

Flame Retardant Flexible Poly(vinyl chloride) Compound for Cable Application

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Received 7 February 2002; accepted 23 November 2002

ABSTRACT: ZnO/MgO, ZnO/CaO, and ZnO/CaO/MgO can form solid solutions. The solid solution for us as flame retardant (SSFR) was obtained by annealing at 1023 K for 4.5 h in a muffle furnace. Flexible poly (vinyl chloride) (PVC) filled with SSFR and Sb₂O₃ was investigated by differential thermal analysis thermogravimetry. Limiting oxygen index (LOI), mechanical properties, and electrical properties were studied. The surface of the char formed after combusting of the PVC compounds was observed through scanning electron microscopy and the effect of the surface area to the LOI was also studied. The data suggested that a small amount of SSFR and Sb₂O₃ have good synergy and can

greatly increase the LOI and the char yield, and that the thermal degradation temperature and the activation energy decreased. It can be concluded that the mechanism of SSFR is a condensed-phase mechanism. Moreover, one can conclude that the surface area can enhance the LOI. All the results showed that SSFR is effective and safe as a flame retardant in flexible PVC. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3137–3142, 2003

Key words: flame retardance; mechanical properties; poly (vinyl chloride) (PVC); degradation; surfaces

INTRODUCTION

Poly(vinyl chloride) (PVC) is the most important halogen-containing polymer. It has a high chloride content (about 56%); therefore, PVC is inherently fire resistant¹ and this property has, in the main, aided PVC usage in a wide range of domestic and commercial materials. For example, it can be used in window frames, in doors, for wallpaper, for gutters, and for house siding. It can also be used as a covering insulation for electrical and communications cable. However, for many applications, it requires an organic plasticizer, such as DOP [di (2-ethylhexyl) phthalate] filled at varying levels to make the PVC materials flexible and easy to process. The plasticizer (DOP) has a dramatic effect on the flammability. When the PVC products contain 40 parts DOP, the limiting oxygen index (LOI) decreases to 22 and becomes a highly flammable material. This can cause a serious fire disaster.

Controlling the fire hazard of PVC has become, more and more, a worldwide concern due to increased usage of these materials. Many studies of flame-retardant and smoke suppression have been carried out. The additive method is one of the most widely used. The additives include various elements, alloys, inorganic compounds as well as several organometallic compounds.² Among these, transition-metal oxides

have been considered.³ According to Starnes and Edelson,⁴ the role of flame retardant and smoke suppression is due to a Lewis acid catalyst. Lewis acids can promote the crosslinking of PVC to form the char rapidly during combustion. Lattimer and Kroenke^{5,6} proposed that the function of the flame retardant was due to changing the thermal degradation pattern of PVC and promoting the formation of the char, via a condensed-phase mechanism. A series of experiments by Moore and George⁷ showed that Sb₂O₃ acts as vapor-phase flame retardant and has little effect on the char yield.

In recent years zinc compounds were used widely because of the high flame retardancy and smoke suppression, of compounds such as zinc borate (ZB),^{8–12} zinc sulfate (ZnSO₄),¹³ and Ongard,¹⁴ and ZnO/MgO solid solution.^{15,16} Use of solid solution flame retardants (SSFR) is reported in several patents, but work on the system and the mechanism of SSFR has not been reported on yet. In this respect some work has been done by us was to check the effect of ZnO/MgO, ZnO/CaO, and ZnO/MgO/CaO solid solution on flame retardancy, thermal degradation, mechanical and electrical properties of plasticized PVC compounds that are required for power cables. The morphology of the condensed phase of the char was also studied through scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The following materials were used: PVC SG2 (Beijing the Second Chemicals Co., Beijing, China); DOP as the

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TABLE I
Flame-Retardant Properties of PVC Compounds

Sample	Composition	LOI	Char yield (%)
B	A + CaCO ₃ 40 parts	22.5	30.3
C	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts	30.0	35.8
D	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + ZnO/MgO/CaO 2 parts	35.0	45.3
E	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + ZnO/CaO 2 parts	34.5	43.2
F	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + ZnO/MgO 2 parts	34.5	44.0
G	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + ZnO 0.8 part,	32.5	38.1
H	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + CaO/MgO 2.4 parts	30.5	36.1
I	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + CaO 1.2 parts	30.5	36.3
J	A + CaCO ₃ 40 + Sb ₂ O ₃ 8 parts + MgO 1.2 parts	30.5	35.1

^a The composition of A is PVC 100 parts, DOP 40 parts, TBLS and DBLP 2 parts, respectively, calcium stearate 0.5 part, coupling agent 1 part. The LOI is 22.5 and char yield is 22.6.

plasticizer (Shanghai Dongfang Chemicals Co., Shanghai, China); tribasic lead sulfate (TBLS) and dibasic lead phosphate (DBLP) as stabilizers and calcium stearate as lubricant (Hebei Baoding Chemicals Co., Baoding City, China); calcium carbonate (CaCO₃) as filler additive; and ZnO, MgO, CaO, and Sb₂O₃ as flame retardant (Tianjin Dengzhong Chemicals Co., Tianjin, China).

Preparation of flame-retardant and PVC samples

The preparation of flame retardant was according to ref. ¹⁵ for the flame retardants as follows: ZnO/MgO (40:60), ZnO/CaO (40:60), ZnO/MgO/CaO (30:35:35) (SSFR), MgO, CaO, ZnO, MgO/CaO. The annealing temperature was 1023 K and the annealing time was 4.5 h. A fine powder of 300 mesh was used.

Samples were prepared by mixing PVC with DOP, CaCO₃, heat stabilizer, lubricant, coupling agent, and some flame retardant, then blending them in a two-roll mill at 443 K for 10 min and compressing at 443 K to form sheets of 100 × 50 × 3 mm. Test specimens were cut from the molded sheets.

Measurements and characterization

LOI values were determined with an HC-1 instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China) according to the ASTM D2863-1970 method.

Char yield values were calculated by the following equation:

$$\text{Char yield (\%)} = w_2/w_1$$

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 N₂ at 623 K for 40 min.

Thermal degradation behavior was measured with a DT-40 thermal analyzer (Shimadu Corp., Japan) under air at a heating rate of 10 K min⁻¹ and an air

following the rate of 60 mL min⁻¹. The temperature range was from room temperature to 1023 K.

The physical mechanical properties were carried out on an LJ-500N mechanical instrument (Chengde Experimental Instrument Factory, Chengde, China). The samples were held in the laboratory for at least 2 days at a room temperature of 293–298 K. The electrical properties were evaluated according to the ASTM D 1531 standard.

The surface structure of the char formed after combustion of PVC compound was observed and diameters of the flame-retardant particles were measured with a SEM-1000B-2 instrument (Chinese Academic of Science Instrument Factory, Beijing, China).

The surface area of the flame retardant was calculated through the formula of $S = 6/\rho d$, where d is the diameter of the particle and ρ is the real density, measured by pycnometer and S is the specific surface area.

RESULTS AND DISCUSSION

Flame-retardant properties

From Table I, it can be seen clearly that only 2 parts of SSFR can increase LOI of PVC compounds by 4–5 units. On the other hand, flame retardants such as CaO, MgO, and MgO/CaO only can increase the LOI marginally (about 0.5 unit), and ZnO at the same level as an SSFR has an intermediate effect on the LOI increasing it by 2.5 units. The data on char yield and the surface area are listed in Table I and Table II and show that when the char yield and the surface area is high, the LOI of PVC compounds is also high. Sb₂O₃ is a highly effective flame retardant in halogen-containing polymers. It forms volatile halide and oxyhalide species during combustion, which act in the vapor phase as free radical scavengers.^{15–17} Consequently, it has little contribution to enhance the char yield. But the conclusion can be that Sb₂O₃ and the SSFR could have good synergy. As shown in Table I, CaCO₃ has little effect on the LOI of PVC compounds: it is only a

TABLE II
The Effect of the Surface Area to the LOI
and the Char Yield

Sample	Specific surface area (m ² /g)	LOI	Char yield (%)
D	54.6427	35.0	45.3
D'	36.1256	34.0	44.3
E	46.6121	34.5	43.2
E'	38.2346	34.0	42.8
F	45.7825	34.5	44.0
F'	35.3698	34.0	42.3
G	30.6105	32.5	38.1
G'	10.3584	31.5	37.2
H	6.7209	30.5	36.1
H'	4.6653	30.5	35.8
I	15.7206	30.5	36.3
I'	9.3216	30.0	36.0
J	37.1765	30.5	35.1
J'	24.4532	30.0	34.6

^a The composition of D', E', F', G', H', I', J' is the same or with the formulations D, E, F, G, H, I, J. The flame retardant in the formulations, D', E', F', G', H', I', J' is not annealed in the muffle furnace.

kind of filler. All the evidence above indicates that the SSFR has a very positive effect on the flame retardancy of PVC compounds.

Thermal analysis

As shown in Figure 1, the thermogravimetry (TG) curves of the thermal degradation of PVC can be divided into two stages: the first stage is mainly due to the emission of hydrogen chloride¹⁸ and the decomposition of DOP. At this stage all the samples except D lost weight by about 40–60%. The thermal decomposition in the second stage is mainly due to the cyclization of conjugated polyethylene to form aromatic com-

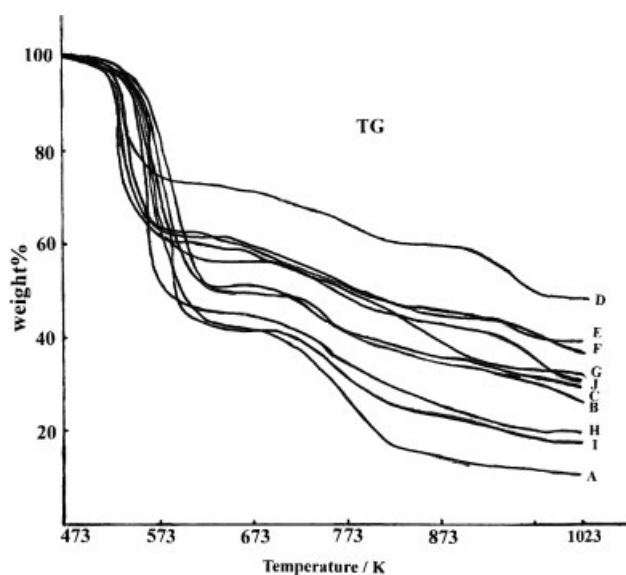


Figure 1 TG curves of PVC samples.

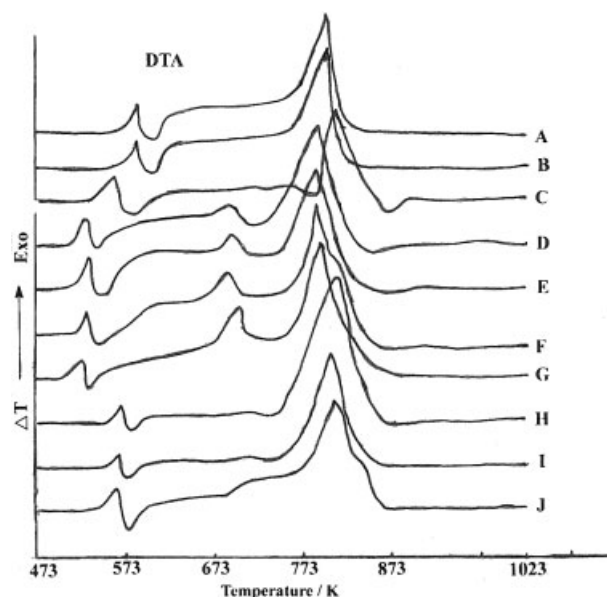


Figure 2 DTA curves of PVC samples.

pounds such as benzene, including atomization, crosslinking, and isomerization.^{19,20} In general, the TG curves show many similarities between the four curves (D, E, F, G). The char residues are very high and increase by 275% (D), 200% (E), and 185% (F), 153% (G) respectively. These results are consistent with the data of LOI and the char yield listed in Table I.

In the first stage of the TG curves for PVC compounds containing SSFR or ZnO, there are smaller weight losses than for the other samples. Incorporation of a small amount of SSFR or ZnO reduces the thermal decomposition temperature in the first stage. From Figure 2, it can be seen that the initial decomposition temperature is lower than that of the pure sample. At about 700 K small peaks appear (D, E, F, G) and this additional intermediate decomposition is due to the delayed evolution of volatiles derived from the plasticizer because ZnO is a stabilizer of PVC compound.²¹ Below about 700 K, ZnO can keep the plasticizer in PVC compound relatively stable and a small amount of plasticizer decomposes. When the temperature is above 700 K, most of the plasticizer decomposes. It is noticeable that formulation D has a smaller weight loss than the other samples. This is probably due to the plasticizer's decomposition, which results in char formation and enhances the LOI.

At the second stage of the TG curves, the PVC compounds containing SSFR or ZnO also have smaller weight losses than that of the other samples. The decomposition temperature is lower than that of pure PVC compound. All the results are due to the SSFR and Sb₂O₃ changing the pattern of thermal degradation and promoting early dehydrochlorination and crosslinking and early formation of char.

TABLE III
Activation Energies and Initial Decomposition
Temperature for the First Stage and Second Stage of
Thermal Degradation of PVC Compound

Sample no.	The first stage		The second stage	
	Exotherm (K)	E (KJ mol ⁻¹)	Exotherm (K)	E (KJ mol ⁻¹)
A	580	197.5	796	112.2
B	564	95.1	815	62.0
C	560	78.5	805	99.9
D	527	123.5	786	98.7
E	531	111.7	788	104.0
F	527	129.1	789	85.3
G	523	124.4	790	93.1
H	564	93.2	797	87.5
I	564	96.5	803	102.9
J	560	82.3	804	100.6

The thermal degradation kinetics of PVC compounds has been studied using the equation of Broido.²² The equation is as follows:

$$\ln(\ln 1/y) = -E/RT + \ln(RZT^2/E\beta)$$

where y is the fraction of initial molecules not yet decomposed, T the temperature of maximum reaction velocity, β the rate of heating (K min⁻¹), Z the frequency factor, and E the activation energy. Using the Broido method, the activation energy can be determined from the slopes by plotting of $\ln(\ln 1/y)$ vs $1/T$. Table III presents activation energies E for all the samples and the decomposition temperatures of the two stages. For the two stages of pyrolysis, the activation energy of PVC compounds decreases below that of a pure PVC sample. The activation energy also

decreases, indicating that the SSFR or ZnO can significantly promote dehydrochlorination of PVC compounds and make early crosslinking forming the char.

Mechanism of the SSFR

The above evidence indicates that the SSFR and Sb₂O₃ are highly effective flame retardants for flexible PVC. Effectiveness is much greater than that of the other flame retardants. It is suggested that the following reasons cause the great increase of the LOI and char yield in the presence of only a small amount of SSFR:

1. There is ZnO in the SSFR, and the ZnO can synergize with the Sb₂O₃. The synergy can enhance LOI significantly.
2. ZnO/CaO, ZnO/MgO, and ZnO/MgO/CaO can form solid solutions. When they are annealed in a muffle furnace, the lattices of ZnO, MgO, and CaO expand greatly increasing. SSFR's specific surface area. The increase of the specific surface area enhance flame retardancy. On the other hand, its big specific surface area can make the PVC compound compact. This is also a point, which can contribute to flame retardancy.
3. The formation of the char. The SSFR react with HCl to form MCl₂ (M = Zn²⁺, Mg²⁺, Ca²⁺), a kind of stronger Lewis acid, which can promote early crosslinking of the PVC compound, leading to rapid charrings. Such a carbonized product is believed to protect the polymer backbone, inhibit heat and O₂ degradation during combustion and hence contribute to flame retardancy. The process of crosslinking and charring is considered to be as follows²³:

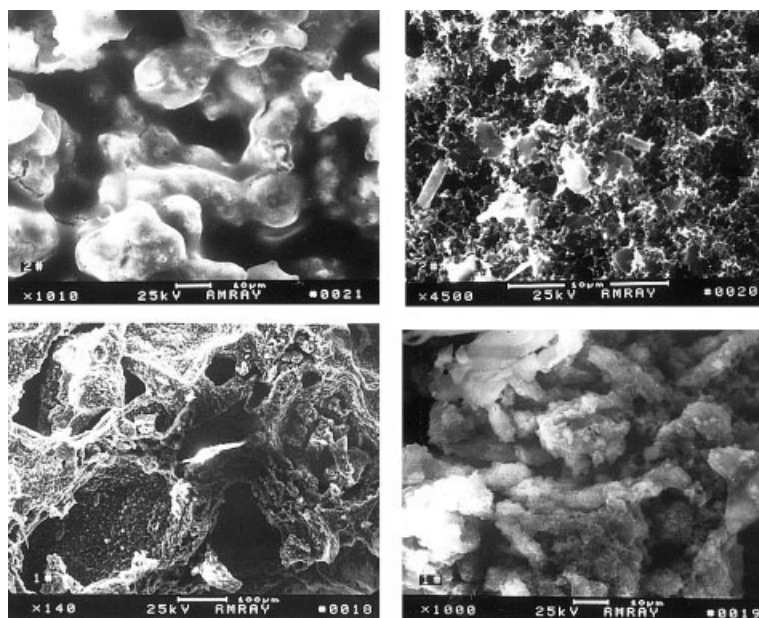
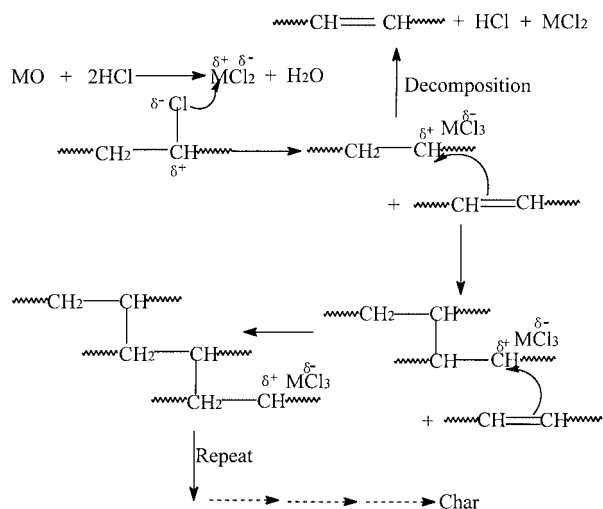


Figure 3 SEM micrographs of the char of pure PVC (1) and PVC containing SSFR (2)



These results are also consistent with the char yields listed in Table I and TG curves in Figure 1.

4. As shown in Figure 3, the char surface of PVC compounds containing SSFR are very different from the char of the pure PVC samples. The former shows a porous honeycomb structure. This kind of structure can inhibit combustible gases and transfer of heat energy to the PVC bulk. This can improve the flame retardancy of PVC. The latter only contains small pores without the honeycomb structure and has little effect on barring the heat transfer and combustible gases from going into the combusting reaction system.
5. The SSFR catalyzes the dehydrochlorination early and decreases the activation energy. The hydrogen chloride can dilute the concentration of O_2 and is a gas-phase flame inhibitor. At the same time, it can be seen that the activation energy of the formulations containing SSFR or ZnO are higher than the other's (except A). This is due to the stabilization influence of ZnO in these four

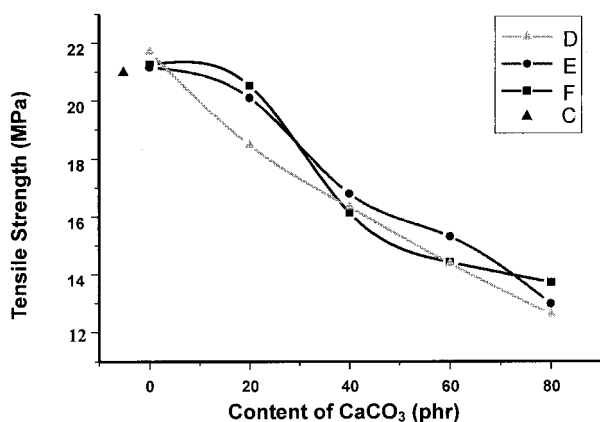


Figure 4 Mechanical properties of PVC compounds (tensile strength).

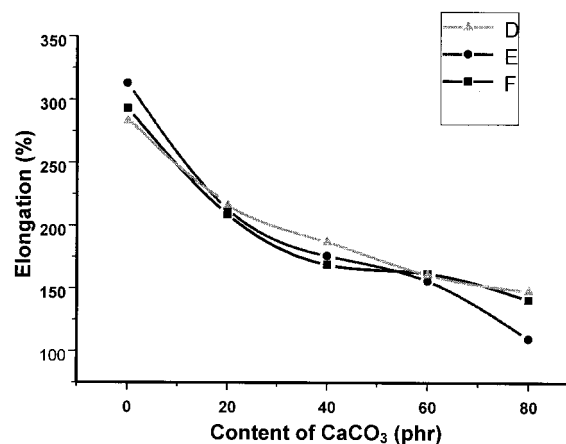


Figure 5 Mechanical properties of PVC compounds (elongation).

formulations. ZnO is not only a flame retardant but also a stabilizer when used in PVC.²¹

Effect of filler and electric properties

To reduce the price of products and to make processing easier, usually some filler is added to the PVC compounds. Calcium carbonate (CaCO_3) is the most widely used filler in PVC compounds. CaCO_3 can actually aid in extrusion and reduce the acid gas of HCl when PVC compound degrades. The tensile strength and elongation values decrease as shown in Figures 4 and 5, with an increase in the content of CaCO_3 . But there is an optimum quantity of CaCO_3 for cable standards. From Figure 4 and Figure 5, it can be concluded that 40 parts CaCO_3 is appropriate for this formulation. The observed electrical properties listed in Table IV show acceptable data for cable standards according to ASTM requirements. The results suggest that the SSFR is suitable for cable applications.

CONCLUSIONS

1. The presence of a small amount of SSFR or ZnO can greatly increase the LOI and the char yield, whereas other flame retardants cannot increase the LOI and the char yield significantly.
2. Good synergy between Sb_2O_3 and SSFR or ZnO has been found, as can be seen in Table I.
3. The SSFR or ZnO can effect early dehydrochlorination, promote PVC crosslinking to form char, and reduce the activation energy. All of these can enhance the flame retardancy.
4. The big specific surface area improves the LOI and enhances char yield.
5. According to the char yield and LOI, it is suggested that the mechanism of SSFR is a condensed-phase mechanism.

TABLE IV
Electrical Properties of PVC Formulations Contained SSFR

Properties	D	E	F	Standard data	Standard
Tan δ (%)	0.042	0.041	0.035	$\leq 5 \times 10^{-2}$	ASTM D 1531
Dielectric constant (MV/m)	106	118	112	≥ 25	ASTM D 1531
Volume resistivity (Ω m) $\times 10^{12}$	34	36	36	$\geq 1 \times 10^{12}$	ASTM D 257

6. The porous honeycomb structure of the char can inhibit heat and the combustible gases from going into the PVC bulk, which also enhances the flame retardancy.

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