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The Effect of Hydrotalcite and Zinc Oxide on Smoke Suppression of Commercial Rigid PVC

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To reduce the smoke release of poly(vinyl chloride) (PVC) during burning, layered double hydroxides (LDHs) and zinc oxide (ZnO) powders were used to modify the polymer. The results indicated that the addition of LDHs-ZnO had a significant effect on smoke suppression. The limiting oxygen index (LOI) reached a maximum value and the smoke density rank (SDR) exhibited a minimum value when the weight percentages of LDHs and ZnO in PVC were 3% and 2%, respectively. Thermal stabilities of the modified PVC and degradation products were investigated by means of thermogravimetry and pyrolysis-gas chromatography-mass spectra (Py-GC-MS). The LDHs-ZnO obviously accelerated the decomposition of PVC to release hydrogen chloride, and the decomposed PVC consequently produced the trans-conjugated polyene sequences, which easily formed cross-linked structures. However, a cyclization reaction in PVC chain without the additives produced aromatic compounds such as benzene, toluene, and naphthalene at 350°C. Even though, an amount of aromatic compounds was released from the PVC modified with LDHs-ZnO at the temperature of 600°C, the content of the decomposed products is relatively lower compared to unmodified PVC.

Keywords PVC, smoke suppression, flame retardance, hydrotalcite, zinc oxide, layered double hydroxide

Introduction

Poly(vinyl chloride) (PVC) has been widely used as wire, cable, and building materials. The polymer will release a large amount of black smoke and toxic gases as it burns; the toxic gases contain chlorinated hydrocarbons, benzene, toluene, naphthalene, and other aromatic compounds. Moreover, some additives such as plasticizer and lubricant can obviously reduce the flame retardance of PVC. All of these limit the extensive application of PVC. Therefore, flame retardance and smoke suppression are paid increasingly more

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attention. Much effort has been made to reduce the flammability and smoke formation of PVC (1–5). Transition metal oxide compounds, such as antimony, tin, zinc, copper, iron and molybdenum, have been reported to be effective as smoke-suppressants for PVC (6–10).

Hydrotalcite has a layered double hydroxides structure, called LDHs. LDHs are an anionic clay in which divalent cations within brucite-like layers are replaced by trivalent cations. The resulting positive charge is compensated by hydrated anions located in the interlayer space between two brucite sheets. The general formula for these materials is $[M^{2+}_{1-x} M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}] \cdot mH_2O$, where M^{2+} and M^{3+} are di- and tri-valent metal cations, respectively, which occupy octahedral positions in hydroxide layers; A^{n-} is an exchangeable anion, such as CO_3^{2-}, NO_3^-, and Cl^-, etc (11, 12). The typical hydrotalcite compound is $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$.

Hydrotalcite has been used as fillers in polymer materials for decades, to improve the mechanical properties and reduce the cost. The effect of hydrotalcite on smoke suppression of PVC was reported recently (13, 14), but the study was mainly aimed at properties of flame retardance and smoke suppression, thermal stability and mechanics of PVC. There was no evidence for the mechanism of the smoke-suppression and the effects of LDHs mixed with other compounds.

In order to enhance the flame retardance and smoke suppression of LDHs in PVC, the effect of a mixture of LDHs and zinc oxide (ZnO) and the mechanism are described in this report.

Experimental

Materials

PVC SG-5 resin with Mn of 63500 (suspension polymerization, no additives) was supplied by Xinxiang Resin Factory, China. Nano-LDHs (chemical purity, particle size 40–60 nm), Jiangsu Chemistry and Chemical Engineering Auxiliary Agent Factory, China. Zinc Oxide (chemical purity), Tianjin Chemical Reagent Factory, China.

Sample Preparation

PVC was blended with LDHs and ZnO in a twin-roller mill at 160°C for 10 min, along with a certain amount of thermal stabilizer and lubricants, plasticizers, and other additives. The polymer blends were compressed into sheets at 14–16 MPa and 170 ± 2°C. The composition of the polymer blends is listed in Table 1.

Measurement

Smoke Density Rank (SDR) was detected on a JCY-3 Smoke Density Analyzer (Nanjing City Jiangbing District Analytical Apparatus Factory, Nanjing, China) according to GB/T8627 method. In this measuring method, the maximum SDR value is 100, and the lower the SDR value, the better smoke suppression the material. Limiting Oxygen Index (LOI) was obtained using a HC-2 Oxygen Index Analyzer (Nanjing Analytical Instrument Factory, Nanjing, China) according to the ASTM D2863 method. TG and DTA of samples were conducted with a Netzsch STA 449C under air at a heating rate of 20°C/min till 600°C. Degradation products were pyrolyzed on a Single-shot Pyrolyzer (Py-2020iS) (Frontier Laboratories Ltd., Japan) under helium gas at 350°C and 600°C, and then the

Table 1
The composition and properties of the modified PVC and compared sample[a]

Samples	LDHs (%)	ZnO (%)	SDR	LOI	Tensile strength (MPa)	Broken elongation (%)
PVC	0	0	88.7	43.0	35.6	44.1
PVC/LDHs3	3	0	69.4	50.0	39.2	36.8
PVC/LDHs3-ZnO1	3	1	65.3	63.0	36.8	34.1
PVC/LDHs3-ZnO2	3	2	63.2	64.0	37.8	36.4
PVC/LDHs3-ZnO3	3	3	67.3	63.0	36.9	33.1
PVC/LDHs3-ZnO4	3	4	76.0	59.5	35.6	33.0

[a] All samples contain tribasic lead sulfate 5%, calcium stearate 2%, dioctyl phthalate 10%, calcium carbonate 5%.

products were detected online with a GC-MS-OP2010 (Shimadzu Co., Japan), where helium gas was used as a carrier gas in gas chromatography (GC) and mass spectrum (MS).

Results and Discussion

Smoke Suppression and Flame Retardance

The commercial PVC was modified with LDHs and ZnO. According to the literature (13) and our previous experiment, 3 wt% LDHs in PVC can obviously reduce the smoke release. The effect of the ZnO content on LOI and SDR of PVC containing 3 wt% LDHs was investigated. As shown in Figure 1, the SDR decreases initially with increasing ZnO, and then the value increases. It exhibits a minimum value of 63.2 at a ZnO content of 2 wt%. On the other hand, the LOI of PVC increases rapidly when the ZnO content is

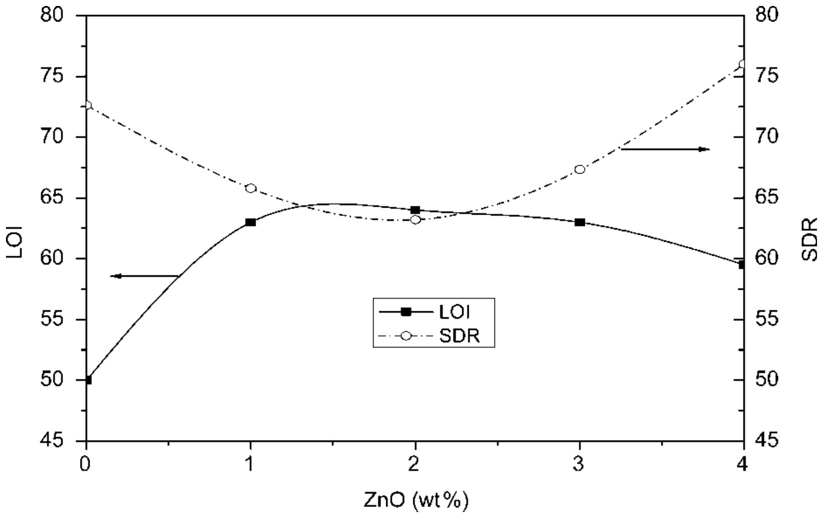

Figure 1. Effects of ZnO contents on LOI and SDR of modified PVC.

below 1%, while the value of LOI decreases when the ZnO content is above 3%. LOI exhibits a plateau at a ZnO content of 1–3wt%. Figure 1 also indicates that the PVC containing 3% LDHs and 2% ZnO can efficiently retard the smoke release, and the LOI increases by 29% and SDR decreases by 49% at this composition, compared to the blank sample. Thus, the samples, PVC and PVC/LDHs3-ZnO2 listed in Table 1, were further investigated.

Analysis of Mass Loss

According to Figure 2 and Table 2, the thermal decomposition of PVC can be divided into two stages. In the first stage, weight loss is between 45–55%, which is attributed to the release of hydrogen, benzene, furan, etc. In this stage, LDHs-ZnO plays an important role of accelerating the decomposition to release hydrogen chloride. The onset decomposition temperature of the PVC/LDHs3-ZnO2 decreases to 250°C from 315°C for PVC, the maximum weight loss increases to 40% from 20%, and the temperature range shortens to 60°C from 100°C. In the second stage, namely, beyond 400°C, both PVC and PVC/LDHs3-ZnO2 exhibit a similar decomposition behavior.

Mechanism of Smoke Suppression

According to the TGA discussed above, the thermal decomposition of PVC can be divided into two stages, in the temperature ranges of 270–370°C and 445–505°C, respectively. We selected two temperatures, 350°C and 600°C, to pyrolyze the polymer and detect the degradation products online by GC-MS.

In the first stage, there are many more strong peaks for PVC, compared to the PVC/ LDHs3-ZnO2, as shown in Figure 3. This demonstrates that the kinds and the amount of degradation products for PVC/ LDHs3-ZnO2 are much lower than that in unmodified PVC. The peaks at 3.78 min, 13.38 min, 14.05 min, and 16.76 min detected for PVC are caused by benzene, 1,4-dihydronaphthalene, naphthalene and 2-vinylnaphthalene, respectively. The data are listed in Table 3. The appearance of these aromatic compounds suggests

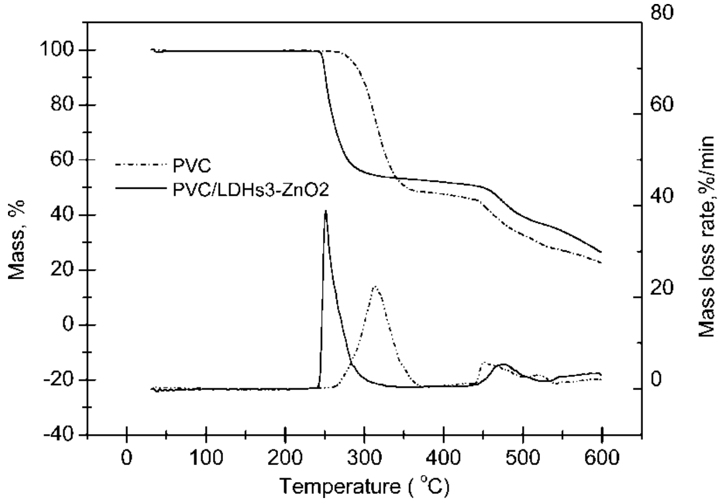

Figure 2. TGA and DTG curves of PVC and PVC/LDHs3-ZnO2.

Table 2
TGA and DTG results of PVC and PVC/LDHs3-ZnO2

Stages	PVC	PVC/LDHs (3%)-ZnO (2%)
First Stage		
Temperature range (°C)	270–370	245–285
T_{max} (°C)	315	250
Weight loss (%)	55	45
R_{max} (%/min)	20	40
Second Stage		
Temperature range (°C)	445–500	445–505
T_{max} (°C)	450	475
Weight loss (%)	25	30
R_{max} (%/min)	5	5

that the main chain of PVC decomposes and cyclizes to form aromatic compounds during this stage, attributed to cis-conjugated polyene structure formed from the PVC chain after releasing HCl; the result is similar to the conclusion reported by McNeill (15). However, these aromatic compounds cannot be found in the spectra of PVC/LDHs3-ZnO2, as shown in Figure 3. The fact demonstrates that LDHs-ZnO in PVC is an effective catalysis for the dehydrochlorination of PVC to form *trans*-conjugated polyene structures; consequently, they do not result in aromatic compounds.

When the pyrolysis temperature rises to 600°C, as shown in Figure 4, PVC still released benzene, toluene, ethylbenzene, p-dimethylbenzene, styrene, and naphthalene, corresponding to the peaks at 3.63 min (strong), 5.58 min (middle), 7.50 min (m), 8.25 min (m), 8.45 min (m) and 14.04 min (m), respectively. But all of those peaks are very weak in the PVC/LDHs-ZnO system, indicating that a small amount of aromatic

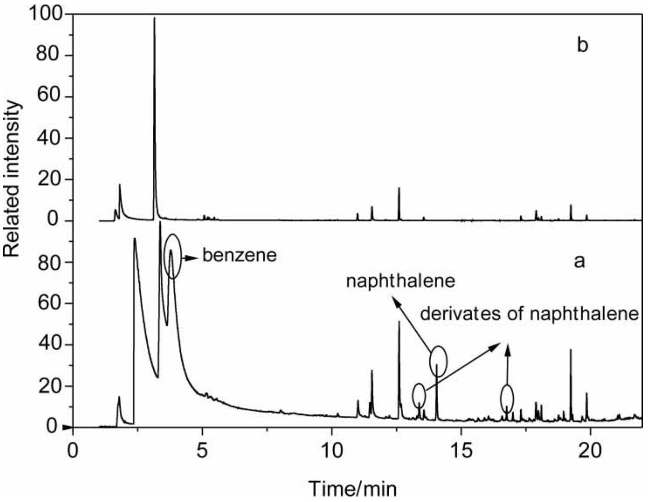

Figure 3. Pyrolysis GC-MS curves of PVC (a) and PVC/LDHs3-ZnO2, (b) 350°C.

Table 3
Pyroysis GC-MS results of PVC and PVC/LDHs3-ZnO2

No.	Components	Relative intensity (350°C) I	Relative intensity (350°C) II	Relative intensity (600°C) I	Relative intensity (600°C) II
1	Hydrogen chloride	91.70	17.91	100	36.03
2	Furan	100	100	46.34	100
3	Benzene	85.81	–	90.04	6.51
4	2-Ethyl-1-hexene	16.68[a]	2.61	9.82	10.71
5	3-Methyl-3-heptene	15.05[a]	–	8.04	8.97
6	Toluene	–	–	15.44	5.67
7	Ethylbenzene	–	–	3.17	–
8	p-Dimethylbenzene	–	–	3.58	2.63
9	Styrene	–	–	5.61	–
10	Chlorohexene	13.45	3.61	4.29	–
11	1-Chloroindane	12.33	–	6.43	–
12	2-propyl-1-pentanol	28.37	7.07	3.99	4.54
13	A(12.60)	52.27	16.68	5.57	9.18
14	1,4-Dihydronaphthalene	12.36	–	3.28	–
15	Butanediol, monobutyl ester	8.58	–	–	2.55
16	Naphthalene	30.63	–	9.32	–
17	2-Methyl-naphthalene	–	–	3.15	–
18	2-Ethenyl-naphthalene	10.61	–	3.16	–
19	Bis(4-chlorobutyl) ether	9.14	2.45	2.44	2.88
20	Phthalic anhydride	12.45	4.83	8.31	12.46
21	B(19.24)	38.50	8.15	4.35	6.40
22	C(19.85–89)	17.21	2.79	3.54	3.25

[a] Peak disturbed by benzene; A, B, and C are not identified; I-PVC, II-PVC/LDHs3-ZnO2.

compounds were released from PVC/LDHs3-ZnO2. The detailed data are listed in Table 3. Thus, the LDHs-ZnO in PVC also had the function of forming trans-conjugated polyene structures from the decomposed PVC chain at 600°C, but *cis*-conjugated polyene structure were partly formed, and aromatic compounds were released.

The results show that the efficiency of the function of LDHs-ZnO in PVC to form trans-conjugated polyene structures from decomposed PVC chain decreases at 600°C,compared to 350°C.

The strong peaks attributing to furan, as listed in Table 3, Figures 3 and 4, have seldom been reported in the literature. The reason for releasing this much furan may be related to the various kinds of organic and inorganic additives in the commercial rigid PVC; the detailed reason is being further investigated.

Conclusions

LDHs and ZnO mixed into PVC retarded smoke release successfully, especially when the weight percentages of LDHs and ZnO in PVC were 3% and 2%, respectively. The thermal

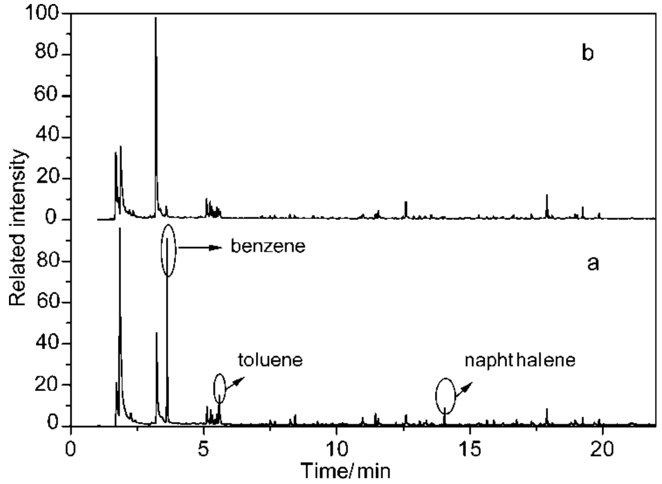

Figure 4. Pyrolysis GC-MS curves of PVC (a) and PVC/LDHs3-ZnO2, (b) 600°C.

decomposition of PVC is divided into two stages: In the first stage of thermal degradation of PVC at 350°C, cyclization of conjugated polyene sequences in the chain produced at the high temperature leads to formation of aromatic compounds. In contrast, LDHs-ZnO can effectively accelerate the decomposition of PVC to release hydrogen chloride and produce trans-conjugated polyene sequences, which form cross-linked structures. Therefore, the addition of LDHs-ZnO in PVC can efficiently control the spatial structures of the decomposed products and aromatic compounds cannot easily be released. In the second stage, LDHs-ZnO plays a similar role on controlling the structures of the decomposed products, along with a slight decrease of efficiency compared to the first stage.

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