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Zinc Hydroxystannate Coated Nano-Magnesium Hydroxide as Flame Retardant for Semirigid Poly(vinyl chloride)

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$ZnSn(OH)_6$ coated $Mg(OH)_2$ (ZHS-MOH) was synthesized by a homogeneous precipitation method with ultrasonic and azeotropic technology. The results of XRD show that the characteristic diffraction peak of $ZnSn(OH)_6$ advanced and the characteristic diffraction peak of $Mg(OH)_2$ reduced respectively with increasing of the mass ratio of $ZnSn(OH)_6$. The particle image of ZHS-MOH and $Mg(OH)_2$ was observed by TEM. TGA and DTA showed the exothermic peak tempareture of $Mg(OH)_2$ increased and the weight loss decreased. The ZHS-MOH was applied into semirigid PVC and it has a higher limiting oxygen index and lower SDR compared with that used $Mg(OH)_2$.

Key Words: $ZnSn(OH)_6$, $Mg(OH)_2$, Flame retardant, Poly(vinyl chloride).

INTRODUCTION

Poly(vinyl chloride) (PVC) is inherently fire retardant due to its higher chlorine content. While PVC used as sheet, such as floor and celling, a large number of plasticizer was added. Then its fire performance is less favorable and hence a potential danger to people's life and riches.

The $Mg(OH)_2$ is a good flame retardant for PVC, but the dosage are high. The inorganic tin compounds have been receiving increasing attention in recent years for its high efficiency[1,2]. $ZnSn(OH)_6$, $ZnSnO_3$ and SnO_2 have been shown to have good flame-retardant and smoke-suppressant properties in halogen-containing polymer such as PVC, neoprene and hypalon[3-5].

The main research objects of this paper is to obtain more effective flame retardant\smoke suppressant by the synergism of $Mg(OH)_2$ and $ZnSn(OH)_6$. $ZnSn(OH)_6$ (10 %) coated nm-$Mg(OH)_2$ (ZHS-MOH) was prepared and applied for the treatment of semi-rigid PVC and the flame retardant\smoke suppressant and mechanical properties of ZHS-MOH was compared with that of nm-$Mg(OH)_2$ and $ZnSn(OH)_6$.

EXPERIMENTAL

PVC TL-100, Tianjin Lejin Dagu Chemical Co.; di-(2-ethylhexyl) phthalate (DOP), Shanghai Dongfang Chemicals Co.; organic tin compound and calcium stearate, Hebei Baoding Chemical Co.; nm-$Mg(OH)_2$ (diameter of 50 nm), Nanjing

Haitai Namicailiao Co.; $Na_2Sn(OH)_6$, ZnO, KOH, urea were purchased from in the market.

Synthesis of ZHS-MOH: The preparation of flame-retardant ZHS-MOH was performed performed according to the reported method[6]: First, nm-$Mg(OH)_2$ was slurried by rapid stirring in 150 mL of an aqueous solution containing urea with ultrasonic under 323 K for 1 h. ZnO, KOH and $Na_2Sn(OH)_6$ were added into another three-necked bottle containing 350 mL of an aqueous solution. Second, to mix the two solutions and heated to 358 K. After 6 h, the solid product was separated by filtration, washed three times with secondary water. The filter azeotropic with the *n*-butanol after it dispersed by supersonic and dried in vacuum drying oven for 24 h at 323 K. The yield of the product was 93 %.

Preparation of PVC samples: Semirigid PVC samples were prepared according to the basic recipe: PVC 100 parts, DOP 30 parts, stabilizer 3 parts, calcium stearate 0.5 parts, stearic acid 0.5 parts, coupling agent 1 part and certain amount flame retardant. That mixer was blend in a two-roll mill at 443 K for 10 min and compressed at 453 K to form sheets. Different shapes, sizes and forms of semi-rigid PVC samples were prepared using appropriated molds, the samples for analysis being ground before use.

Measurements and characterization: TEM carried out on JEM-100SX transmission electron microscopy. XRD carried out on X-ray diffractometer (Y-2000) (Cu target Kα, λ = 0.1541 nm, Japan),the shift step 0.06 % and the angle step 20-80°. TG and DTA carried out on a DT-40 thermal analyzer (Shimadzu Corp., Japan) under air at a heating rate of 10 K min^{-1}. The LOI values were determined in accordance with ASTM D2863 by means of a General Model HC-1 LOI instrument. Smoke density rating (SDR) was determined with the JCY-1 instrument according to ASTMD 2843 method, the size of the test specimens was 25.3 mm × 25.3 mm × 3 mm. The tensile strength and elongation measurements were carried out on LJ-5000N mechanical instrument according to ISO 10810.

RESULTS AND DISCUSSION

XRD and TEM analysis: The XRD patterns of $Mg(OH)_2$ and MOH-ZHS were showed in the Fig. 1. It can be found that with increasing of the mass ratio of $ZnSn(OH)_6$ coated on $Mg(OH)_2$, the characteristic diffraction peak of $ZnSn(OH)_6$ advanced obviously contrast to the reduced of $Mg(OH)_2$. The characteristic diffraction peak of $ZnSn(OH)_6$ have been obviously reduced when 10 % $ZnSn(OH)_6$ coated nm-$Mg(OH)_2$.

The images of nm-$Mg(OH)_2$ and MOH-ZHS (coated ratio 10 %) were showed in Figs. 2 and 3, respectively. The direct of the nm-MOH partical is 150 nm and it increased to 200 nm after coated. The coated particle's disapersity become well compared with that of the nm-MOH, the appearance of reunites decreased.

These results indicated that nm-$Mg(OH)_2$ could be coated by $ZnSn(OH)_6$ well even 10 % coated ratio.

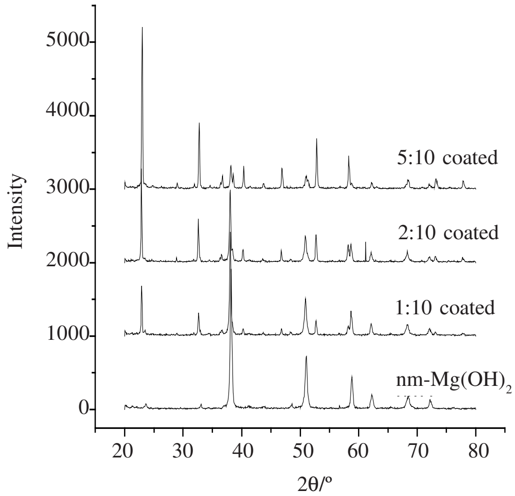
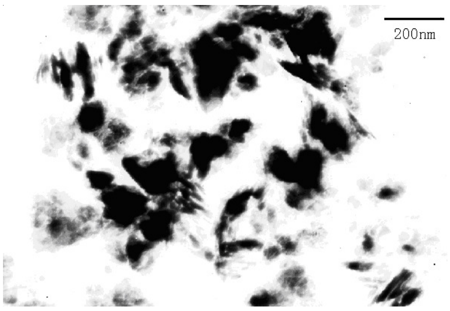


Fig. 1. XRD pattern of different coated rates of $ZnSn(OH)_6$ coated nm-$Mg(OH)_2$



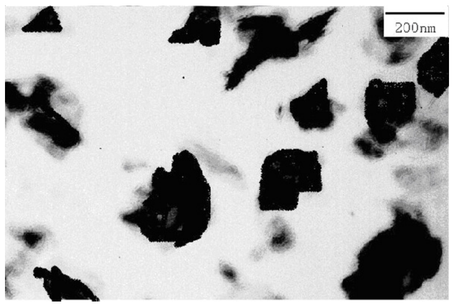


Fig. 2. TEM images of nm-$Mg(OH)_2$ Fig. 3. TEM images of and MOH-ZHS

TG/DTA analysis: From the TG/DTA of nm-$Mg(OH)_2$ curve (Fig. 4) analysis that, it has an obvious weight loss and exothermic process from 326-440 ºC, in this process the weight loss was 31.15 %, which was consistent with theoretical dehydration of nm-$Mg(OH)_2$ 31.03 %. Compared with nm-$Mg(OH)_2$, the TG/DTA curve of ZHS-MOH (Fig. 5) divided into two different stages: one stage is from 237-340 ºC and the second stage is from 340-470 ºC, the whole rate of the weight loss obtained 31.15 %. The results indicated that the initial decomposition temperature of the coated nm-$Mg(OH)_2$ compared with uncoated nm-$Mg(OH)_2$ had elevated 14 ºC. The reason is the production of $ZnSnO_3$ which synthesized by dehydration of $ZnSn(OH)_6$ from 237-340 ºC[7] coated on the surface of nm-$Mg(OH)_2$. The $ZnSnO_3$ played the inhibitory action to the thermal decomposition process of nm-$Mg(OH)_2$ and had promoted the $Mg(OH)_2$ decomposition temperature and degeneration time.

Flame retardant and smoke suppressant properties: As shown in Table-1, the LOI was improved along with the increasing content of the additives. When at the same additive level, the flame retardant properties of ZHS-MOH was the best

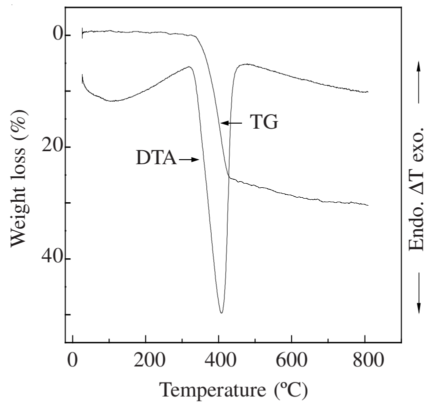


Fig. 4. TG/DTA of nm-$Mg(OH)_2$

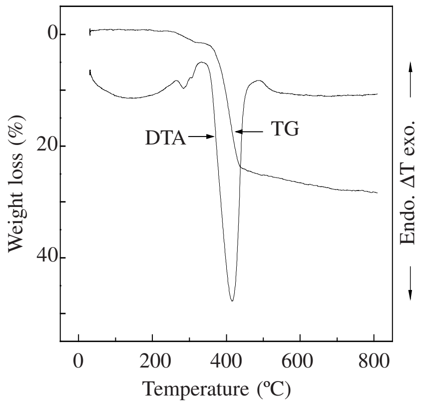


Fig. 5. TG/DTA of MOH-ZHS

TABLE-1
SOME PROPERTIES OF THE PVC SAMPLES

Samples	Flame retardents	Contents (phr)	LOI (%)	SDR (%)	Tensile strength (MPa)	Impact strength (kJ/m^2)
I	Blank	0	28.5	90.08	24.4	5.1
II(a)		2	31.7	86.30	23.8	3.8
II(b)	$ZnSn(OH)_6$	3	32.5	86.51	23.3	3.5
II(c)		4	32.5	86.89	23.7	3.7
III(a)		20	31.8	60.25	21.8	8.4
III(b)	nm-$Mg(OH)_2$	30	33.6	53.95	23.1	7.2
III(c)		40	35.4	40.35	25.6	6.0
IV(a)		20	40.3	57.39	23.2	10.4
IV(b)	ZHS-MOH (10 %)	30	43.8	64.75	22.6	7.4
V(c)		40	45.3	–	24.2	5.8

among the three kinds of additives [$ZnSn(OH)_6$, nm-$Mg(OH)_2$ and ZHS-MOH]. For example, when added 20 parts of additives, the LOI of sample IV(b) was 11.3 units higher than that of sample II(b), 10.2 units higher than that of sample III(b) and 15.3 units higher than the black sample. These indicated that $ZnSn(OH)_6$, nm-$Mg(OH)_2$, ZHS-MOH are effective flame retardant for semi-rigid PVC and ZHS-MOH has the best effect when at the same effective additive level.

As shown in Table-1, the SDR were decreased along with the order of sample II(b)-sample V(b), which indicated the smoke suppressant properties of $ZnSn(OH)_6$, nm-$Mg(OH)_2$, $ZnSn(OH)_6$ coated nm-$Mg(OH)_2$ and $ZnSn(OH)_6$ coated nm-$Mg(OH)_2{\cdot}O_2$ coated $CaCO_3$ was the best among the given additive in Table-1. The SDR of samples II(b), III(b), IV(b) and V(b) were 86.51, 53.95, 76.18 and 64.75 %, respectively and that of them was 3.57, 36.13, 13.90 and 25.33 % lower than the semi-rigid PVC (sample (1)). Theses indicated that the addition of nm-$Mg(OH)_2$ and $ZnSn(OH)_6$ coated nm-$Mg(OH)_2$ can greatly decrease the formation of smoke.

The mechanical properties were also shown in Table-1. To different particle size, when 20 parts nm-$Mg(OH)_2$ and ZHS-MOH was added into the PVC samples, the impact strength 8.44 and 10.45 kJ/m^2 higher than that of black sample (5.12 kJ/m^2), respectively, the sample's impact strength of $ZnSn(OH)_6$ was lower than that of black sample. The more addition added to the PVC, the worse impact properties of PVC. The addition of the ZHS-MOH improved the impact strength but little effecte to the tensile strength of the non-flame retardant PVC.

Conclusion

The well-coated ZHS-MOH can be prepared by a homogeneous precipitation method with ultrasonic and azeotropic technology and the exothermic peak tempareture of $Mg(OH)_2$ increased after coated by $ZnSn(OH)_6$. The ZHS-MOH was a more efficently flame retardant and smoke-suppressant agent than the $Mg(OH)_2$ as used in the PVC. More the addition of ZHS-MOH has little influence on the tensile strength of the PVC samples.

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