Zinc Hydroxystannate and Zinc Stannate as Flame-Retardant Agents for Flexible Poly(vinyl chloride)

Jianzhong Xu, Chunyan Zhang, Hongqiang Qu, Chunming Tian

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

Received 1 November 2004; accepted 6 March 2005
DOI 10.1002/app.22282
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The flame-retardant and smoke-suppressant properties of inorganic tin compounds such as zinc hydroxystannate (ZHS) and zinc stannate (ZS) were investigated in a comparison with alumina trihydrate, magnesium hydroxide, and Sb_2O_3 through the limiting oxygen index test and smoke density test. The flame-retardant mechanisms were studied through the char yield test, SEM, quantitative analysis, thermogravimetry and differential thermal analysis. The thermal degradation in air of flexible PVC treated with the above compounds was studied by thermal analysis from ambient temperature to 800°C. The results showed that tin compounds such as ZHS and ZS could be used as a highly effective flame retardant for flexible PVC, and it appears that the tin compound may exert its action in both the condensed and vapor phases, but mainly in condensed phases as a Lewis acid. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1469–1475, 2005

Key words: flame retardance; poly(vinyl chloride) (PVC); degradation; zinc hydroxystannate; zinc stannate

INTRODUCTION

Poly(vinyl chloride) (PVC), a well-known and economical polymer, is used in numerous electrical applications. The high chloride content (56.8%) of PVC makes it relatively resistant to ignition and burning. For many applications of rigid PVC, additions of flame-retardant or smoke-suppressant additives are not required. PVC is compatible with a wide range of formulating ingredients such as plasticizers, which make it flexible and less resistant to ignition unless flame-retardant and smoke-suppressant additives are incorporated.

In recent years, concerns have been widely expressed about the inherent toxicity of halogenated flame retardants and their persistence in the environment.[1] Halogen-free fame retardancy is commonly achieved by the incorporation of inorganic fillers, typically alumina trihydrate (ATH) or magnesium hydroxide (MDH), into the host polymer.[2] Although these fillers are essentially nontoxic and relatively inexpensive, the high levels required for adequate flame retardancy often lead to processing difficulties and a marked deterioration in other critical polymer characteristics, including mechanical, physical, and electrical properties.[3] Although antimony trioxide is an efficient flame retardant in PVC compositions, it is found to increase the amount of smoke and toxic gases. Recently, inorganic tin compounds have been developed as flame retardants in PVC because of their reduced toxicity such as zinc hydroxystannate (ZHS) and zinc stannate (ZS). Cusack et al.[4–8] indicated that zinc hydroxystannate and zinc stannate could be use as a highly effective flame retardant. The advantage of zinc hydroxystannate and zinc stannate as flame retardants is less toxicity than that of antimony compounds. As a result, ZHS and ZS have been used as alternative synergists to antimony trioxide in halogen-containing polymers, given that Sb_2O_3 itself is coming under increasing environmental scrutiny because of its classification in the EC as a category 3 carcinogen.[9]

Few studies have been reported of the flame-retardant mechanism of ZHS, ZS, and other tin compounds.[10] The purpose of our present study is to compare the flame-retardant and smoke-suppression properties of samples that are treated with tin compounds and other flame retardants such as $Al(OH)_3$, $Mg(OH)_2$, and Sb_2O_3. Through the char yield test, SEM, quantitative analysis, thermogravimetry (TG), and differential thermal analysis (DTA) we analyzed the mechanism of tin compounds as flame-retardant agents for flexible PVC.

EXPERIMENTAL

Materials

The materials used were PVC SG2 (Beijing Second Chemicals Co., Beijing, China); DOP [di(2-ethylhexyl) phthalate] as the plasticizer (Shanghai Dong-

Correspondence to: H. Qu (Hqqu@163.com).

fang Chemicals Co., Shanghai, China); organic tin compound as stabilizer and calcium stearate as lubricant (Hebei Baoding Chemicals Co., Baoding City, China); $Al(OH)_3$ and $Mg(OH)_2$ (Shandong Shouguang Chemicals Co., Shouguang City, China); ZnO (Tianjin Third Chemicals Co., Tianjin, China); SnO_2 (Tianjin, Tianda Chemical Co., Tianjin, China); Sb_2O_3 as flame retardant (Tianjin Dengzhong Chemical Co., Tianjin, China); NaOH, $SnCl_4$, and $ZnSO_4$ as agents (Tianjin Dengzhong Chemical Co.) for the preparation of ZHS and ZS.

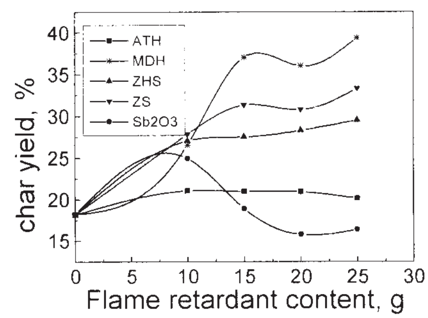


Figure 2 Char yield values of the PVC samples.

Preparation of flame retardants and PVC samples

Preparation of flame retardants was carried out in accordance with procedures reported in the literature[11] for the flame retardants $ZnSnO_3$ and $ZnSn(OH)_6$. Samples were prepared by mixing PVC with DOP, heat stabilizer, lubricant, coupling agent, and flame retardants, then blending them in a two-roller mixer at 170°C for 10 min and compressing them at 180°C to form sheets of $100 \times 50 \times 3$ mm. The test specimens were cut from the molded sheets. The basic recipe of the samples is as follow as: PVC, 100 parts; DOP, 40 parts; stabilizer, 3 parts; calcium stearate, 1 part; coupling agent (NDZ-311) 1 part; and some flame retardants. It had been reported that the organic tin compound as stabilizer and calcium stearate as lubricant had little effect on the flame retardancy and the smoke generated from burning flexible PVC.[10] Furthermore, the content of the stabilizer and the lubricant in samples with and without the flame retardants were all at the same level.

Measurements and characterization

The limiting oxygen index (LOI) value is the minimum amount of oxygen in an oxygen–nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. The higher the LOI value, the more effective the flame-retardant treatment. LOI values were determined in accordance with ASTM D2863-2000 by means of a General Model HC-1 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China).

The smoke density rating (SDR) values were determined in accordance with ASTM D2843-1993 by means of a General Model JCY-1 instrument (Nanjing Jiangning Analysis Instrument Factory).

Char yield values were calculated by the following equation:

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

where w_1 and w_2 are the weight of PVC samples before combustion and the residue after combustion of PVC samples respectively. This experiment was carried out in a muffle furnace under N_2 at 400°C for 30 min.[12]

DTA and TG analyses were carried out on a DT-40 thermal analyzer (Shimadzu Corp., Kyoto, Japan). DTA and TG were performed under air at a heating rate of 20°C min^{-1} and the air-following rate was 60 ml min^{-1}; α-Al_2O_3 was taken as the reference material. The temperature range was from room temperature to 800°C.

The morphology of the char formed after combustion of the samples was investigated by means of scanning electron microscopy (SEM-AMARRY-1000B-2, Chinese Academic of Science Instrument Factory, Beijing, China). Before observation, the surfaces of the char were covered with gold.

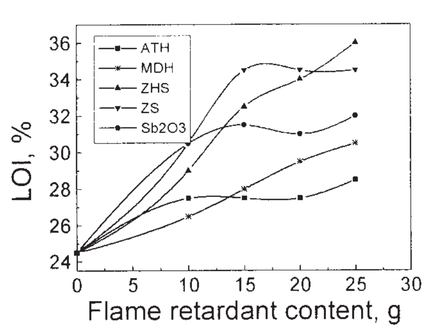


Figure 1 LOI values of the PVC samples.

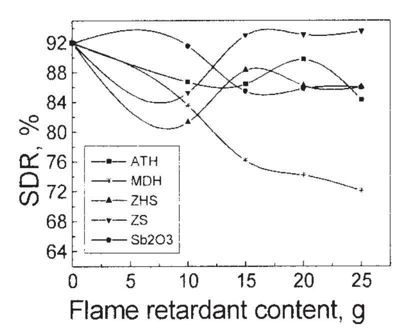


Figure 3 SDR values of the PVC samples.

TABLE I
Flame-Retardant Properties of Samples Treated with ZnO or SnO_2

Flame retardant	Content (g)	LOI (%)	SDR (%)
None	0	24.5	92.0
ZnO	10	26.5	90.4
	15	26.5	93.8
	20	27.0	93.5
	25	26.5	91.6
SnO_2	10	27.5	87.1
	15	32.5	89.6
	20	33.0	88.2
	25	32.5	82.8

RESULTS AND DISCUSSION

Flame retardant and smoke suppressant

In Figure 1 it can be seen that the PVC samples containing a flame retardant of ZHS, ZS, or Sb_2O_3 substantially enhance the LOI and the other formulations containing ATH or MDH marginally enhance the LOI when incorporated at levels of 10 to 25 parts into the PVC compound. When the additive level is at 10 parts, the LOI of ZHS, ZS, and Sb_2O_3 can reach 29.0, 30.5, and 30.5, respectively, and the LOI can be increased 5–6 units. LOI values of other formulations can be enhanced by only 1–2.5 units. When the additive level reaches 25 parts, the LOI for the tin-containing compound ZS or ZHS can reach 35.0 and 36.0 respectively, whereas Sb_2O_3 can reach only 32.0. These results indicate that tin compounds ZHS and ZS have a higher efficiency as flame retardants for PVC than that of Sb_2O_3 or other compounds, ATH and MDH.

In Figure 2 it can be seen that MDH, ZS, and ZHS can apparently improve the char yield, but Sb_2O_3 enhancing the char yield only slightly. The reason is that Sb_2O_3 is a highly effective flame retardant in a halogen-containing polymer, but it forms volatile halide and oxyhalide species during combustion, which act in the vapor phase as free-radical scaven-

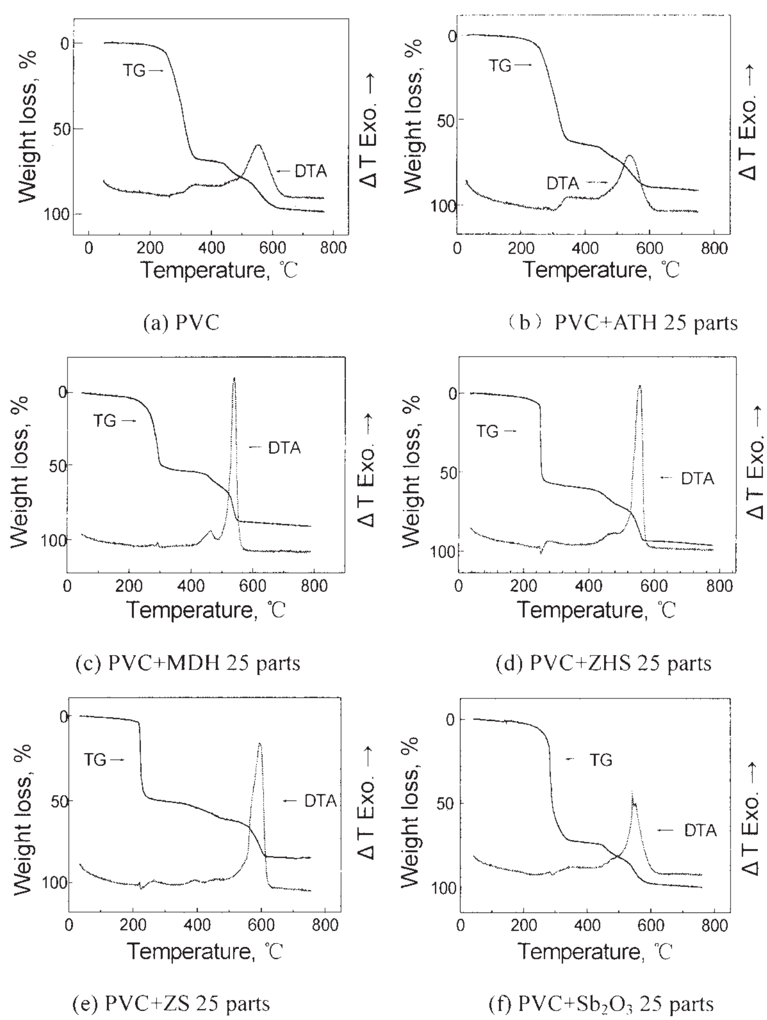
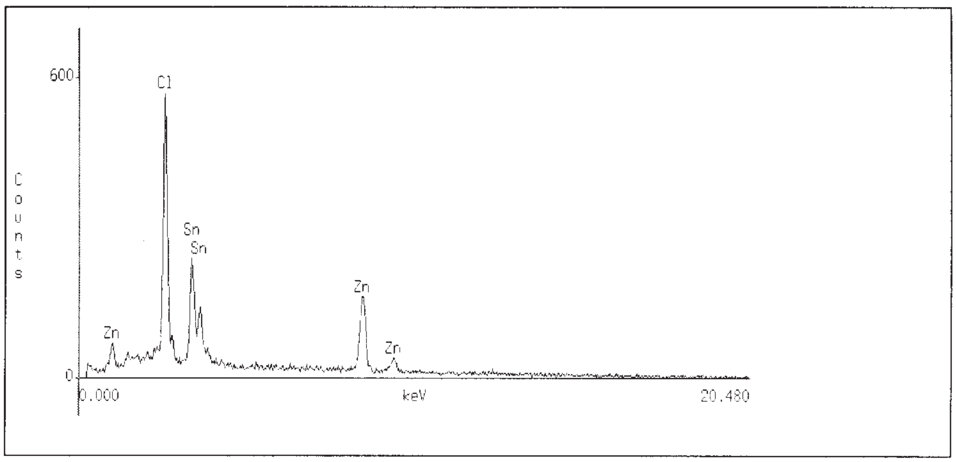


Figure 4 TG and DTA curves of the PVC samples.

TABLE II
TGA and DTA Results of the Samples

Sample	Temperature of exothermic (°C)	$T_{1\%}$ (°C)	First stage		Second stage		Third stage	
			Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)
a	552	210	210–353	68.27	440–517	10.01	517–619	16.53
b	538	197	197–352	61.35	440–515	10.77	515–591	12.31
c	537	185	185–325	51.23	442–521	13.88	521–554	18.57
d	565	172	172–279	56.80	415–494	10.19	494–572	22.08
e	596	176	176–268	49.63	374–491	9.24	529–613	20.77
f	543	183	183–345	76.99	442–534	13.02	534–599	12.27



Accelerating Voltage: 25 KeV Take Off Angle: 9.09028°
Live Time: 100 seconds Dead Time: 2.896

```
Quantitative Analysis
Mon Mar 15 10:57:04 2004
Filter Fit Method
Chi-sqd = 1.14    Livetime = 100.0 Sec.
Standardless Analysis
Element  Relative    Error      Net     Error
          k-ratio   (1-Sigma)   Counts  (1-Sigma)
Cl-K   0.28034 +/- 0.00680     7711 +/-   187
Zn-K   0.29465 +/- 0.01672     2980 +/-   169
Sn-L   0.42501 +/- 0.02466     4601 +/-   267
```

```
PROZA Correction  Acc.Volt.= 25 kV  Take-off Angle=
9.09 deg
Number of Iterations = 6
Element  k-ratio   ZAF   Atom %  Element  Wt % Err.
         (calc.)                  Wt %   (1-Sigma)
  Cl-K   0.1713  2.069  59.15   35.45    +/- 0.86
  Zn-K   0.1801  1.186  19.33   21.36    +/- 1.21
  Sn-L   0.2597  1.663  21.53   43.19    +/- 2.51
  Total                100.00  100.00
```

Figure 5 Quantitative analysis of the residual char of sample (e).

gers,[13–15] and consequently it enhances the char yield only slightly.

From Figure 3 we can see that the SDR values of the samples treated with flame retardants (except Sb_2O_3) are lower than that of the sample of plasticized PVC, especially ZHS, which reduces the SDR by 11 units (from 92.0 to 81.0), when 10 parts flame retardant are incorporated. The flame retardant (except MDH) has a slight effect on the SDR when its content is more than 10 parts.

Table I shows that the addition of ZnO has a negligible effect on flame retardancy and smoke suppression; only 2 units of the LOI increased at the content level from 10 to 25 g, and the smoke suppression is almost at the same level as (or even worse than) that of the plasticized PVC. After adding SnO_2, the flame retardancy and smoke suppression were enhanced, the LOI increased 8 units, and the SDR decreased about 9%. However, the flame retardancy and the smoke suppression properties of ZHS or ZS are much better than these of ZnO and SnO_2 added separately, compared with the data in Figures 1 and 3.

Thermal analysis

Many papers have reported[12,16,17] on the thermal degradation of PVC. According to these reports, the curves of thermal degradation can be divided into two stages. Sometimes there would be more stages than two depending on the different compositions. As shown in Figure 4, the TG curves of the thermal degradation can be divided into three stages. The thermal decomposition in the first stage is mainly attributed to the emission of hydrogen chloride and the degradation of DOP.[12,18] It can be seen from Table II that all the samples lost weight, about 50–65 wt % at the first stage. In fact, for the sample of plasticized PVC without fire-retardant additives, just over 65 wt % is lost, with somewhat smaller losses for the samples that were treated with flame retardants (except the sample treated with Sb_2O_3, which is about 77 wt % higher than the others; this is because Sb_2O_3 acts in the vapor phase as a flame retardant for PVC). Incorporation of flame retardants reduces the initial decomposition temperature $T_{1\%}$ ($T_{1\%}$ is defined as the temperature at which 1% of the initial weight has been lost[19]), especially the ZS and ZHS: $T_{1\%}$ and the decomposition temperature range at the first stage are decreased about 40 and 30°C, respectively, and the decomposition temperature at the second stage was also decreased. ZHS increases the weight loss from 6.99 to 51.70% between 249 and 256°C; ZS also greatly increases the weight loss of the PVC thermal decomposition from 3.08 to 40.77% between 219 and 230°C. These results indicate that ZS and ZHS catalyze dehydrochlorination of PVC and promote early crosslinking to lead to rapid charring, decreasing the SDR and increasing the LOI and char yield of the samples. These results are consistent with the data of LOI, SDR, and the char yield in Figures 1 to 3. The second stage is where the carbonaceous backbone undergoes chain scission and thus lower molecular weight compounds (and smoke) are produced.[20] The third stage tends to be, just as for many other polymers, a very slow reaction that is the oxidation of the unstable char. With respect to the second and third weight stages, the only possible systematic statement is that both the temperature range and the percentages of weight loss are at the same level, respectively, and much smaller than those for the first stage.[12]

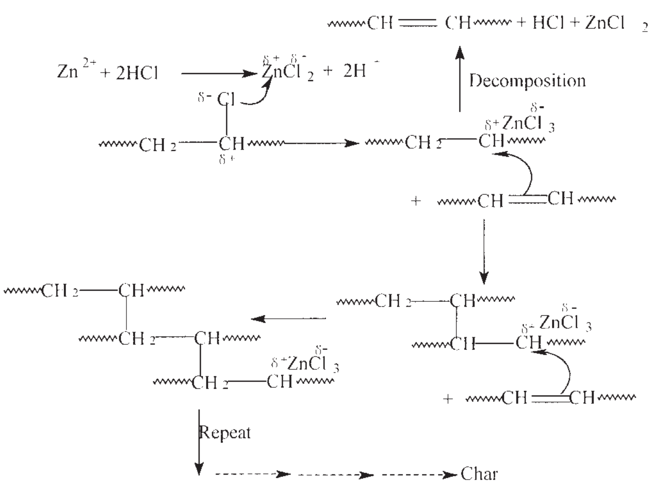
As shown in Figure 4, the DTA curve of the sample treated with ATH is similar to that of the sample plasticized PVC. Incorporation of ATH has only a slight effect on the DTA curves of the PVC, except the small endothermic peak at about 300°C, which is consistent with the temperature range of the endothermic dehydration of ATH.[16] The DTA curve of the sample treated with the other flame retardants has a sharp exothermic peak, in contrast with that of the plasticized PVC and the sample treated with ATH. The temperature of the exothermic peak was increased when ZS or ZHS was added, revealing that the stability of the residual char was enhanced.

Mechanism of the ZHS and ZS

Many studies have been reported about the flame-retardant mechanism of inorganic hydroxide and Sb_2O_3.[21,22] Zinc-containing compounds can increase the LOI and greatly reduce smoke formation during the pyrolysis and combustion of PVC.[23] The study of the mechanism of tin compounds was focused on SnO_2: SnO_2 as flame retardant and smoke suppressor mainly act in the condensed phase.[24] Bulewicz et al.[25] A proved through the experiment that the tin element mainly exists as SnO and $SnCl_2$ in the residual char of the PVC sample treated with SnO_2, which also indicates that SnO_2 mainly acts in the condensed phase. From Figure 5, we can see the atom proportion of tin and zinc in the residual char is about 1 (equal to the atom proportion of tin and zinc in the ZS or ZHS); even the quantity of tin is greater than that of zinc, which may be explained by the addition of organic tin compound as plasticizer. This indicates that the mechanism of flame-retardant action of tin (IV)–halogen systems is different from that of antimony–halogen systems; the mechanism of flame retardance stemming from the tin compound is principally one of action in the condensed phase.

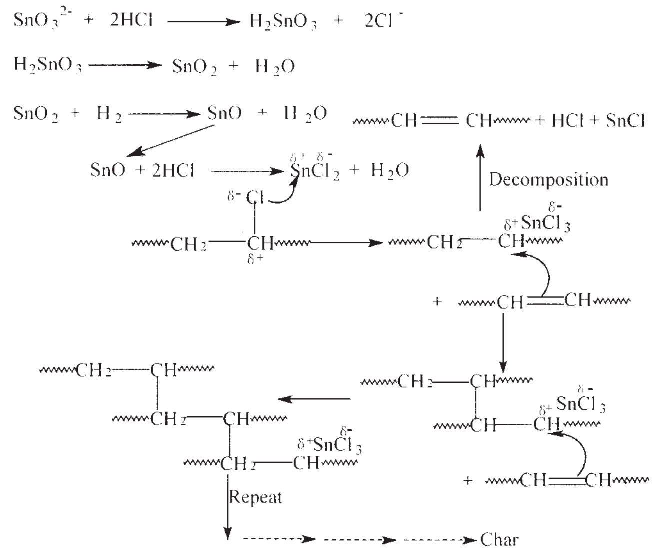
The above evidence indicates that the ZS and ZHS are highly effective flame retardants for flexible PVC. Effectiveness is much greater than that of the other flame retardants. According to the results described above, we suggest that the following reasons explain the great increase of the LOI and char yield and decrease of the SDR:

1. There is Zn^{2+} in the ZS and ZHS, and the Zn^{2+} reacts with HCl to form $ZnCl_2$, a kind of stronger Lewis acid, which catalyzes the dehydrochlorination and promotes early crosslinking to the PVC compound, leading to rapid charrings. The hydrogen chloride released is an effective gas-phase flame inhibitor and such a carbonized product is believed to protect the polymer backbone, inhibiting heat and O_2 degradation during combustion and thus contributing to flame retardancy. The process is schematically shown as follows[12]:



Scheme 1

2. There is SnO_3^{2-} both in the ZS and ZHS; and the SnO_3^{2-} reacts with HCl to form the final products, $SnCl_2$ and H_2O, $SnCl_2$ also acts as a kind of Lewis acid in the condensed phase, and cooperates with $ZnCl_2$ to enhance the flame retardance of PVC. The process is shown in Scheme 2.[12,26]
3. A small amount of tin compound volatilizes as oxyhalide and acts in the vapor phase.[27]
4. As shown in Figure 6, the morphology of the char formed after combustion of PVC containing ZS or ZHS in air is quite different from that of char formed after combustion of the pure PVC sample. The morphology of char formed in PVC shows a cindery structure with some small pores, whereas the morphology of char formed in PVC/ZS or PVC/ZHS shows a densified structure. The densified structure can form a barrier to inhibit combustible gases and transfer of heat energy to the PVC bulk, which is beneficial to the improvement of flame retardance.



Scheme 2

CONCLUSIONS

1. Compared with the inorganic hydroxide and Sb_2O_3, ZS and ZHS can greatly increase the LOI and the char yield, demonstrating that ZS and ZHS are effective flame retardants for flexible PVC.
2. ZS and ZHS reduced the initial decomposition temperature and the decomposition temperature range at the first stage, enhanced the temperature of the exothermic peak and the stability of the residual char, promoted the dehydrochlorination of PVC during thermal decomposition.
3. The action of ZS and ZHS as flame retardants of PVC, which catalyze the dehydrochlorination and promote early crosslinking to the PVC compound, leading to rapid charring, is mainly a result of the Lewis acid mechanism in the condensed phase. A small amount of tin compound volatilizes as oxyhalide and acts in the vapor phase.
4. The density structure of the char can inhibit heat and combustion gases from going into the PVC bulk, thus also enhancing the flame retardancy.

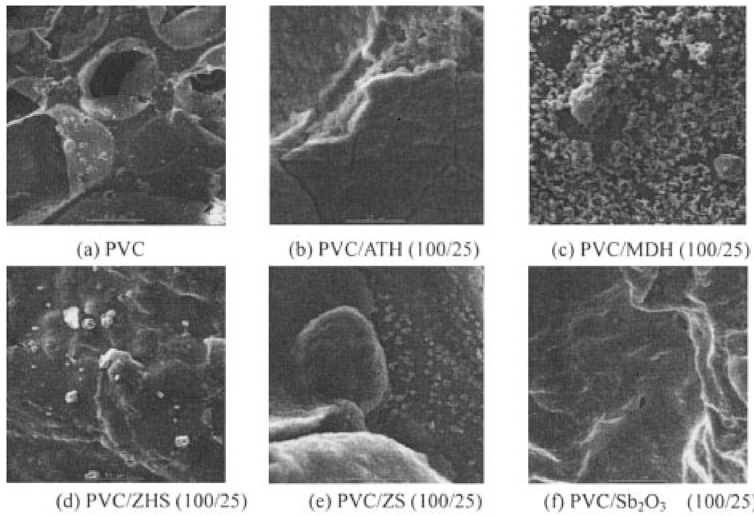


Figure 6 SEM micrographs of the char.

References

1. Purser, D.; Grand, A. F.; Wilkie, C. A. Fire Retardancy of Polymeric Materials; Marcel Dekker: New York, 2000.
2. Davis, J.; Pritchard, G. Plastics Additives: An A–Z Reference. Chapman & Hall: London, 1998.
3. Horn, W. E.; Grand, A. F.; Wilkie, C. A. Fire Retardancy of Polymeric Materials; Marcel Dekker: New York, 2000.
4. Andre, F.; Cusack, P. A.; Monk, A. W.; Seangprasertkij, R. Polym Degrad Stab 1993, 40, 267.
5. Bains, R. S.; Cusack, P. A.; Monk, A. W. Eur Polym J 1990, 26, 1221.
6. Cusack, P. A.; Heer, M. S.; Monk, A. W. Polym Degrad Stab 1997, 58, 229.
7. Cusack, P. A.; Hornsby, P. R. J Vinyl Addit Technol 1999, 5, 21.
8. Cusack, P. A.; Heer, M. S.; Monk, A. W. Polym Degrad Stab 1991, 32, 177.
9. Anon. Antimony and Its Compounds: Health Hazards and Precautionary Measures. UK Health and Safety Executive Guidance Note EH 19 (Revised). HSE Books: Sudbury, UK, 1997.
10. William, J. K. J Appl Polym Sci 1981, 26, 1167.
11. Jiaqiang, X.; Yanli, L.; Xinshu, N. J Chin Ceram Soc 2002, 30, 321.
12. Chunming, T.; Hai, W.; Xiulan, L. J Appl Polym Sci 2003, 89, 3137.
13. Gupta, M. K. U.S. Pat. 4,593,060 (1986).
14. Hastie, J. W. J Res NBS, 1973, 77A, 733.
15. Costa, L.; Goberti, P.; Paganetto, G. Polym Degrad Stab 1990, 30, 13.
16. Tong, N.; Shaoyun, G. J Appl Polym Sci 2000, 77, 3119.
17. Gumargalieva, K. Z. Polym Degrad Stab 1996, 52, 73.
18. Brauman, S. K.; Fishman, N.; Brolly, A. S. J Fire Retard Chem 1976, 3, 66.
19. Cullis, C. F.; Hirschler, M. M. Polymer 1983, 24, 834.
20. Brauman, S. K. J Fire Retard Chem 1976, 3, 117.
21. Hornsby, P. R.; Watson, C. L. Polym Degrad Stab 1990, 30, 73.
22. Costa, L.; Goberti, P.; Paganetto, G. Polym Degrad Stab 1990, 30, 13.
23. Stoeva, S.; Karaivaniva, M.; Benev, D. J Appl Polym Sci 1992, 46, 119.
24. Donaldson, J. D.; Donbavand, J.; Hirschler, M. M. Eur Polym J 1983, 19, 33.
25. Bulewicz, E. M.; Padley, P. G. Mechanism of SnO_2 on Flame Retardant in Polymer, Proceedings of the Ninth Symposium on Combustion. Academic Press: New York, 1963.
26. Cullis, C. F. Developments in Polymer Degradation. Applied Science Publishers: London, 1981; Part 3, p. 283.
27. Brauman, S. K. J Fire Retard Chem 1976, 3, 117.