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A novel intumescent flame retardant and smoke suppression system for flexible PVC

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Triazine derivatives containing a hydroxystannate or zinc hydroxystannate (ZHS) group were synthesized as a novel intumescent flame retardant (IFR) and smoke suppressant for flexible PVC, and their structure and thermal stability were evaluated by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), respectively. Limiting oxygen index (LOI) and smoke density rating (SDR) tests demonstrated that melamine hydroxystannate (MASN) and a composite of MASN and ZHS (MAZSN) are effective flame retardants and smoke suppressants for flexible PVC at levels of 5–30 parts per hundred parts of base resin (phr). The thermal degradation of the flame-retardant flexible PVC was investigated by TGA, differential thermal analysis (DTA), and scanning electron microscopy (SEM). The results showed that adding MASN and MAZSN not only decreased the initial decomposition temperature and increased the weight loss rate at the first stage, but also promoted char formation and expansion at the second stage. Moreover, flame retardants consisting of MASN or MAZSN and the PVC matrix form a novel IFR and smoke suppression system, in which the PVC matrix acts as the carbonization agent and $Sn(OH)_6^{2-}$ and Zn^{2+} provide the acid (Lewis acid). When combustion occurs, $Sn(OH)_6^{2-}$ and Zn^{2+} catalyze dehydrochlorination and promote early crosslinking of PVC, and hydrogen chloride and melamine (MA), acting as the blowing agent, enhance the intumescence of the char. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: flame retardant; smoke suppression; poly(vinyl chloride); thermal analysis; intumescent flame retardant

INTRODUCTION

Poly(vinyl chloride) (PVC) is a commodity thermoplastic with the advantages of low cost, formulation versatility, and inherent flame retardancy; it has been used in building materials, sealing strips, wire and cables.^[1] Owing to its high chlorine content (56.8%), unplasticized PVC products do not contribute to fire propagation, and most rigid PVC formulations will pass most flammability tests without the need to incorporate flame retardants. However, a large quantity of black smoke is produced when unplasticized PVC is forced to burn, which is a significant problem in applications where fire hazard is a concern.^[2] Therefore, the addition of smoke suppressants is necessary when rigid PVC is used. In flexible PVC, the plasticizers compromise the resistance to fire in most instances.

To meet specifications such as those for the limiting oxygen index (LOI) value, heat release, smoke evolution, and extent of burning in cable tests, flame retardants and smoke suppressants are often incorporated into plasticized PVC.^[3] Many types of chemical compound have been reported as flame and smoke retardants for PVC, including metal alloys, inorganic compounds, coordination compounds, and organic compounds.^[4] Each type has advantages and disadvantages. Antimony compounds, especially Sb₂O₃ and Sb₂O₅, are widely used as flame retardants for PVC and have shown good flame retardancy but increased smoke production.^[5,6] Although inorganic fillers, typically alumina trihydrate (ATH) and magnesium hydroxide (MDH), are essentially non-toxic and relatively inexpensive, the high levels required for adequate flame retardancy often lead to processing difficulties and a remarkable deterioration in other critical polymer characteristics, including mechanical, physical, and electrical properties.

In recent years, researchers became interested in the use of certain tin compounds, such as tin(IV) oxide (SnO_2) , zinc stannate $(ZnSnO_3, ZS)$ and zinc hydroxystannate $(ZnSn(OH)_6, ZHS)$, as flame retardant and smoke suppressant additives for PVC^[7,8] because tin compounds can act as a Lewis acid, predominantly in the condensed phase, and increase the amount of char residue.^[9] Although these compounds show high flame retardant efficiency and low toxicity, they are not economical for wide use as flame retardants. Therefore, the preparation of effective, low-cost fillers as flame-retardant and smoke-suppressant additives for polymeric materials, especially for halogen-containing polymers, has been a very hot topic in recent years.^[1,0-12]

In recent decades, intumescent flame retardants (IFR) producing low smoke and toxicity without corrosive gas generation have drawn more and more attention in the flame retardation of materials.^[13] An IFR generally consists of three components: an acid source, a carbonization agent, and a blowing agent.^[14] A typical and widely adopted IFR system is an ammonium polyphosphate (acid source)/pentaerythritol (carbonization agent)/melamine (MA) (blowing agent) mixture.^[15] IFRs have been studied and used widely as effective flame retardants, but reports of the use of IFR in flexible PVC have been very limited.

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Scheme 1. Synthesis of MASN and MAZSN.

In the present work, triazine derivatives containing a hydroxystannate or ZHS group as a novel IFR were synthesized. The thermal stability of these compounds was evaluated by thermogravimetric analysis (TGA). The effects of the novel IFR on flame retardancy, smoke suppression, and thermal degradation in flexible PVC are also discussed.

EXPERIMENTAL

Materials

Sodium hydroxystannate (Na₂Sn(OH)₆, \geq 99%), zinc chloride (ZnCl₂, \geq 98%), and hydrochloric acid (HCl, 36–38%) were all purchased from Tianjin Kemiou Chemical Reagent, Tianjin, China. Melamine was purchased from Jinglong Fengli Chemical Co., Hebei Province, China.

A suspension PVC (TL-1000, M_W : 63,100) employed in this study was purchased from Beijing the Second Chemicals Co., Beijing, China. Dioctyl phthalate (DOP) was used as the plasticizer (Shanghai Dongfang Chemicals Co., China), an organic tin compound, namely diisooctyl-2,2'-[(dioctylstannylene)bis(thio)] diacetate, was used as stabilizer and calcium stearate was used as lubricant (Baoding Chemicals Co., Baoding, China).

Preparation of the flame retardants and PVC samples

Two IFRs were synthesized with MA, $\rm Na_2Sn(OH)_{6},$ and $\rm ZnCl_2,$ as follows. $^{[16]}$

MA (12.6 g, 0.1 mol) and 200 ml (1.0 mol I^{-1}) hydrochloric acid were mixed in a three-neck flask at 85°C with continuous agitation. Next, 26.6 g of solid Na₂Sn(OH)₆ (0.1 mol) was dissolved in 100 ml of distilled water and then added to the clear solution of MA hydrochloride. The batch was agitated at 83–87°C for an additional 4 hr and then cooled to room temperature and filtered. Then, the wet cake was re-slurried and re-filtered twice in 80 and 50 ml of water, respectively. After that, the cake was dried for 16 hr at 80°C and then crushed into powder. Finally, 30.2 g of melamine hydroxystannate (MASN) was obtained.

MA (12.6 g, 0.1 mol) and 200 ml (1.0 mol l⁻¹) hydrochloric acid were mixed in a three-neck flask heated at 85°C with agitation. Next, 100 ml (1.0 mol⁻¹) of ZnCl₂ aqueous solution and 200 ml of Na₂Sn(OH)₆ (1.0 mol⁻¹) aqueous solution were added to the clear solution of MA hydrochloride over 10 min at 83–87°C. The batch was agitated at

83–87°C for an additional 4 hr and then cooled to room temperature and filtered. The wet cake was then re-slurried in 150 ml of water and re-filtered. It was re-slurried again in 100 ml of water and filtered once more. The cake was then dried for 16 hr at 80°C, and 53.8 g of a composite of MASN and ZHS (MAZSN) was obtained.

The synthetic routes of MASN and MAZSN are as follows (Scheme 1). The test specimens were prepared as follows. First, the PVC was mixed with DOP, heat stabilizer, lubricant, and the selected flame retardant. The basic recipe of each sample is: PVC, 100 parts per hundred parts of base resin (phr); DOP, 40 phr; stabilizer, 3 phr; calcium stearate, 1 phr; and flame retardant. The mixture was then blended with a two-roll mill at 170°C for 10 min and compressed into sheets 140 mm \times 50 mm \times 3 mm in size. The sheets were cut into standard specimens.

Structural characterization

X-ray diffraction (XRD) was performed on a Japan Rigaku K/max- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 1.542$ Å, $2\theta = 10-65^{\circ}$) at the scanning rate of 0.02 C sec⁻¹.



Figure 1. EDS results of MASN and MAZSN.

| Table 1. | Quantitative | analysis | results | of MASN | |
|----------|--------------|----------|---------|---------|--|
|----------|--------------|----------|---------|---------|--|

| Element | Weight | Weight | Atom | Atom | Formula |
|------------------------------------|--|--|---|--|--|
| line | % | % error | % | % error | |
| C K N K O K Sn K Total | 10.66 24.50 29.57 35.27 100.00 | $\pm 0.83 \\ \pm 3.63 \\ \pm 1.93 \\ \pm 0.48$ | 18.37 36.20 38.28 6.15 100.00 | $\pm 1.05 \\ \pm 3.93 \\ \pm 1.83 \\ \pm 0.06$ | C _{2.99} N _{5.89} O _{6.22} Sn ₁ |

| Table 2. Quantitative analysis results of MAZSN | | | | | |
|---|--|--|---|--|---|
| Element line | Weight % | Weight % error | Atom % | Atom % error | Formula |
| C K N K O K Zn K Sn K Total | 6.07 12.59 32.01 10.38 38.95 100.00 | $\pm 0.83 \\ \pm 1.48 \\ \pm 1.23 \\ \pm 0.33 \\ \pm 0.64$ | 12.94 23.12 51.43 4.08 8.43 100.00 | $\pm 1.57 \\ \pm 2.39 \\ \pm 1.74 \\ \pm 0.11 \\ \pm 0.12$ | C _{3.17} N _{5.67} O _{12.61} Zn ₁ Sn _{2.07} |

Fire testing

The LOI is the minimum percentage oxygen for maintaining specimen's flaming combustion under specified laboratory conditions. In this work, the LOI values were determined with General Model HC-2 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China) according to ASTM D2863-2000.

The Smoke density rating (SDR) values were determined in accordance with ASTM D 2843-1993 using a General Model JCY-1 instrument (Nanjing Jiangning Analysis Instrument Factory).

Thermal analysis

Thermal analysis including TGA, differential thermogravimetry analysis (DTG) and differential thermal analysis (DTA) was conducted with a WCT-2 (Beijing Optical Instrument Co. Ltd., China) thermoanalyzer instrument. About 7 mg of the specimens were heated from 20 to 800° C at a linear heating rate of 20° C min⁻¹. All runs were performed in air at a flow rate of 50 ml min^{-1} .

Scanning electron microscopy (SEM)

The morphologies of the chars obtained from the fire test were studied by SEM (AMARRY-1000B-2, Chinese Academy of Sciences Instrument Factory, Beijing, China). The char surfaces were covered with gold before observation.

RESULTS AND DISCUSSION

Quantitative analysis of MASN and MAZSN

The quantitative analysis of MASN and MAZSN was analyzed with energy dispersive spectrum (EDS), and the results were shown in Figure 1 and Tables 1 and 2. As shown in Figure 1 and Tables 1 and 2, the elements type and content consistent with the target compounds, which indicate that the compounds are with high purity.



Figure 2. XRD patterns for prepared flame-retardant crystallites (a-d).



Structure and thermal decomposition behavior of MASN and MAZSN

The structures of MA, MASN, and MAZSN were characterized by XRD analysis (Figure 2). MA belongs to the monoclinic system, and its powder diffraction pattern allows complete indexing consistent with reported results.^[17,18] The intensity of the characteristic diffraction peaks decreased significantly in the products MASN and MAZSN. When the same method was used to prepare ZHS, a non-crystalline product was obtained.

Figure 3 shows the TGA/DTG/DTA curves of the flame retardants. As shown in Figure 3a, the weight loss rate is high within the first degradation stage from 271 to 379° C in the TGA curve of MA because the MA is sublimated. After that, the weight loss rate decreases, and MA decomposes into a large amount of non-flammable gases, such as NH₃, CO₂, and N₂, and a small amount of graphitic carbon nitride.^[17,18] The total weight loss may reach 99%. The DTA curve for MA (Figure 3a) shows an obvious endothermic peak between 286 and 403°C with a peak temperature of 367°C, corresponding to the decomposition of MA.

As shown in Figure 3b, the thermal decomposition process of MASN is very similar to that of MA, but the MA content of MASN is significantly reduced, so the weight loss in MASN is also less.

Figure 3c shows that the decomposition temperature of MAZSN is lower than that of MA, which is because the decomposition temperature of the ZHS contained in MAZSN is 220°C.^[19] Between 227 and 350°C, the dehydration reaction of ZHS overlaps with the sublimation reaction of MA, so a distinct endothermic peak appears at 265°C in the DTA curve. Moreover,

an obvious small exothermic peak appears at 445°C in the DTA curve of MAZSN but not in those of MA and MASN, corresponding to the oxidation and decomposition of the char residue generated by the combustion of MAZSN.

Flame retardancy and smoke suppression

The LOI test is an indicator of the ease of combustion in an oxygen–nitrogen atmosphere through downward burning of a vertically mounted sample. The test method is generally reproducible to an accuracy of $\pm 0.1\%$, providing a useful comparison of the relative flammability of different materials, but the correlation with large-scale fires is highly questionable.^[20]

Figure 4 shows the observed LOI results for the flexible PVC samples. The presence of MASN or MAZSN causes an obvious increase in LOI, though the increase is not directly proportional to the level added. When 5 phr of MASN or MAZSN is added to the PVC sample, the LOI increases from 25.2% to 27.9% and 29.6%, respectively. When the additive level reaches 30 phr, the LOI for samples containing MASN or MAZSN reaches 29.9% and 32.5%, respectively. Because there is no obvious increase in LOI for the MA-treated samples at the experimental additive levels, we can conclude that MASN and MAZSN are efficient flame retardants for flexible PVC, but MA is not.

Figure 5 shows the SDR of the flexible PVC samples. The SDR values of the samples treated with flame retardants are lower than that of untreated PVC; in particular, the addition of 30 phr of MAZSN decreased the SDR by 15 units (from 91.8% to 76.9%). While the SDR results for the MA-treated samples contradict the LOI results, MA obviously reduced the SDR.



Figure 3. TGA/DTG/DTA curves of the flame retardants (a-c).



Figure 4. LOI of the PVC samples.

In previous work,^[9] the addition of 25 phr of Sb₂O₃ increased the LOI from 24.7% to 32.0% and decreased the SDR from 92.0% to 86.0%. When the additive level reaches 25 parts, the LOI for ZS or ZHS reached 35.0% and 36.0%, respectively, and the SDR reached 86.0% and 93.6%, respectively. These results indicate that ZHS, ZS, and Sb₂O₃ are more efficient flame retardants for PVC, but their smoke suppression is very limited. The potential toxicity of Sb₂O₃ and the higher price of these compounds also limit their applicability as flame retardants for PVC. The addition of 25 phr of ATH increases the LOI only from 24.7% to 28.5% and decreases the SDR from 92.0% to 84.3%, indicating that the efficiency of ATH as a flame retardant for PVC is very limited. The addition of MA greatly reduces the cost of the novel flame retardant system for PVC, and the novel system is a more efficient flame retardant and smoke suppressant, so it is more suitable for application in PVC.

Thermal analysis

The thermal decomposition behavior is a very important factor in the flame retardant behavior of materials. It plays a crucial role in heat release and weight loss behavior during burning, which



Figure 5. SDR of the PVC samples.

are not evaluated in LOI and SDR tests. The thermal degradation of treated and untreated PVC samples was studied in order to understand the combustion behavior of flexible PVC.

As shown in Figure 6 and Table 3, the TGA curves can be divided into two stages. The thermal decomposition in the first stage, from 240 to 370°C, is due mainly to the emission of hydrogen chloride and the degradation of DOP.^[21,22] The weight loss for each sample is about 58-67 wt% during the first stage. In fact, for the untreated plasticized PVC sample, just over 67 wt% is lost, with somewhat smaller losses for the samples treated with flame retardants. The weight loss of the sample treated with MA decreased from 67.1% to 62.6% (sample b), whereas the final decomposition temperature, the temperature at the maximum rate of weight loss (T_{max}) , and the maximum rate of weight loss (WLR_{max}) increased slightly. The reason is that MA can decompose and absorb heat from 295 to 400°C, producing large amounts of gas (as shown in Figure 3a). Although the gas production expands the char layer and decreases the SDR, the product interferes with HCl in the gas phase, so MA does little to improve the LOI of the flexible PVC. When MASN or MAZSN is added, the weight loss decreases from 62.6% to 58.3% and 59.6%, respectively, but the temperature range is narrower. T_{max} decreases from 305.7 to 288.7°C and 270.1°C, respectively, in the first stage and WLR_{max} increases from 1.94 mg min^{-1} to 2.32 and 7.41 mg min⁻¹, respectively. The reason is that both MASN and MAZSN contain $Sn(OH)_6^{2-}$, which reacts with HCl to form the final products $SnCl_2$ and H_2O .^[9] $SnCl_2$ acts as a kind of Lewis acid in the condensed phase and can catalyze dehydrochlorination and promote early crosslinking of the PVC compound, leading to rapid charring. The hydrogen chloride released acts as both an effective gas-phase flame inhibitor and a synergist of MA to expand the char, so this carbonized product is believed to protect the polymer backbone and inhibit heat and O_2 degradation during combustion, hence contributing to flame retardancy. The MAZSN contains Zn^{2+} , which reacts with HCl to form ZnCl₂, which in turn can cooperate with SnCl₂ to enhance the flame retardancy of PVC. Thus, the MAZSN-treated sample shows better flame retardancy.

The second stage is where the carbonaceous backbone suffers chain scission, and thus low-molecular-weight compounds (and smoke) are produced and the unstable char is oxidized.^[21] The





Figure 6. TGA/DTG/DTA curves of the PVC samples (a-d).

WLR_{max} in the second stage of the MA-treated sample (sample b, Figure 6b) is at the same level as in the untreated PVC (sample a, Figure 6a), but the final degradation temperature and T_{max} increased notably, indicating that there were more char residues in the second stage, and the stability of the char was improved. For the MASN- and MAZSN-treated samples, the weight loss increased from 29.2% to 33.4% and 30.4%, respectively, and both the final degradation temperature and T_{max} in the second stage increased, indicating that the stability of the char was improved.

As shown in Figure 6 and Table 3, the DTA curves of all the PVC samples had an exothermic peak at about 540–630°C, which corresponds to oxidation of the unstable char. The DTA curve of the MA-treated PVC sample (Figure 6b) is similar to that of the untreated PVC sample (Figure 6a), although a small endothermic

peak appeared at about 300°C, corresponding to the endothermic decomposition of MA. However, the DTA curves of the MASNand MAZSN-treated samples differ significantly from that of the untreated PVC. The exothermic peak becomes very sharp, and the exothermic peak temperature (TE) clearly increases, indicating that the structure of the char residue changed.

Char morphology

As shown in Figure 7, the thickness of the sample for SDR test is 6.0 mm, and after SDR tests the thickness of the char residue increase to 37.0–42.0 mm (increased 500–600%). Compared with the standard IFR system, the new IFR systems has a more outstanding expansion character, and the char residue has a denser structure.^[23]

| Table 3. TG/DTG/DTA results of the PVC samples | | | | | | | | | |
|--|-------|---------|--------------------|-------------------------|------------------|---------|---------------------|-------------------------|------------------|
| | | | The first stage | | | | The seconc stage | 1 | |
| Sample | TE | T range | Weight | WLR _{max} | T _{max} | T range | Weight | WLR _{max} | T _{max} |
| | (°C) | (°C) | loss (%) | (mg min ⁻¹) | (°C) | (°C) | loss (%) | (mg min ⁻¹) | (°C) |
| a | 540.9 | 244–350 | 67.1 | 1.43 | 297.3 | 437–617 | 29.2 | 0.36 | 538.6 |
| b | 624.2 | 242–372 | 62.6 | 1.94 | 305.7 | 423–670 | 32.4 | 0.30 | 619.3 |
| c | 630.2 | 249–341 | 58.3 | 2.32 | 288.7 | 407–673 | 33.4 | 0.46 | 628.5 |
| d | 595.3 | 244–295 | 59.6 | 7.41 | 270.1 | 427–653 | 30.4 | 0.51 | 587.3 |

Note: sample a = PVC; sample b = PVC/MA 15 phr; sample c = PVC/MASN 15 phr; sample d = PVC/MAZSN 15 phr; TE = the exothermic peak temperature; T_{max} = the temperature at the maximum weight loss rate of the stage; WLR_{max} = the maximum weight loss rate in the stage.



Figure 7. Photographs and SEM micrographs of char: (a) PVC + MA (15 phr); (b) PVC + MASN (15 phr); (c) PVC + MAZSN (15 phr).

The surface morphology of the char residue after the SDR test was investigated with SEM; photographs and images are shown in Figure 7. The morphology of the char formed in air from PVC containing MASN or MAZSN is quite different from that of char containing MA after the SDR test. Although the char of the PVC sample containing MA is sufficiently intumescent, it shows an alveolate and breakable structure, with some crevasses and small pores in the surface (Figure 7a); therefore, heat and flammable volatiles could easily penetrate the char layer into the flame zone during the process of burning, so the sample's flame retardancy is poor. The morphology of char formed in PVC containing MASN or MAZSN shows a tight, swollen structure, and the obtained swollen charred layers are formed of closed cells. The closed structural cells also promote the thermal protection properties of the charred layers, which agree well with the above-mentioned LOI and thermal property results.

CONCLUSIONS

Investigation of MASN and MAZSN showed that they can be used as efficient flame retardants and smoke suppressants for flexible PVC. MASN or MAZSN and the PVC matrix form a novel intumescent flame-retardant and smoke-suppression system. The PVC acts as the carbonization agent and $Sn(OH)_6^{2-}$ and Zn^{2+} act as the acid source in the flame retardants. The latter can act as a kind of Lewis acid in the condensed phase, catalyzing dehydrochlorination and promoting early crosslinking to the PVC compound. Hydrogen chloride and MA, acting as the blowing agent, can promote the intumescence of the char. On the other hand, the released hydrogen chloride can act as an effective gas-phase flame inhibitor, and the metal ions can promote the stability of the char residue. Thus, this IFR system forms a swollen, stable char layer in fire and can be used as an efficient flame retardant and smoke suppressant for flexible PVC.

SYMBOLS AND ABBREVIATIONS

| ATH | alumina trihydrate |
|--------------------|--|
| DOP | dioctyl phthalate |
| DTA | differential thermal analysis |
| DTG | differential thermogravimetry analysis |
| HCI | hydrochloric acid |
| IFR | intumescent flame retardant |
| LOI | limiting oxygen index |
| MA | melamine |
| MASN | melamine hydroxystannate |
| MAZSN | composite of MASN and ZHS |
| MDH | magnesium hydroxide |
| WLR _{max} | maximum rate of weight loss |
| phr | parts per hundred parts of base resin |
| PVC | poly(vinyl chloride) |
| SEM | scanning electron microscopy |
| SDR | smoke density rating |
| TE | exothermic peak temperature |
| TGA | thermogravimetric analysis |
| T _{max} | temperature at the maximum rate of weight loss |
| XRD | X-ray diffraction |
| ZS | zinc stannate |
| ZHS | zinc hydroxystannate |
| | |

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