A Study on the Flame-Retardance of Poly(vinyl chloride) Incorporated with Metal Hydroxystannates

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ABSTRACT: In this article some metal hydroxystannates were synthesized. It shows that the ZHS with $Fe_2SnO_3.3H_2O$ imparts fairly good flame retardance to the plasticized poly (vinyl chloride) (PVC). The thermal stability and flammability on heating and burning were explored by TG/DTA. Study on mechanical properties of PVC had also been performed. J Appl Polym Sci 112: 82–88, 2009

Key words: poly(vinyl chloride); flame retardance; smoke density; thermal property

INTRODUCTION

Low-cost and easily processed commercial poly (vinyl chloride) (PVC) was widely used in cable, automobile, architecture, and other industries.[1–3] The high chloride content (56.8%) of PVC makes it relatively resistant to ignition and burning. However, the addition of plasticizers for improving the flexibility of PVC gives the poor fire-retardance of PVC at the same time and makes more smoke evolved in burning. This problem has been recognized as an increasingly important issue,[4] it is necessary to improve the fire-retardance of PVC by addition of flame retardants (FRs) into the polymers.

In recent years, concerns have been widely expressed about the inherent toxicity of halogenated FRs and their persistence in the environment. Halogen-free flame retardancy is commonly achieved by the incorporation of inorganic fillers' such as alumina trihydrate (ATH) and magnesium hydroxide (MH) have been widely used as commercial sFR for thermoplastics.[5] Although ATH and MH can significantly increase the resistance to ignition of a polymer and reducing smoke and toxic gas generation during combustion, the addition level is always more than 50%, which will greatly reduce the mechanical properties.[6] Therefore, a lot of studies have been carried out to improve the FR efficiency of MH or ATH, or look for the new highly effective inorganic FR.

Zinc stannate (ZS) and zinc hydroxystannate (ZHS), as nontoxic and highly effective FRs have been studied by the International Tin Research Institute (ITRI) and arisen the attention of other researchers[7–9] in the past three decades. In order to further reduce the cost of the flame retardant, but not reduce the flame retardancy at the same time, some researchers have explored the coating method to prepare ZS or ZHS coated inorganic fillers, which have been found to exhibit significantly enhanced FR and smoke-suppressant properties for PVC at relatively low addition level.[10,11] On the basis of the work of the former literature, a series of hydroxystannate, composite hydroxystannate, and their corresponding coated inorganic fillers have been prepared, and their FR and smoke effect suppressant effects on semirigid PVC have been studied by our team. The aim of our present work is to investigate the FR and smoke suppressant properties of the homemade composite FRs—some mixtures of ZHS and other hydroxystannates, and their effect on the mechanical properties of semirigid PVC were also studied.

EXPERIMENTAL

Materials

The used materials: PVC SG5 (Beijing the Second Chemical Co, Beijing, China), DOP [die (2-ethylhexyl) phthalate] (Shanghai Dongfang Chemicals Co, Shanghai, China), organic tin compound as stabilizer and calcium stearate as lubricant (Hebei Baoding Chemical Co, Baoding City, China), $Na_2Sn(OH)_6$ (Tianjin Suzhuang Chemical Co, Tianjin, China), NaOH, urea, ZnO, $ZnSO_4{\cdot}7H_2O$ (Tianjin the Third Chemical Co., Tianjin, China).

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Preparation of FRs and PVC samples

The FRs were prepared according to the reference.[12] Samples were prepared by mixing PVC with DOP, heat stabilizer, lubricant, coupling agent, and a certain of FRs, then blending them in a two-roller at 343 K for 10 min and compress them at 353 K to form sheets of 100 mm × 50 mm ×3 mm. The test specimens were cut from the molded sheets. The based recipe of the samples is as follow: PVC 100 g, DOP 30 g, stabilizer 3 g, calcium stearate 0.5 g, stearic acid 0.5 g, coupling agent 1 g, and some FRs.

Measurements and characterization

Limiting oxygen index

The flame redundancy of plastics was measured by using limiting oxygen index (LOI) method. The LOI value is the minimum amount of oxygen in oxygen–nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. The LOI values were determined in accordance with ASTM D2863-2000 by HC-3 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China).

Char yield

Char yield values were calculated by the equation of

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

There w_1 and w_2 were the weight of PVC samples before combustion and the residue after combustion of the PVC samples, respectively.[13] This experiment was carried out in a muffle furnace under N_2 at 673 K for 30 min.

Smoke density rating

Smoke density rating (SDR) were determined with JCY-1 instrument (Nanjing Analysis Instrument Factory, Nanjing) according to ASTMD 2843 method, the size of test specimens were 25.3 mm × 25.3 mm × 3 mm. SDR is the absorbency. The process of determine is that in 4 min of the burning of sample the absorbency were determined 16 times (D is the average of smoke density. The larger of the absorbency of the concentration of smoke is higher). The expressions of SDR: $SDR = [D_1 + D_2 + D_3 + \ldots\ldots + D_{15} + 1/2D_{16}]/16]$.

Thermal analysis

The thermal stability of the resins may be assessed by the temperature range of their mass losses measured by thermogravimetry (TG),[10] while the effects of additives on the heat changes during decomposition can be studied by differential thermal analysis (DTA). TG and DTA were carried out on a DT-40 thermal analyzer (Shimadzu Corp., Japan), under air at a heating rate of 10 K min^{-1} and the air flow rate was 60 mL min^{-1}, α-Al_2O_3 was taken as the reference material. The temperature range is from room temperature to 1073 K.

Mechanical property

The tensile strength and elongation measurement were determined with LJ-5000N mechanical instrument (Chengde Experimental Instrument Factory, Chengde) according to ISO: 10810 method. The cross head speed was 50 mm/min. The impact strength was carried out on XCJ-40 Charpy impact test machine (Chengde Experimental Instrument Factory, Chengde) according to ISO: 179 method. For each sample, the average value reported was derived from at least five specimens.

RESULTS AND DISCUSSIONS

Flame retardant property

Figure 1 showed the LOI values of the FR semirigid PVC samples treated with different composite hydroxystannates. As shown in Figure 1, the LOI of the FR semirigid PVC samples treated with different composite hydroxystannates were gradually increased from 30.5% to 41.0% as the addition of the composite hydroxystannate ranged from 0.5 to 2.0 parts; the LOI of the FR semirigid PVC sample treated with the composite hydroxystannate ZHS+$Fe_2Sn_3(OH)_{18}$, ZHS+ $NiSn(OH)_6$, and ZHS+ $CuSn(OH)_6$ was better than that of ZHS+ $MgSn(OH)_6$, ZHS+ $SrSn(OH)_6$, ZHS+ $MnSn(OH)_6$, and ZHS+ $CoSn(OH)_6$ at the same addition level, respectively, which may be ascribed to the different synergetic effect of the metal elements; the LOI of the FR semirigid PVC treated with the composite hydroxystannate-ZHS+$Fe_2Sn_3(OH)_{18}$ was the highest among the studied composite hydroxystannates at the same addition level, the LOI was 36.5% only with 0.5 part addition, and the LOI was 41.0% as the addition was increased to 1.5 parts, which showed that there may be a good synergetic effect of zinc, iron, and tin.

The result showed that the studied composite hydroxystannates were very effective FRs for semirigid PVC and the FR property of ZHS+$Fe_2Sn_3(OH)_{18}$ was the best.

Char formation property

Figure 2 provided the char yield of the FR semirigid PVC samples treated with different composite

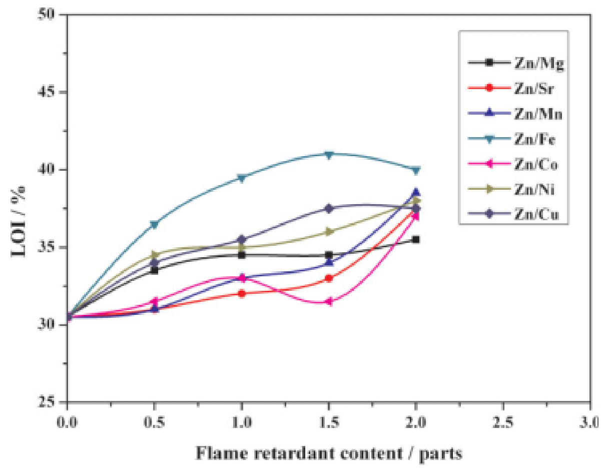

Figure 1 LOI of the flame retardant semirigid PVC samples. (Note: Zn/Mg, Zn/Sr, Zn/Mn, Zn/Fe, Zn/Co, Zn/Ni and Zn/Cu represents the flame retardant semirigid PVC sample treated with ZHS+$MgSn(OH)_6$, ZHS+$SrSn(OH)_6$, ZHS+$MnSn(OH)_6$, ZHS+$Fe_2Sn_3(OH)_{18}$, ZHS+$CoSn(OH)_6$, ZHS+ $NiSn(OH)_6$ and ZHS+ $CuSn(OH)_6$, respectively.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydroxystannates. As indicated in Figure 2, in most of the cases, the char yield of the FR semirigid PVC samples treated with different composite hydroxystannates was lower than that of the pure semirigid PVC, which showed that the composite hydroxystannates may not display their promotion of char formation as the addition level was lower than 2 parts.

Smoke suppressant property

The smoke suppressant properties of the studied composite hydroxystannates were investigated by SDR, the corresponding data of SDR and maximum

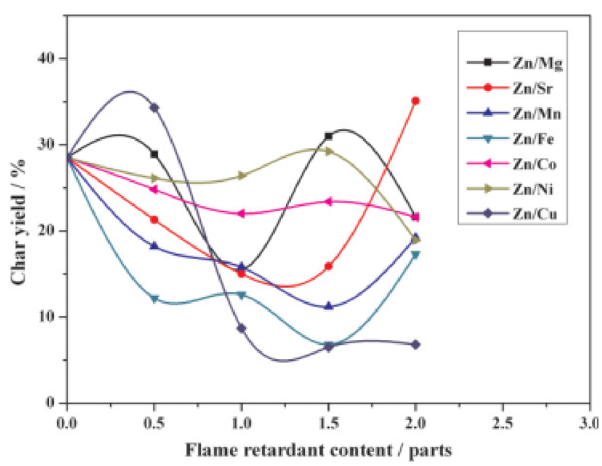

Figure 2 Char yield of the flame retardant semirigid PVC samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Smoke Density of the Semirigid PVC Treated with Two Parts of Different Composite Hydroxystannate

Flame retardants	SDR (%)	MSDR (%)
None	89.13	100
ZHS+$MgSn(OH)_6$	46.69	60.36
ZHS+$SrSn(OH)_6$	62.42	76.29
ZHS+$MnSn(OH)_6$	39.93	59.26
ZHS+$Fe_2Sn_3(OH)_{18}$	46.83	58.25
ZHS+$CoSn(OH)_6$	54.88	69.82
ZHS+$NiSn(OH)_6$	35.49	48.77
ZHS+$CuSn(OH)_6$	52.42	64.95

of smoke density rating (MSDR) of the FR semirigid PVC sample treated with two parts of the composite hydroxystannates were shown in Table I. As observed in Table II, the SDR and MSDR of the pure semirigid PVC was 89.13 and 100%, respectively; the SDR of the FR semirigid PVC treated with the composite hydroxystannates was decreased to 35.49–62.42% with 30–54% reduction, and the MSDR was decreased to 48.77–76.29% with 24–51% reduction; the SDR and MSDR of the FR semirigid PVC was 35.49% and 48.77%, respectively, which showed the lowest value among the studied FR samples. The result of SDR and MSDR indicated that the studied composite hydroxystannates were good smoke suppressants for semirigid PVC and ZHS+$NiSn(OH)_6$ was the best among them.

Thermal analysis

Figures 3 and 4 showed the TG curves of the pure semirigid PVC and FR semirigid PVC treated with selected composite hydroxystannates, respectively, and the corresponding data of TG and DTA was shown in Table II. The FR semirigid PVC sample treated with two parts of ZHS+$Fe_2Sn_3(OH)_{18}$, ZHS+$CuSn(OH)_6$, and ZHS+$SrSn(OH)_6$ were selected to investigate the thermal degradation and FR mechanism of the composite hydroxystannates. As observed from Figure 3, the TG curves of the pure and FR semirigid PVC samples showed two degradation stages, the first stage was mainly due to the emission of hydrogen chloride and the degradation of DOP,[14,15] and the second stage was attributed to the process of crosslinking formation of aromatic volatiles, Diels–Alder reactions and eventually charring.[16] The gradient of TG curves for the FR semirigid PVC samples were obviously different from that of pure semirigid PVC. As shown in Table II, $T_{1\%}$ was increased 17–30 K with the addition of the selected composite hydroxystannate, which showed the addition of the composite hydroxystannate increased the thermal stability of the semirigid PVC.

TABLE II
TG and DTA Results of the PVC Samples

			First stage		Second stage		
Sample	T_m (K)	$T_{1\%}$ (K)	TR_1 (K)	ML_1 (%)	TR_2 (K)	ML_2 (%)	TML (%)
A	825	479	479–604	67.7	664–886	29.3	97.0
B	816	506	506–604	63.7	636–850	27.2	90.9
C	839	496	496–601	64.1	638–874	33.4	97.5
D	826	503	503–614	65.6	657–894	25.4	91.1

Note: A-pure semi rigid PVC; B-the flame retardant semi-rigid PVC samples treated with [ZHS+$Fe_2Sn_3(OH)_{18}$]; C-the flame retardant semi-rigid PVC samples treated with [ZHS+$CuSn(OH)_6$]; D-the flame retardant semi-rigid PVC samples treated with [ZHS+$SrSn(OH)_6$]; T_m—the temperature of exothermic peak, $T_{1\%}$—the temperature at which the mass loss of the samples was 1%; TR_1,TR_2—the temperature range of the first stage and second stage, respectively; ML_1, ML_2—the mass loss of the first stage and the second stage, respectively; TML—the total mass loss.

The weight loss of the first degradation stage (ML_1) was slightly decreased by 3–6%, which showed the addition of the composite hydroxystannate inhibited the evolution of hydrogen chloride and the degradation of DOP at some degree, finally resulted in the decrease of smoke production; and that of the second stage (ML_2) of the FR semirigid PVC treated with ZHS+$CuSn(OH)_6$ was increased by 14%, which indicated the composite hydroxystannate may display its role in gas phase; the ML_2 of the FR semirigid PVC treated with ZHS+$Fe_2Sn_3(OH)_{18}$ and ZHS+$SrSn(OH)_6$ was decreased a 8–13%, which indicated the promoting effect of char formation; the total mass loss (TML) of the FR semirigid PVC was increased, except for sample C.

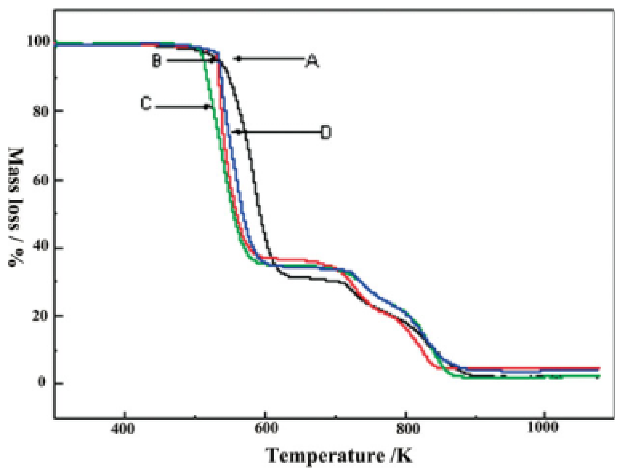

Figure 3 TG curves of the pure semirigid PVC and flame retardant semirigid PVC. (Note: A-pure semirigid PVC; B-the flame retardant semirigid PVC samples treated with two parts of [ZHS+$Fe_2Sn_3(OH)_{18}$]; C-the flame retardant semirigid PVC samples treated with two parts of [ZHS+$CuSn(OH)_6$]; D-the flame retardant semirigid PVC samples treated with two parts of [ZHS+$SrSn(OH)_6$]). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As shown in Figure 4 and Table II, the DTA curves of the samples treated with the FRs have sharper exothermic peak respectively, and an obvious endothermic peak respectively, at 520–540 K contrast with the pure semirigid PVC.

FR and smoke suppression mechanism of the composite hydroxystannates

The FR and smoke suppressant results of the studied composite hydroxystannate indicate that the studied composite hydroxystannates were effective FRs and smoke suppressants for semirigid PVC. According to the results of our former study and the work of other researchers,[17,18] the FR mechanism of the composite hydroxystannates can be explained from the following aspects:

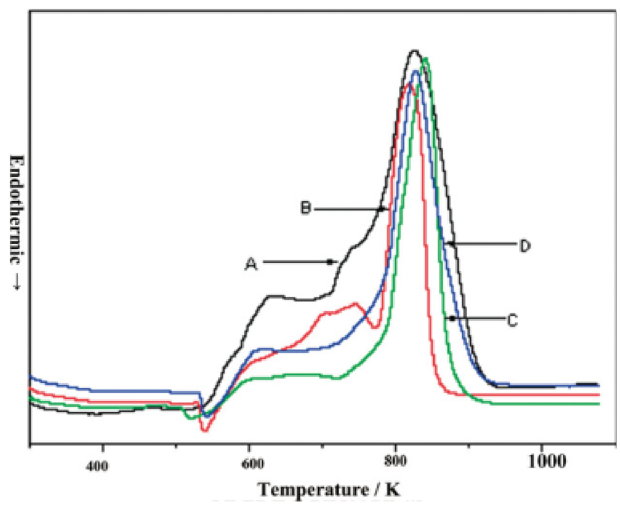

Figure 4 DTA curves of the pure PVC and flame retardant semirigid PVC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

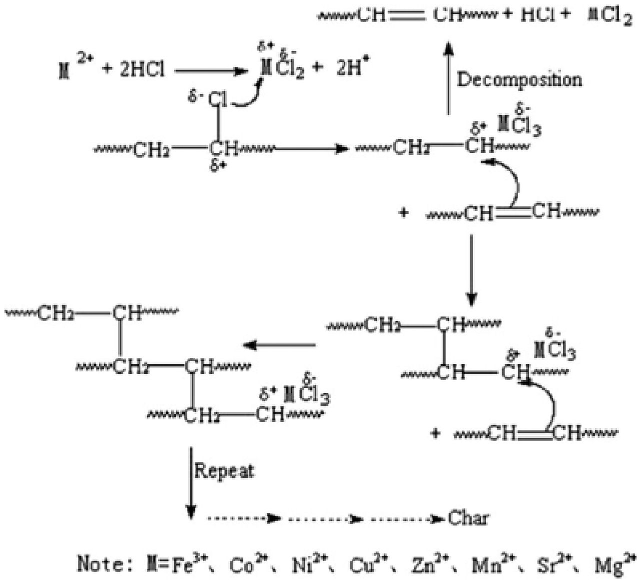

Figure 5 The sketch map of the flame retardant process of M^{n+} in the composite hydroxystannates.

The sketch map of the FR process of M^{n+} in the composite hydroxystannates was demonstrated in Figure 5. As shown in Figure 5, the M^{n+} (M^{n+} = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Sr^{2+}, Mg^{2+}) in the composite hydroxystannates reacted with HCl to form MCl_n, a kind of stronger Lewis acid, which catalyzed the dehydrochlorination and promoted early crosslinking of the PVC compound, leading to rapid char formation. The carbonized product is believed to protect the polymer backbone, inhibit heat and O_2 transfer during combustion.[17] The metal cation may react with the free radicals to interrupt chain transmission to improve the FR effect.

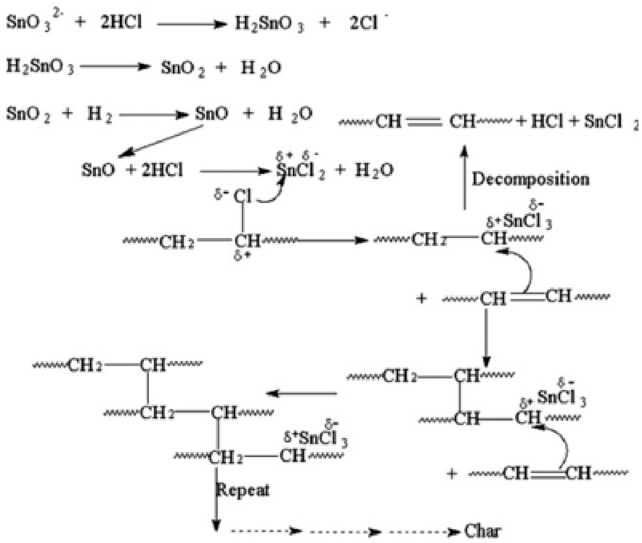

Figure 6 The sketch map of the flame retardant process of SnO32-in the composite hydroxystannates.

The sketch map of the FR process of SnO_3^{2-} in the composite hydroxystannates was presented in Figure 6. As shown in Figure 6, the SnO_3^{2-} in the hydroxystannates reacted with HCl to form $SnCl_2$ and H_2O. $SnCl_2$ also acts as a kind of Lewis acid in the condensed phase, which is incorporated with MCl_n to enhance the flame retardance of PVC.[17,18]

It was the integrated effect of M^{n+} and SnO_3^{2-} that improved the FR and smoke suppressant effect, which displayed their roles in both condensed and gas phase.

Analysis of mechanical property

Figures 7–9 showed the tensile strength, elongation at break, and impact strength of the FR semirigid PVC treated with different composite hydroxystannate, respectively. As shown in Figure 7, the tensile strength of the FR semirigid PVC basically decreased with the increase of the composite hydroxystannate, except for several exception; that the FR semirigid PVC was 22.0–24.8 MPa decreased by 4–15% as the addition of the composite hydroxystannate ranged from 0.5 parts to 1.5 parts, and that was decreased to 19.0–23.5 MPa decreased by 9–26%. This result showed the studied composite hydroxystannate had little bad effect on the tensile strength of the corresponding FR sample, which may be due to small addition level of the composite hydroxystannate.

As observed from Figure 8, the elongation at break of the FR semirigid PVC was increased by 20–89% along with the addition of the corresponding

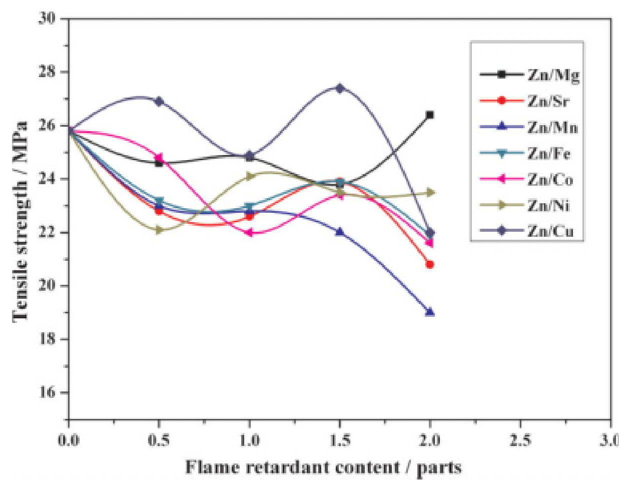

Figure 7 Tensile strength of the flame retardant semirigid PVC sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydroxystanate, which showed the toughening effect of the studied composite hydroxystannate on the semirigid PVC matrix.

As Figure 9 indicated, the impact property of the FR semirigid PVC could be divided into two groups, except for some exception. One group was the FR semirigid PVC treated with ZHS+$MgSn(OH)_6$, ZHS+$Fe_2Sn_3(OH)_{18}$, and ZHS+$CuSn(OH)_6$ respectively, the impact strength of which was 1.4–5 times, except for the exception of the sample treated with two parts of composite hydroxystannate—ZHS+ $MgSn(OH)_6$, the impact strength of which was about 26 times as that of the pure semirigid PVC. The other group was the FR semirigid PVC treated with ZHS+$SrSn(OH)_6$, ZHS+$MnSn(OH)_6$, ZHS+$CoSn(OH)_6$, and ZHS+$NiSn(OH)_6$, respectively, except for the sample treated with 1.0 part of ZHS+$NiSn(OH)_6$, the impact strength of which was 23–29 times as that of pure semirigid PVC when the addition level was ranged from 0.5 to 1.5 parts, and that of which was 2–3 times as that of pure semirigid PVC when the addition level was two parts. The result of impact strength of the FR samples showed the different composite hydroxystannate with different addition level had different effect on the impact strength, which may be attributed the different particle size of the different composite hydroxystannate and the detailed cause of which should be carried out in our future work.

In a word, the above results showed that the studied composite hydroxystannate basically had a little bad effect and greatly increased toughening effect on the semirigid PVC matrix.

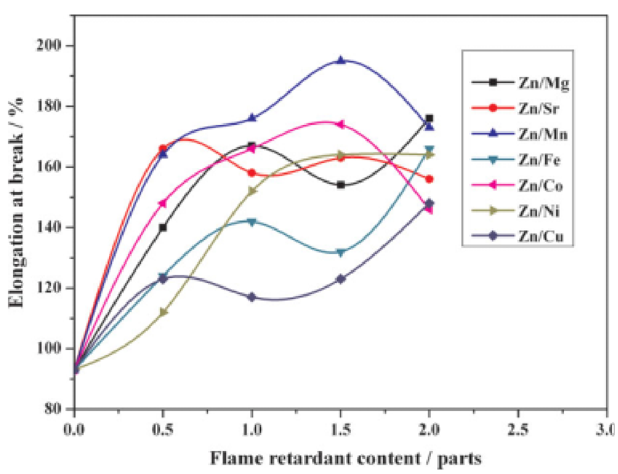

Figure 8 Elongation at break of the flame retardant semirigid PVC sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

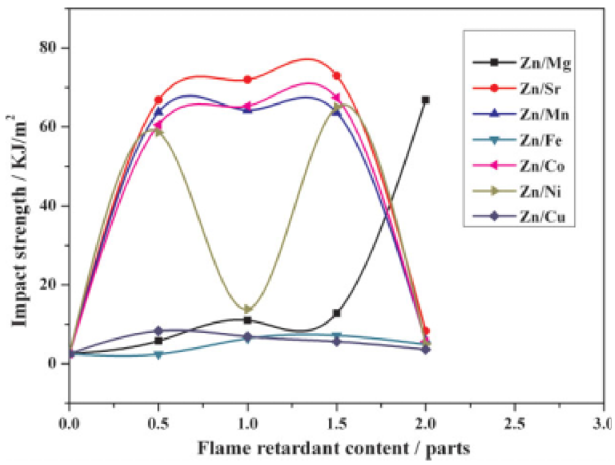

Figure 9 Impact strength of the flame retardant semirigid PVC sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

The result of LOI, char yield, and smoke suppressant properties showed that the studied composite hydroxystannates—ZHS+$MgSn(OH)_6$, ZHS+$SrSn(OH)_6$, ZHS+$MnSn(OH)_6$, ZHS+$Fe_2Sn_3(OH)_{18}$, ZHS+$CoSn(OH)_6$, ZHS+$NiSn(OH)_6$, and ZHS+$CuSn(OH)_6$ were all good FR and smoke suppressant agents for semirigid PVC. The LOI of the semirigid PVC treated with two parts of ZHS+$Fe_2Sn_3(OH)_{18}$ was 40% increased by 31% and the SDR of which was 46.83% decreased by 47% as compared with the corresponding property of pure semirigid PVC.

TG-DTA analysis showed the addition of the composite hydroxystannate increased the thermal stability of the semirigid PVC, inhibited the evolution of hydrogen chloride. The FR and smoke suppressant properties of the studied composite hydroxystannates was a integrated effect of M^{n+} and SnO_3^{2-}, which displayed their roles in both of condense and gas phase.

The mechanical properties showed the studied composite hydroxystannates had a little bad effect and greatly increased toughening effect on the semirigid PVC matrix.

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