

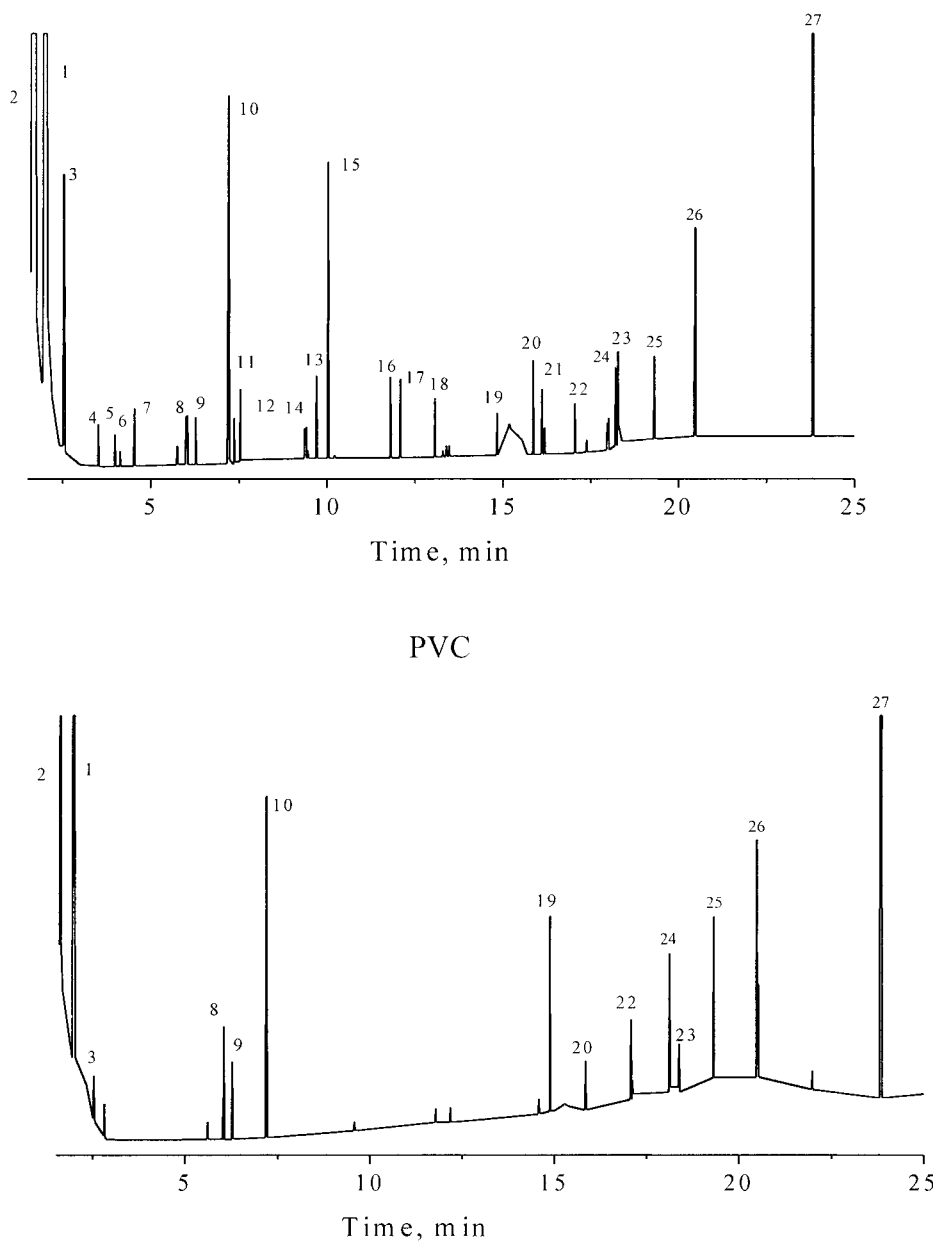
$$= -E/R[\Delta(1/T)/\Delta \ln(1 - \alpha)] + n \quad (5)$$

The kinetic parameters for thermal degradation of PVC can be calculated through linear regression according to eq. (5) and iteration according to eq. (3). The results are listed in Table II. The relative coefficient for linear regression and iteration is a very important parameter to evaluate whether the equation could describe the thermal degradation kinetics. In general, if the relative coefficient is larger than 0.95, the thermal degradation kinetics of PVC could be well described by this equation. The data listed in Table II demonstrate that the relative coefficients approach 1. This indicates that linear regression and iteration equations are completely correct. Because  $(1 - \alpha)$  is less than 1, increase of  $n$  indicates a decrease of the thermal degradation rate. The data listed in Table II also show that the presence of ZB and ZB-ATH reduces the activation energy and reaction order for dehydrochlorination of PVC. The activation energy decreases with increase of the ZB-ATH content, revealing that the presence of ZB and ZB-ATH can greatly promote dehydrochlorination of PVC.

The results discussed above indicate that ZB and ZB-ATH show joint flame-retardant and smoke-suppressant effectiveness for PVC. Al-



**Figure 6** UV spectra of PVC and PVC/ZB-ATH (100/5) decomposed at 250°C for 5 min.



**Figure 7** GC-MS curves of PVC and PVC/ZB-ATH.

though ATH is not a good flame retardant and smoke suppressant for PVC, ZB and ATH have a good synergistic effect on the flame retardance and smoke suppression of PVC. We suggest that following the reasons cause the great increase of flame retardance for PVC in the presence of a small amount of ZB-ATH:

1. Both ZB and ATH contain a certain amount of water of hydration. ATH can undergo an endothermic dehydration by releasing 34% by weight of water in the

temperature range of 220–450°C. ZB can release about 15% by weight of water in the temperature range of 290–450°C. The temperature of ZB-ATH-filled PVC during burning can decrease due to endothermic dehydration reactions. In the meantime, the aqueous vapor released by dehydration can dilute the concentration of combustible gases. Hence, the LOI of PVC greatly increases in the presence of ZB-ATH.

2. The  $B_2O_3$  moiety of ZB can form a glassy layer, inhibiting the oxygen in air to enter

- the burning system and further oxidation of the char.
- ZB-ATH catalyzes the dehydrochlorination of PVC and decreases its activation energy. The hydrogen chloride released is also an effective gas-phase flame inhibitor.
  - As shown in Figure 5, the morphology of the char formed after combustion of PVC in air is quite different from that of char formed after combustion of PVC/ZB-ATH (100/5). The morphology of char formed in PVC shows a densified structure with only small pores, while the morphology of char formed in PVC/ZB-ATH shows a porous honeycomb structure. The porous honeycomb structure can form a barrier to inhibit combustible gases and heat energy to go into the PVC bulk, which is beneficial to the improvement of flame retardance.

### Mechanism of Smoke Suppression

Two main kinds of mechanisms of smoke suppression in rigid PVC for metal-containing compounds were proposed: One is the Lewis acid mechanism<sup>15</sup> and the other is the reductive coupling mechanism.<sup>13</sup> They are all supported by some experimental results. But the final results for these mechanisms are that all the metal compounds promote early crosslinking of PVC during decomposition to increase char formation. It is due to the Lewis acid mechanism that zinc-containing compounds can greatly reduce smoke formation during the pyrolysis and combustion of PVC.<sup>9</sup> ZnCl<sub>2</sub>, which formed along with the thermal decomposition of PVC, acts as an effective catalyst for the ionic dehydrochlorination of PVC due to its strong Lewis acidity. Dehydrochlorination of PVC under the influence of ZnCl<sub>2</sub> occurs with a formation of *trans*-polyene structures fol-

**Table III GC-MS Results of PVC and PVC/ZB-ATH (100/5)**

No.	Components	Abundance ( $\times 10^{-4}$ )		Relative Abundance Ratio (I/II)
		I	II	
1	1,2-Ethanediol	15.1	26.1	0.58
2	Benzene	80.4	8.8	9.14
3	Toluene	5.75	1.01	5.69
4	Ethylbenzene	0.95	0.18	5.28
5	1,2-Dimethylbenzene	0.78	0.37	2.11
6	Benzene monochloride	0.44	0.10	4.40
7	Styrene	1.65	0.20	8.25
8	A	1.08	2.47	0.44
9	1-Ethyl-2-methylbenzene	1.00	1.72	0.58
10	2-Ethyl-1-hexanol	7.76	7.18	1.08
11	2-Propenylbenzene	0.88	0.22	4.00
12	1-Ethynyl-4-methylbenzene	1.63	0.30	5.43
13	1,2-Dihydronaphthalene	1.75	0.52	3.37
14	B	0.68	0.20	3.40
15	Naphthalene	6.41	0.30	21.37
16	1-Methylnaphthalene	1.56	0.20	7.80
17	2-Methylnaphthalene	1.46	0.12	12.17
18	2-Ethenylnaphthalene	1.04	0.10	10.40
19	Butylated hydroxytoluene	0.82	4.12	0.20
20	2,4-Dihydroxy-3,6-dimethylbenzaldehyde	1.49	0.78	1.91
21	C	1.00	0.26	3.85
22	D	0.68	1.67	0.41
23	Diphenylethyne	1.20	0.94	1.28
24	Heptadecane	1.20	3.65	0.33
25	Pentadecane	1.30	5.55	0.23
26	Ethyl ester hexadecanoic acid	3.87	4.89	0.79
27	Ethyl ester octadecanoic acid	14.37	9.68	1.48

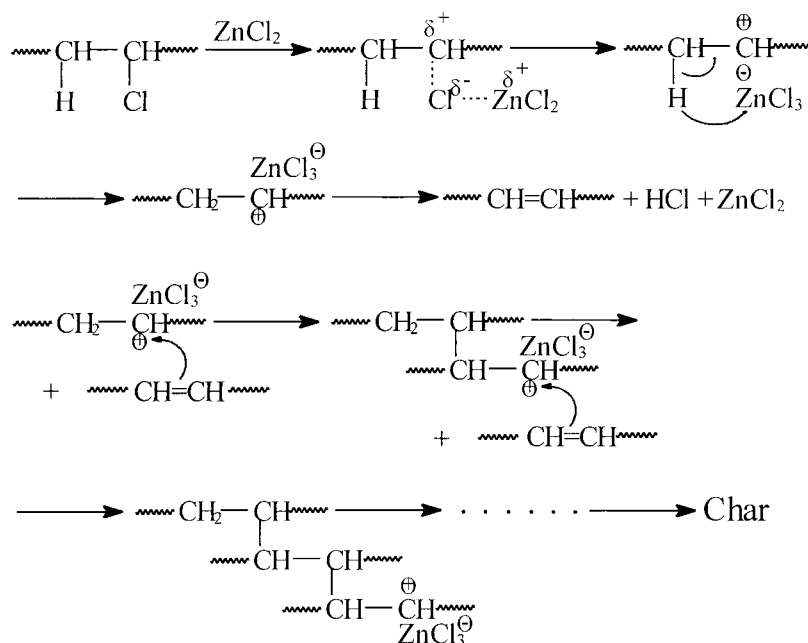
I, PVC; II, PVC/ZB-ATH (100/5). A, B, C, and D represent unidentified products.

lowed by intermolecular cyclization, resulting in increased char formation and a decrease in smoke production. To the best of our knowledge, there is scarce evidence in the literature on how zinc compounds produce char and decrease smoke formation. In our work, we found good correlation between smoke reduction and char formation for ZB and ZB-ATH. To find evidence on how ZB-ATH produces char and decreases smoke formation, the toxic gases released under air pyrolysis of PVC and a condensed-phase structure were characterized by GC-MS and a UV spectrophotometer, respectively.

PVC decomposed at temperatures between 150 and 250°C with the evolution of hydrogen chloride and discoloration. The color of PVC will change from intense yellow to brown as conjugated polyene sequences develop. In our work, we observed the color of PVC to change from intense yellow to brown when PVC decomposed at 250°C; however, the color of PVC in PVC/ZB-ATH quickly became black when PVC decomposed at 250°C. As shown in Figure 6, two characteristic peaks of conjugated polyene sequences in the range of 200–300 nm are shown in the UV spectrum of PVC decomposed for 5 min at 250°C, while no characteristic peaks of conjugated polyene sequences in the range of 200–300 nm are shown in the UV spectrum of PVC/ZB-ATH (100/5) decomposed for 5 min at 250°C, indicating that incorporation of ZB-ATH causes a series of crosslinking reactions of PVC after evolution of hydrogen chloride.

GC-MS was used to characterize volatile products released in the thermal decomposition process of PVC and PVC/ZB-ATH at 600°C. Figure 7 and the data listed in Table III demonstrate that the presence of ZB-ATH can greatly decrease the amount of aromatic products (i.e., benzene, toluene, ethyl benzene, naphthalene, etc.) formed during PVC decomposition. The peak of hydrogen chloride appears ahead of the solvent, ethanol, so it cannot be observed in gas chromatography curves. There is hardly any styrene, benzene chloride, and methylnaphthalene products detected in the PVC/ZB-ATH system. The total amount of gas products released in PVC/ZB-ATH during decomposition is much lower than that in PVC, indicating that ZB-ATH is a very good smoke suppressant for PVC. Figure 7 also shows that the peaks after 20 min are mainly the peaks of aliphatic products including pentadecane, heptadecane, ethyl ester hexadecanoic acid, and ethyl ester octadecanoic acid. The content of aliphatic products in the PVC/ZB-ATH blend is higher than that in PVC. This also indicates that ZB catalyzes dehydrochlorination of PVC and promotes early crosslinking to lead to rapid charring, reducing smoke formation.

According to the results described above, we suggest that ZB could promote PVC crosslinking during decomposition to lead to rapid charring as the following reactions:





When PVC/ZB-ATH is heated, small amounts of zinc chloride are formed by ZB absorbing the hydrogen chloride released. The zinc chloride formed is a strong Lewis acid and reacts with PVC by accepting a chloride-forming primary carbonium ion. The primary carbonium ion then decomposes into alkene, hydrogen chloride, and zinc chloride. The zinc chloride then reacts again as the above mode. The carbonium ions formed react with unsaturated groups in PVC, as in cationic polymerization, to produce char by a series of crosslinking reactions of PVC and, subsequently, reduce smoke formation. A similar mechanism for iron compounds' reducing smoke formation was proposed by Carty et al.<sup>19</sup>

## CONCLUSIONS

1. Incorporation of a small amount of ZB and ZB-ATH can greatly increased the LOI of PVC and char formation and inhibit smoke production. The mixture of ZB with ATH had a good synergistic effect on the flame retardance and smoke suppression of PVC.
2. The thermal stability of ZB-filled PVC improved in the presence of ATH.
3. ZB and ZB-ATH reduced the activation energy and reaction order for dehydrochlorination of PVC, promoting dehydrochlorination of PVC during thermal decomposition.
4. Incorporation of a small amount of ZB and ZB-ATH greatly decreased the aromatic products released during combustion and increased the aliphatic products due to a series of crosslinking reactions of PVC after evolution of hydrogen chloride during combustion.

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## REFERENCES

1. Carty, P.; White, S. *Polym Networks Blends* 1997, 7(3), 121.
2. Carty, P.; White, S. *Polym Networks Blends* 1995, 5(4), 205.
3. Carty, P.; Metcalfe, E.; Annison, W. N. *J Appl Polym Sci* 1990, 41, 901.
4. Carty, P.; White, S. *Polymer* 1995, 36, 1109; 1994, 35, 343.
5. Carty, P.; White, S. *Polym Degrad Stab* 1994, 44, 93.
6. Guo, S.; Ning, Y. *J Polym Sci-Phys* accepted.
7. Skinner, G. A.; Haines, P. J. *Fire Mater* 1986, 10(2), 63.
8. Carty, P.; White, S. *Polym Degrad Stabil* 1995, 47, 305.
9. Stoeva, S.; Karaivaniva, M.; Benev, D. *J Appl Polym Sci* 1992, 46, 119.
10. Starnes, W. H., Jr.; Oliver Huang, C.-H. *Polym Prepr Div Polym Chem* 1989, 30, 527.
11. Green, D. W.; Dallavia, A. J., Jr. *J Vinyl Technol* 1988, 10, 178.
12. Brauman, S. *J Appl Polym Sci* 1981, 26, 353.
13. Lattimer, R. P.; Kroenke, W. J. *J Appl Polym Sci* 1981, 26, 1191; 1981, 26, 1167.
14. Kroenke, W. J.; Lattimer, R. P.; Getts, R. G. *J Appl Polym Sci* 1984, 29, 3788; 1986, 32, 3737.
15. Starnes, W. H.; Edelson, D. *Macromolecules* 1979, 12, 97.
16. Iida, T.; Goto, K. *J Polym Sci-Chem* 1977, 15, 2427.
17. Cusack, P. A.; Killmeyer, A. J. In *Fire and Polymers—Hazards Identifications and Prevention*; Nelson, G. L., Ed.; American Chemical Society: Washington, DC, 1990; p 199.
18. Guo, S.; Wang, Z.; Li, C.; Xu, X. *Polym Mater Sci Eng (in Chinese)*, 1997, 13(3), 100.
19. Carty, P.; Metcalfe, E.; White, S. *Polymer* 1992, 33, 2704.