

Mechanochemical Improvement of the Flame-Retardant and Mechanical Properties of Zinc Borate and Zinc Borate–Aluminum Trihydrate-Filled Poly(vinyl chloride)

Hong Pi, Shaoyun Guo, Yong Ning

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, Sichuan, People's Republic of China

Received 8 January 2002; accepted 21 October 2002

ABSTRACT: In this study, the effect of the high-energy mechanical milling of a mixture of poly(vinyl chloride) (PVC) with zinc borate (ZB) or ZB–aluminum trihydrate (ATH), a mixture of ZB and ATH, on the flame-retardant and mechanical properties of ZB and ZB–ATH filled PVC was examined. The high-energy mechanical milling of PVC/ZB and the PVC/ZB–ATH mixture produced chemical bonding between PVC and ZB or ZB–ATH, increasing the interfacial interaction of PVC/ZB and PVC/ZB–ATH blends, which resulted in a great increase in the limiting oxygen index, the impact and yield strengths, and the elongation at break of PVC/ZB and PVC/ZB–ATH blends. The

results from ultraviolet spectroscopy and gas chromatography–mass spectroscopy show that mechanochemical modification of ZB and ZB–ATH much more effectively suppressed the release of aromatic compounds in PVC/ZB and PVC/ZB–ATH blends during burning. Mechanochemical modification provided an excellent route for the improvement of the flame-retardant and mechanical properties of flame-retardant-additive-filled PVC. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 753–762, 2003

Key words: flame retardance; mechanical properties; poly(vinyl chloride) (PVC)

INTRODUCTION

Poly(vinyl chloride) (PVC) has been widely used in many building, electrical housing, and electrical insulation applications because of its high level of combustion resistance. However, although PVC has good flame retardancy because of its high chloride content, there has been a growing realization that PVC is not a safe material from the point of view of fire hazards because it releases high levels of smoke and toxic gases (i.e., hydrogen chloride, benzene, and other aromatic compounds) during burning.^{1,2} So smoke suppression during the burning of PVC could have profound consequences because PVC has been increasingly used to produce building materials.

Additives, such as compounds containing antimony, tin, zinc, copper, iron, and molybdenum, are widely used to reduce flammability and smoke formation;^{3–16} the most important commercial smoke suppressants are zinc and molybdenum compounds.

Many previous investigations have been aimed at studying the effects of these compounds on the flame retardancy and smoke suppression of PVC and the chemistry of PVC decomposition.^{17–19} Zinc borate (ZB) has the unique characteristic of being both a fire retardant and a smoke suppressant in PVC.^{11,20} In our previous work,¹⁰ some evidence on how ZB increases char residue and decreases smoke suppression was found, and the synergistic effect of the combination of ZB and aluminum trihydrate (ATH) on flame retardancy and smoke suppression was studied. The results show that a mixture of ZB with ATH (ZB–ATH) had a good synergistic effect on the flame retardancy and smoke suppression of PVC. Previous articles also reported that almost all of the additives studied were inorganic compounds filler. The presence of the additives could decrease the mechanical properties of PVC because of poor adhesion between PVC and the additives; meanwhile, the effects of additives on the flame retardancy and smoke suppression of PVC also rely on good dispersion in the PVC matrix and good adhesion with PVC.¹¹

Mechanochemical reactions of polymers and polymer blends have a profound effect on the properties of polymers in a relatively unpredictable manner. They provide a potential route for the preparation of innovative polymeric materials with special properties and for the enhancement of the compatibility of incompatible polymer blends.^{21–26} To enhance the flame-retardant and mechanical properties of ZB and ZB–ATH-

Correspondence to: S. Guo (nic7702@scu.edu.cn).

Contract grant sponsor: Special Funds for Major State Basic Research Projects of China; contract grant number: G1999064800.

Contract grant sponsor: National Natural Science Foundation of China.

Contract grant sponsor: State Education Ministry of China.

TABLE I
Treatment of ZB and ZB-ATH

Sample	Treatment conditions
ZB-1	Untreated
ZB-2	Vibromilled for 2h, steel ball/(ZB:PVC = 2:3) = 10:1, ambient temperature
ZB-ATH-1 ^a	Untreated
ZB-ATH-2 ^b	Vibromilled for 2 h, steel ball/(ZB-ATH:PVC = 2:3) = 10:1, ambient temperature

^a ZB/ATH = 50/50 (by mass).

filled PVC, the mechanochemical modification of ZB and ZB-ATH by high-energy mechanical milling and its effect on the flame-retardant and mechanical properties of PVC were studied in this work. The effect of the mechanochemical modification of flame-retardant and smoke-suppressant additives on the release of aromatic compounds during the burning of PVC was characterized by ultraviolet (UV) spectroscopy and gas chromatography-mass spectrometry (GC-MS).

EXPERIMENTAL

Materials

The PVC used was PVC-S700 from Shangdong Qilu Petrochemical Co. (Zibo, Shangdong, China), with a number-average molecular weight of 4.49×10^4 . The mercaptide organotin heat stabilizer thermolite 175 was from 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 ATH were from Hebei Hongxing Chemicals Co. (Chang Zhou, China).

Mechanochemical modification of ZB and ZB-ATH

Mechanochemical modification was performed in a high-energy ball-milling machine with a vibromilling frequency of 22.3 Hz at ambient temperature. The sample code and treatment conditions are listed in Table I.

Sample preparation

Samples were prepared by the mixture of PVC with ZB, ZB-ATH, and a certain amount of the mercaptide organotin heat stabilizer and lubricants, then blending in a twin roller at 170°C for 10 min, and compression molding at 180°C. The test specimens were cut from the molded sheets.

Measurement and characterization

The limiting oxygen index (LOI) was determined with an LOI1045 instrument (Jiangning Analyzer Factory, Nanjing, China) according to ASTM D 2863.

Stress-strain behavior was measured on an Instron universal testing machine (model 4302, Canton, MA), with specimen dimensions of $25 \times 6.5 \times 1$ mm and a crosshead speed of 20 mm/min. Izod notched impact strength test was carried out according to the regulations mentioned in GB1843-80 with an XJ140A impact tester (Wuzhong Factory, Shanghai, China).

To confirm the effect of mechanochemical modification on the interfacial interaction of ZB and ZB-ATH-filled PVC, the tensile fractured surfaces were sputtered with silver-palladium alloy under vacuum and examined with a Hitachi X-650 scanning electron microscopy (SEM) instrument (Tokyo, Japan) with an accelerating voltage of 20 kV.

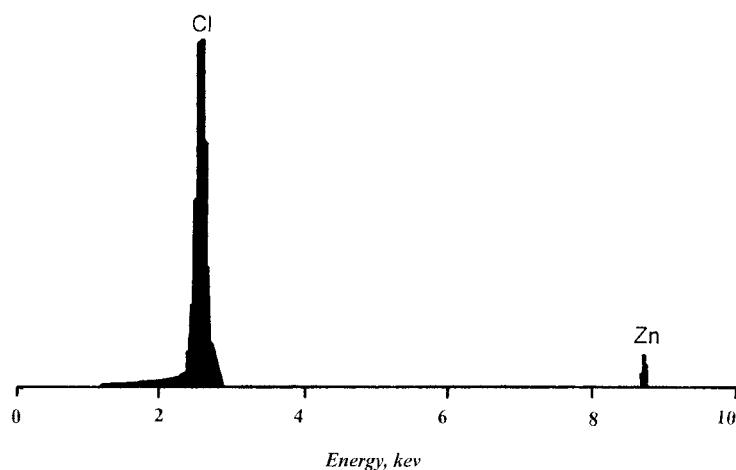


Figure 1 X-ray energy spectrum of the extracted PVC/ZB mixture after milling.

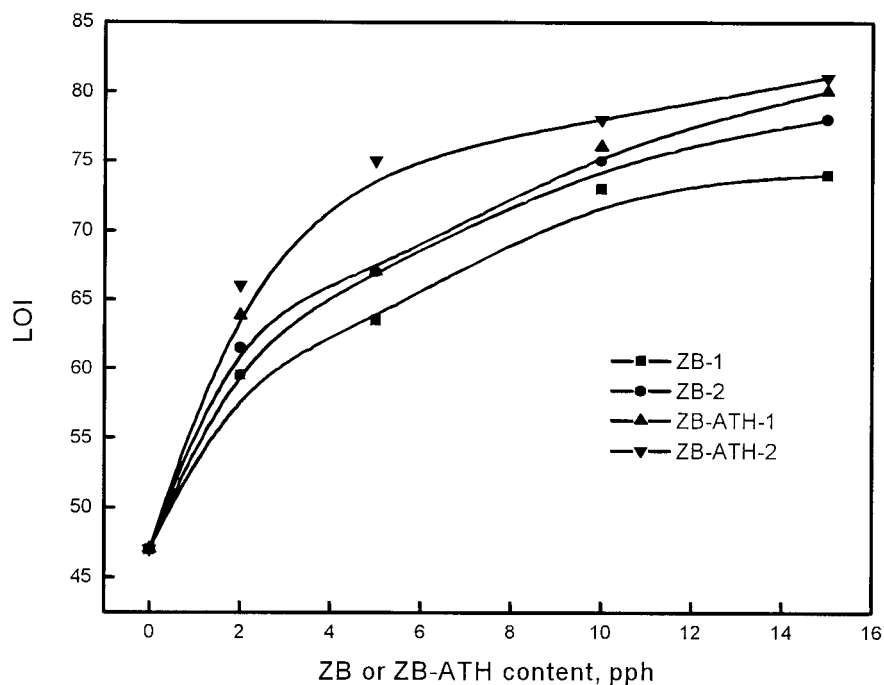


Figure 2 Effects of the ZB and ZB-ATH content on the LOI of PVC.

The extraction test was conducted in a Soxhlet extractor (Suguang Corp., Chengdu, China). A certain amount of the ZB and PVC/ZB mixture was extracted before and after high-energy mechanical milling in a Soxhlet extractor for a period of 2 h by chlorhydric acid to dissolve out ZB. The extracted samples were dried in a vacuum oven for 24 h and were then examined in an X-ray energy spectrometer (the Hitachi

X-650 SEM instrument) to characterize the chemical bonding between PVC and ZB under high-energy mechanical milling.

Certain amounts of PVC and PVC/ZB and PVC/ZB-ATH were weighed, and the weights based on PVC in the samples were equal. The samples were decomposed in air at 600°C. The toxic gases released under air pyrolysis of PVC at 600°C were dissolved in

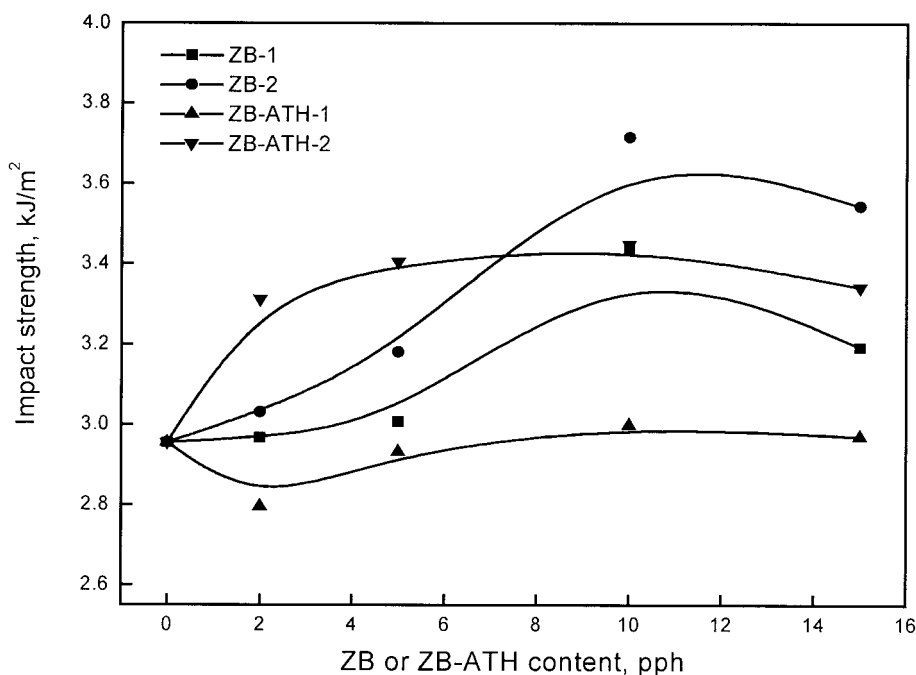


Figure 3 Effects of the ZB and ZB-ATH content on the impact strength of PVC.

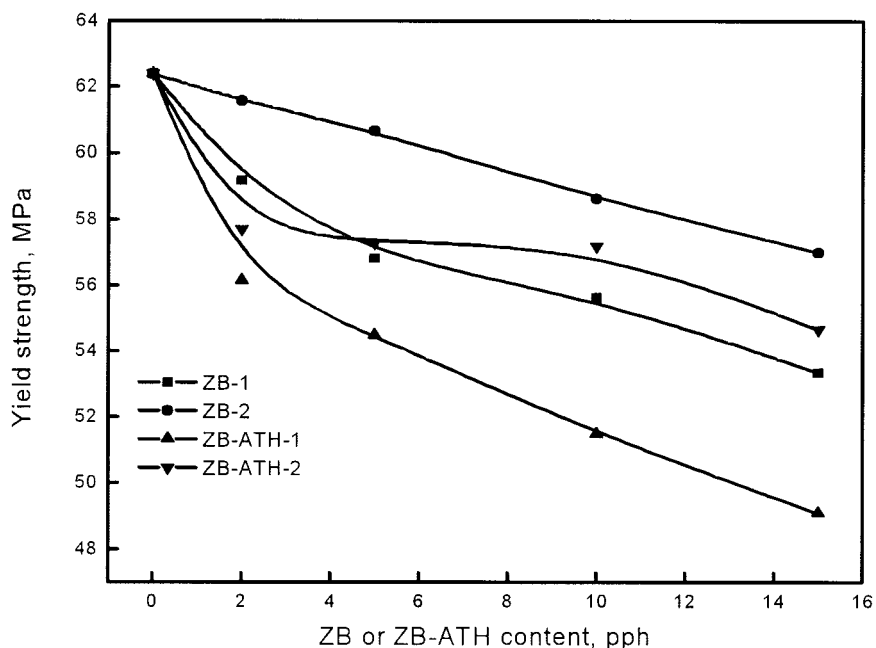


Figure 4 Effects of the ZB and ZB-ATH content on the yield strength of PVC.

100 mL of ethanol and were then detected with a HP5890 II gas chromatograph and a HP5972 mass spectrometer (Hewlett-Packard Co., Wilmington, DE). Nitrogen and helium were used as carrier gases in gas chromatography and mass spectrometry, respectively. The UV absorption spectra of an ethanol solution of toxic gases released from PVC, PVC/ZB, and PVC/ZB-ATH were recorded with a UV-visible UV-240 spectrophotometer (Shimadzu Corp., Kyoto, Japan). According to the relative intensity of the peaks, the

relative content of toxic gases released were measured to investigate the effect of mechanochemical modification on the toxic gases released during burning.

RESULTS AND DISCUSSION

Chemical bonding between PVC and ZB during milling

Our previous work²⁵ showed that a complex combination of the shearing, extension, tearing, collision,

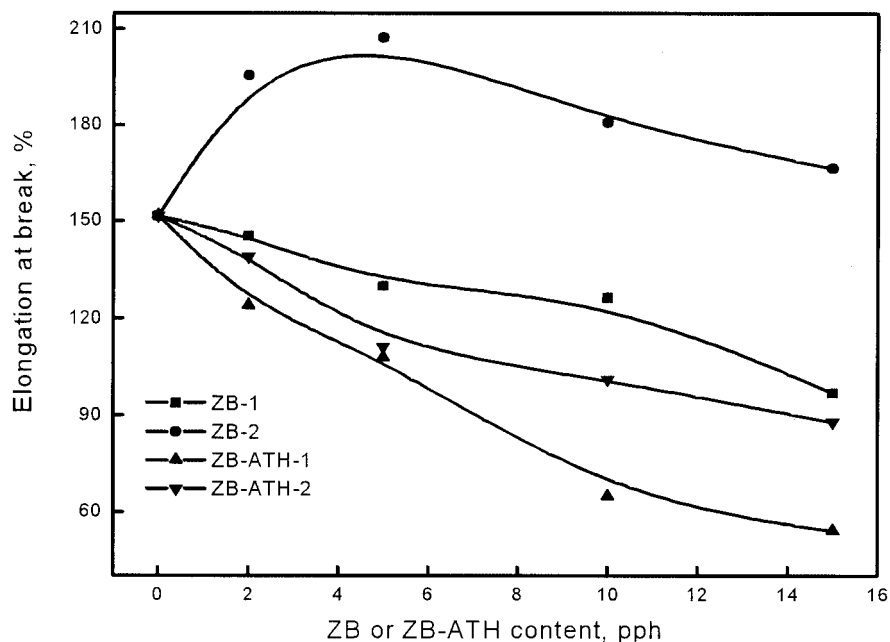


Figure 5 Effects of the ZB and ZB-ATH content on the elongation at break of PVC.

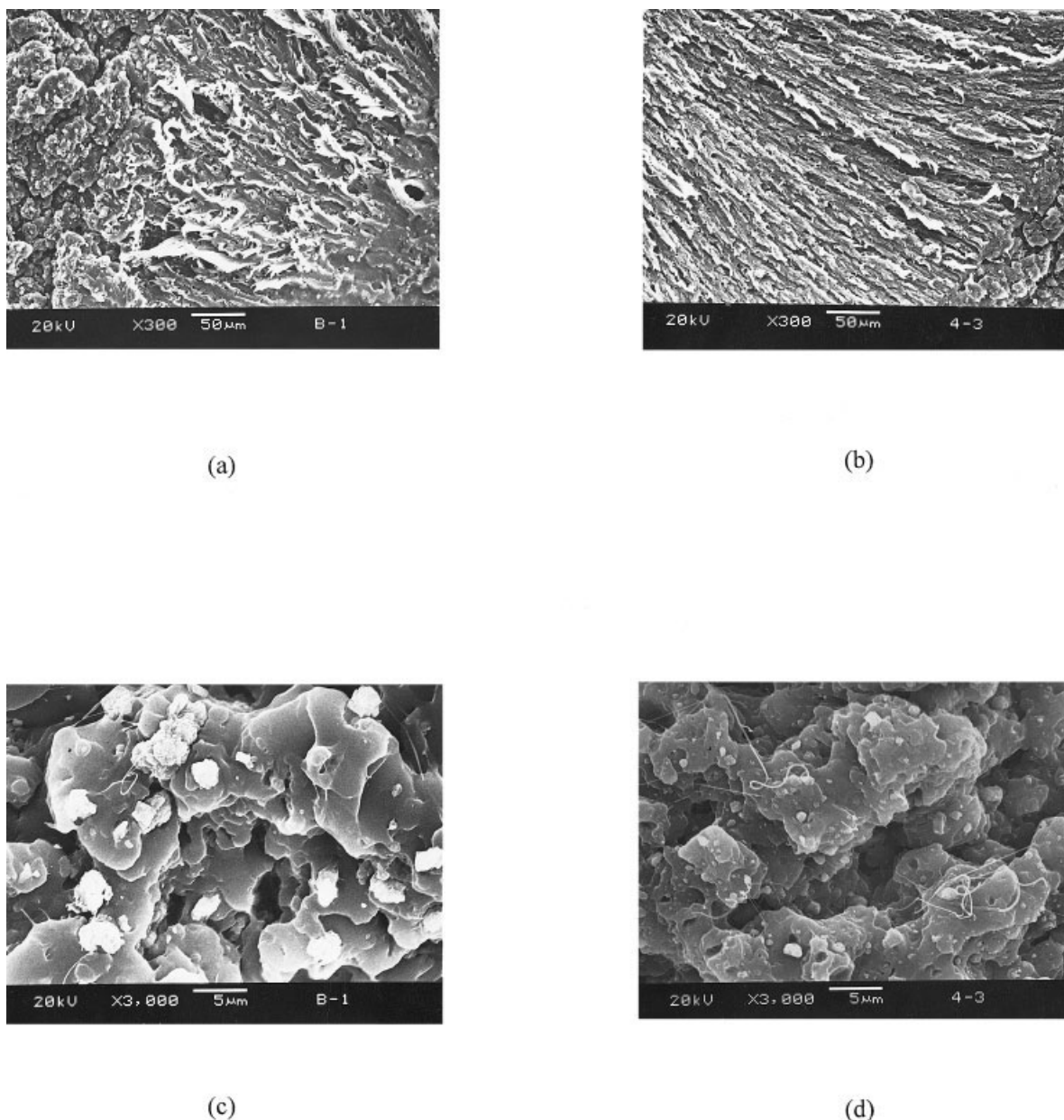


Figure 6 SEM micrograph of PVC/ZB-1 (100/10) and PVC/ZB-2 (100/10) blends: (a) ZB-1 (300 \times), (b) ZB-2 (300 \times), (c) ZB-1 (3000 \times), and (d) ZB-2 (3000 \times).

fracture, and cold-drawing of PVC powder during vibromilling could induce chain scission and generate free radicals. Chain scission was accompanied by a reduction in molecular weight in the presence of a radical acceptor. When PVC/ZB mixture was milled, the pulverization of ZB during milling may have generated high-active fresh surfaces, so it was conceivable that PVC free radicals generated during milling may have combined with high-active new surfaces of the ZB pulverized powder. Extraction results show that ZB and ZB in the PVC/ZB mixture before milling could be completely dissolved out. Although only some parts of ZB in the PVC/ZB mixture after milling were dissolved out, the characteristic energy spectrum

of zinc still appeared on the X-ray energy spectrum after extraction (Fig. 1). This indicated that chemical bonding between PVC and ZB took place during milling. The chemical bonding between ZB and PVC enhanced the interfacial interaction in ZB and ZB-ATH-filled PVC and was, therefore, anticipated to have a profound effect on their flame-retardant and mechanical properties.

Effect of the mechanochemical treatment of ZB and ZB-ATH on the flame retardancy of PVC

As shown in Figure 2, the LOI of PVC/ZB and PVC/ZB-ATH went up with increasing ZB and ZB-ATH

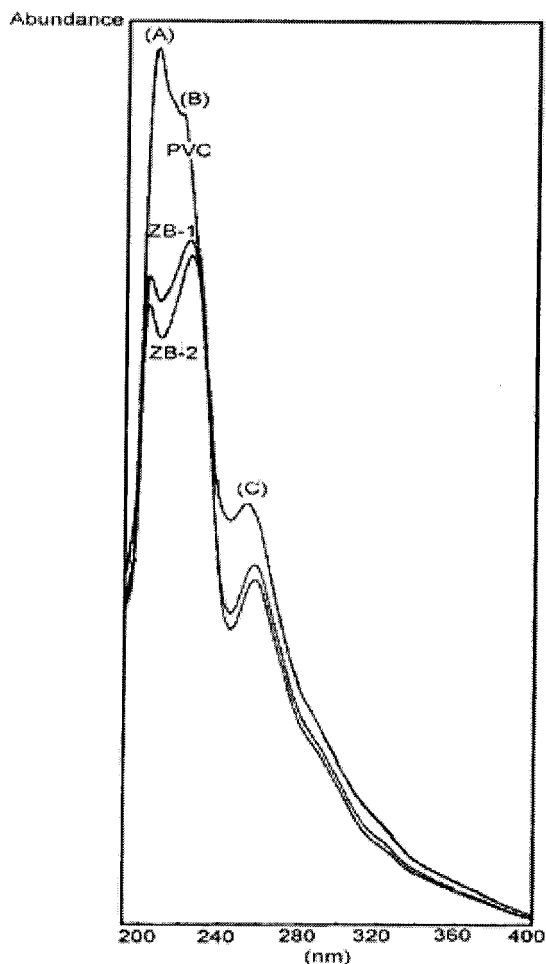


Figure 7 UV spectra of PVC, PVC/ZB-1 (100/5), and PVC/ZB-2 (100/5).

content. The LOI of PVC/ZB-2 and PVC/ZB-ATH-2 was much higher than that of corresponding PVC/ZB-1 and PVC/ZB-ATH-1. Compared with that of PVC/ZB-1 (100/5) and PVC/ZB-ATH-1 (100/5), the LOI of PVC/ZB-2 (100/5) and PVC/ZB-ATH-2 (100/5) increased by 5 and 10, respectively. This benefited from the following:

- The particle size of ZB and ZB-ATH was decreased, and the specific surface areas increased during milling.
- Chemical bonding between PVC and ZB or ZB-ATH promoted their dispersion in the PVC matrix.

Effect of the mechanochemical treatment of ZB and ZB-ATH on the mechanical properties of PVC

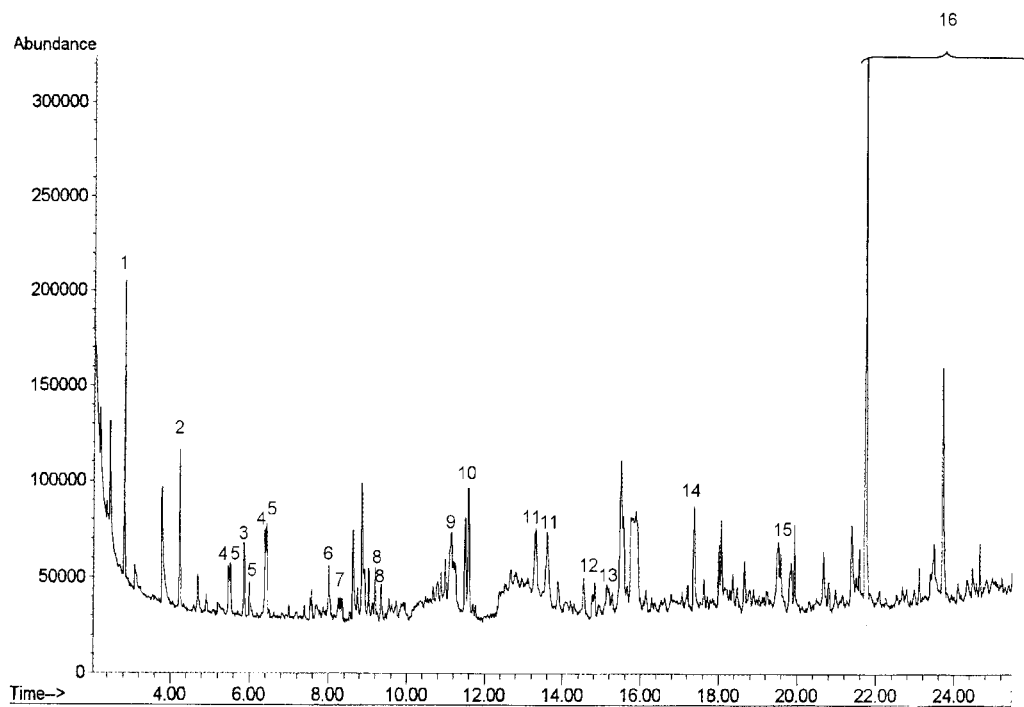
As shown in Figure 3, the impact strength of PVC/ZB-ATH-1 almost remained unchanged with increasing ZB-ATH-1 content, whereas the impact strength of PVC/ZB-ATH-2 increased with rising ZB-ATH-2 content, and the impact strength of PVC/ZB-ATH-2

was higher than that of PVC/ZB-ATH-1. Figure 3 also shows that although the presence of ZB-1 caused an increase in the impact strength of PVC, the impact strength of PVC/ZB-2 was higher than that of PVC/ZB-1. Figure 4 shows that the yield strength of PVC decreased with increasing ZB and ZB-ATH content, but the yield strength of PVC/ZB-2 and PVC/ZB-ATH-2 was much higher than that of the corresponding PVC/ZB-1 and PVC/ZB-ATH-1. As shown in Figure 5, the elongation at break of PVC/ZB-2 and PVC/ZB-ATH-2 was much higher than that of PVC/ZB-1 and PVC/ZB-ATH-1. Surprisingly, the elongation at break of PVC/ZB-2 was higher than that of neat PVC. As shown in Figures 2–5, although the mixture of ZB and ATH (ZB-ATH) had a good synergistic effect on the flame retardance and smoke suppression of PVC, it had a negative effect on the mechanical strength of PVC.

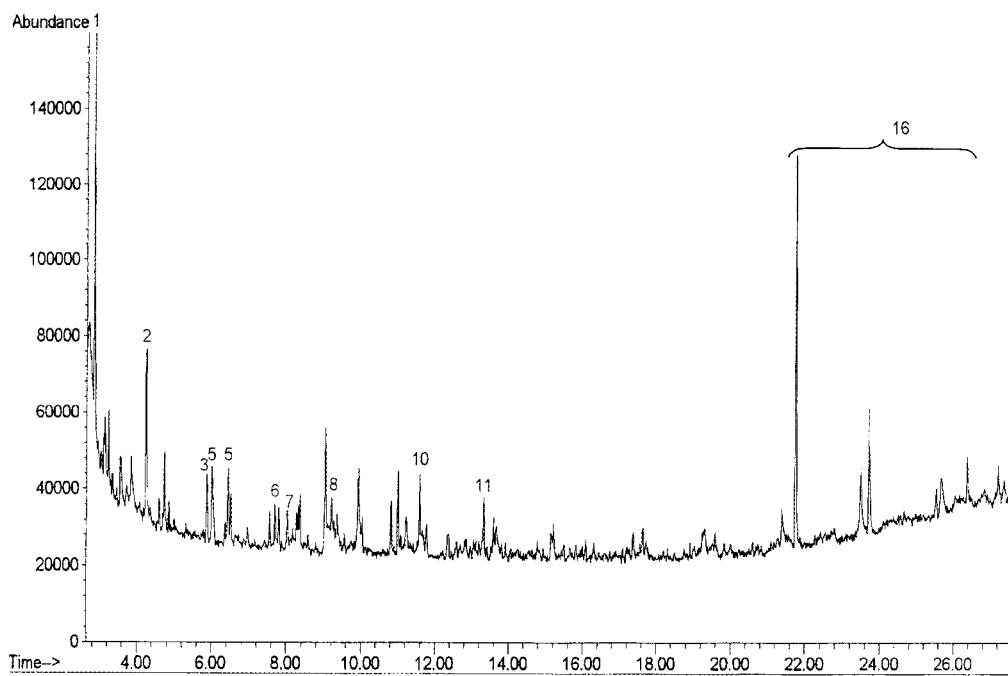
As discussed previously, PVC and ZB or ZB-ATH were pulverized during high-energy mechanical milling. The particle size of ZB and ZB-ATH and PVC decreased, and the distribution of particle size became narrower, promoting the homogenous dispersion of ZB and ZB-ATH in PVC, resulting in an improvement in the mechanical strength of PVC/ZB and PVC/ZB-ATH blends. More important, the chemical bonding of PVC with ZB or ZB-ATH was generated during mechanical milling. PVC molecules chemically bonded on ZB or ZB-ATH particles acted as coupling agents, which enhanced the interfacial interaction between PVC and ZB or ZB-ATH in PVC/ZB and PVC/ZB-ATH blends, causing a great increase in the impact strength, elongation at break, and yield strength of PVC/ZB and PVC/ZB-ATH blends. As shown in Figure 6, the SEM micrograph of the tensile fractured surface in the PVC/ZB-1 blend showed a lot of debonded ZB particles [Fig. 6(a)], whereas the debonded ZB particles almost disappeared on the SEM micrograph of the tensile fractured surface in the PVC/ZB-2 blend [Fig. 6(b)]. The larger magnified SEM micrograph in PVC/ZB-1 blend showed a lot of large aggregated ZB particles [Fig. 6(c)], whereas the larger magnified SEM micrograph in PVC/ZB-2 blend showed a homogeneous dispersion of ZB in the PVC matrix [Fig. 6(d)]. This also revealed the enhancement of interfacial interaction in PVC/ZB and PVC/ZB-ATH blends through the mechanochemical treatment of ZB and ZB-ATH.

Characterization of the products released during burning

In our previous work,¹⁰ we found that the smoke suppression of ZB on PVC followed this mechanism:



(a)



(b)

Figure 8 GC-MS spectra of (a) PVC, (b) PVC/ZB-1 (100/5), and (c) PVC/ZB-2 (100/5).

TABLE II
Characteristic Components of Pyrolyzed Gases

No.	Name	Abundance ($\times 10^{-3}$)		
		I	II	III
1	Benzene	238.3	214.9	88.8
2	Toluene	167.3	105.6	28.7
3	Ethyl benzene	82.6	43.4	19.4
4	Styrene	58.6	—	—
		108.4		
5	(<i>o</i> -, <i>m</i> -, and <i>p</i> -) Dimethyl-benzene	56.9	41.7	27.8
		40.4	48.1	23.7
		79.3		
6	1-Ethyl-2-methyl benzene	65.0	26.1	16.9
7	Trimethyl benzene	29.6	25.1	10.7
8	Indene	64.2	22.1	—
		54.1		
9	Benzoic acid	166.8	—	—
10	Naphthalene	121.3	51.0	34.2
		162.8		
11	Methyl naphthalene	78.7	46.9	27.0
		90.3		
		216.5		
12	Ethyl naphthalene	33.1	—	—
13	Dimethyl naphthalene	35.1	—	—
14	Fluorene	172.9	—	—
15	Phenanthrene or anthracene	51.3	—	—
16	Aliphatic products	Strongest	Stronger	Weak

I = PVC; II = PVC/ZB-1 (100/5); III = PVC/ZB-2 (100/5).

pounds during burning, but the amount of all of the aromatic compounds released was greatly decreased and some aromatic compounds could not be detected because of their very low content in the presence of ZB. The results also show that ZB effectively suppressed the release of aromatic compounds during burning of PVC. More important, compared with that of PVC/ZB-1 (100/5), the amount of aromatic compounds released in PVC/ZB-2 (100/5) during burning was further obviously decreased, indicating that the mechanochemical modification of ZB and ZB-ATH was a very effective route for the improvement of their smoke-suppression efficiency. This was consistent with the UV spectra.

CONCLUSIONS

1. The incorporation of a small amount of ZB and ZB-ATH can greatly increase the LOI of PVC and suppress the release of aromatic compounds during the burning of PVC.
2. The mechanochemical modification of ZB and ZB-ATH can decrease their particle sizes and distribution and enhance the interfacial interaction of PVC/ZB and PVC/ZB-ATH, causing a great increase in the impact and yield strengths

and elongation at break of PVC/ZB and PVC/ZB-ATH.

3. The mechanochemical modification of ZB and ZB-ATH increases the LOI of PVC/ZB and PVC/ZB-ATH and greatly reduces the amount of aromatic compounds released in PVC/ZB and PVC/ZB-ATH during burning, indicating that mechanochemical modification provides a very effective route for further improvement of the flame-retardant and smoke-suppressant properties of PVC/ZB and PVC/ZB-ATH.

References

1. Gordon, E. H.; Arthur F. G.; Walter G. S. In *Fire and Polymers: Hazards Identifications and Prevention*; Nelson, G. L., Ed.; American Chemical Society: Washington, DC, 1990; p 12.
2. Montaudo, G. *Polym Degrad Stab* 1991, 33, 229.
3. Carty, P.; White, S. *Polym Networks Blends* 1997, 7, 121.
4. Carty, P.; Whilte, S. *Polym Networks Blends* 1995, 5, 205.
5. Carty, P.; Metcalfe, E.; Annison, W. N. *J Appl Polym Sci* 1990, 41, 901.
6. Carty, P.; White, S. *Polymer* 1995, 36, 1109; *Polymer* 1994, 35, 343.
7. Carty, P.; White, S. *Polym Degrad Stab* 1994, 44, 93.
8. Guo, S.; Ning, Y. *J Polym Sci Part B: Polym Phys* 1999, 37, 2828.
9. Pi, H.; Guo, S. *Polyvinyl Chloride* 2001, 4, 28 (in Chinese).

10. Ning, Y.; Guo, S. *J Appl Polym Sci* 2000, 77, 3119.
11. Guo, S.; Wang, Z.; Li, C.; Xu, X. *Polym Mater Sci Eng* 1997, 13(3), 100 (in Chinese).
12. Shen, K. K.; Griffin, T. S. In *Fire and Polymers: Hazards Identifications and Prevention*; Nelson, G. L., Ed.; American Chemical Society: Washington, DC, 1990; p 157.
13. Stoeva, S.; Karavanova, M.; Benev, D. J. *J Appl Polym Sci* 1992, 46, 119.
14. Frank, M.; Robert, S.; Sam, M.; Green, J. *J Vinyl Additive Technol* 1995, 1(3), 159.
15. Iida, T.; Goto, K. *J Polym Sci Polym Chem Ed* 1977, 15, 2435.
16. Skinner, G. A.; Haines, P. J. *Fire Mater* 1986, 10(2), 63.
17. Kroenke, W. J.; Lattimer, R. P.; Getts, R. G. *J Appl Polym Sci* 1984, 29, 3788; *J Appl Polym Sci* 1986, 32, 3737.
18. Starnes, W. H.; Edelson, D. *Macromolecules* 1979, 12, 97.
19. Iida, T.; Goto, K. *J Polym Sci Polym Chem Ed* 1977, 15, 2427.
20. 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.
21. Porter, R. S.; Casale, A. *Polym Eng Sci* 1985, 25, 129.
22. Cassle, A.; Porter, R. S. *Polymer Stress Reaction*; Academic: New York, 1979; Vol. 2.
23. Shen, Y.; Keqiang, C.; Qi, W.; Xi, X. *J Macromol Sci Chem* 1986, 23, 1415.
24. Keqiang, C.; Suming, C.; Xi, X. *J Macromol Sci Pure Appl Chem* 1992, 29, 55.
25. Xu, X.; Guo, S. *J Appl Polym Sci* 1997, 64, 2273.
26. Chen, G.; Guo, S.; Li, H. *J Appl Polym Sci* 2002, 86, 23.
27. Huang, L. Z.; Bao, Z. Y. *Ultraviolet Spectroscopy and Its Application*; China Science and Technology: Beijing, China, 1992 (in Chinese).