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Research of the properties of flame-retardant flexible PVC

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Abstract
Effects of the inorganic flame retardants on the oxygen index of flexible Polyvinyl chloride (PVC) have been systematically studied in this paper. Firstly, effects of single groups on PVC flame retardant properties were studied, including aluminum hydroxide (ATH), antimony trioxide (Sb_2O_3). Study found that antimony trioxide is the better flame retardant for PVC. Adding 4phr Sb_2O_3 into PVC，the LOI can reach 29.4%. Then we studied effects of binary system, aluminum hydroxide - antimony trioxide(Sb_2O_3-ATH) and zinc - aluminum hydroxide(ZB-ATH), on PVC flame retardant properties. The LOI can be as high as 30.3 when the amount of ATH is 20phr and Sb_2O_3 is 3phr, while the LOI increased by 5% by adding 3 phr ZB and 20phr $Al(OH)_3$ into PVC, the SDR can decrease to 66.98. Study found that both zinc borate and antimony trioxide have synergistic effects on aluminum hydroxide.

1. Introduction

Polyvinyl chloride (PVC) is one of the earliest industrialized plastic. Its current output is outranked only by polyethylene, since it exhibits corrosion resistance and good insulation properties for many purposes. PVC is widely used in a number of industries and fields, including construction, furniture, automobile and medical applications. For example, it is mainly applied in cracking resistant sheath of heat-resistant wires, cables and electrical cable in electrical industry; used as the steering wheel or the top cover plate in the auto industry; made in all kinds of pipes, plates, sheets and decoration materials for building industry. Polyvinyl chloride can also be processed into pipe, chemical reagent containers products to make a chemical equipment.

PVC products are divided into hard ware and soft ware. Soft ware products have very low oxygen index due to the addition of a plasticizer [1]. A way of achieving enhanced flame retardant activity is to add flame retardants, such as chlorinated paraffin, phosphate, aluminum hydroxide, antimony trioxide, zinc borate, red phosphorus, etc.

The use of antimony trioxide (Sb_2O_3) as flame retardants for PVC has been reported for a long time, which is more effective when used with aluminum hydroxide. Aluminum hydroxide (ATH) functions as a flame retardant by decomposing into water and metal oxide upon heating. The released water vapor dilutes the combustible ambience while removing the combustion heat [2]. It is believed that antimony trioxide reacts with the HCl to form antimony trichloride, which inhibits the flame reactions via scavenging of free radicals and release part of

chlorine into the flame [3]. Zinc borate (ZB) is commonly used as flame retardant for PVC. This material also behaves as smoke suppressant.

In this study, we added aluminum hydroxide, zinc borate, antimony oxide and their compounded systems as flame retardants into PVC matrix .The flame retardant properties were characterized by LOI.

2. Experiments

2.1. Materials

Polyvinyl chloride (SG-4) were obtained from Qilu Petrochemical Corporation, Shandong, and China. Antimony trioxide were obtained from Star Better chemical materials Co., Ltd, Beijing, China. Aluminum hydroxide were obtained by Aluminum Corp oration of China Limited，Shandong，China. Zinc borate obtained from Beijing Western Instrument Technology Co. Ltd, China. Dioctyl Phthalate (DOP) supplied by Tianjin Fuchen Chemical Reagent Factory was used as Plasticizer. The Ca/Zn composite stabilizer were obtained from Bayer polyurethane Co.LTD, Shanghai, China.

2.2. Preparation of PVC and Flame Retardant PVC Composites

The DOP plasticizer and the Ca/Zn composite stabilizer were mixed into The PVC resin powder with an electric stirrer at 200 rpm for 30 min to make flexible PVC, which is also called soft PVC. Here PVC/plasticizer / stabilizer=100/40/1.8 (shown in table 1).

According to a certain proportion(shown in table 1) , soft PVC and flame retardant were mixed in the Double Roller at 160-165 ℃ for 7min.The resultant mixture was immediately poured into a mold of Pressure Machine to produce plate PVC pieces at 180 ℃ for 10min . Different test samples of specific shapes were cut by a cutting machine.

Table 1. *Foaming formulation of rigid polyurethane foams.*

Ingredients	Dosage/phr①
Soft PVC	
PVC resin	100
DOP	40
Ca/Zn composite stabilizer	1.8
Flame retardant PVC Composites	
Soft PVC	100
aluminum hydroxide	0~20
zinc borate	0~3
antimony trioxide	0~4

①The dosages of all ingredients are expressed in parts by weight.

2.3. Measurements

Limiting oxygen index (LOI) tests were measured according to GB/T 2406—1993 by using a oxygen index instrument (JF-3), made by Nanjing Jiangning Analtical Instrument Factory, China).The size of the specimen was 120*6.5*3mm^3. In order to overcome problems of poor repeatability of data, ten or more specimens for each sample were used.

The smoke density was measured according to GB/T 8627—2007 by using a smoke density chamber (JCY-2, made by Nanjing Jiangning Analtical Instrument Factory, China). The specimen size for the LOI measurement was 25*25*3 mm^3. The maximum smoke density was measured from the peak maxima of the curve of the light absorption time. Total amount of smoke present in the chamber for 4 min time.

Tensile strength tests were performed according to GB/T 1040.1-2006 with a electronic universal testing machine (AMETEK LR30K, Britain).Five or more specimens per material were tested and the mean value of each item was determined. The distance between points was defined as 60mm, and the drawing speed was defined as 50mm/min to obtain stress-strain curves.

The morphology of various PVC samples were observed using a Hitachi H-800 scanning electron microscope (SEM),at an accelerate voltage of 20KV. The surface of the samples used for SEM were gold-sputtered with a conductive layer before observation.

3. Results and Discussion

3.1. One Component Systems

3.1.1. Antimony Trioxide

As shown in Figure 1, we can see that the LOI values of PVCs increase with the increase of Sb_2O_3, where the maximum LOI has risen to 29.4% in presence of 4phr Sb_2O_3. So Sb_2O_3 can perform a good flame retardant effect. The increase in LOI revealed the resistance of the material to the inflammability. It is believed that antimony trioxide reacts with the HCl evolved from burning PVC to form antimony oxchlorides, and then decomposes to form antimony trichloride ($SbCl_3$). The antimony trichloride is the main contributor in the inhibition of the flame reactions via scavenging of free radicals and introducing a source of chlorine into the flame [4].

The effects of Sb_2O_3 on mechanical properties of PVC composites were also investigated. Tensile strength and elongation results are given in Figure 2. This reveals that the addition of Sb_2O_3 at the amounts of 1~4wt% did not have a considerable negative effect on mechanical properties.

Combining with the mechanical properties and flame retardant properties, the amount of Sb_2O_3 in the compounded system will be fixed to 3phr.

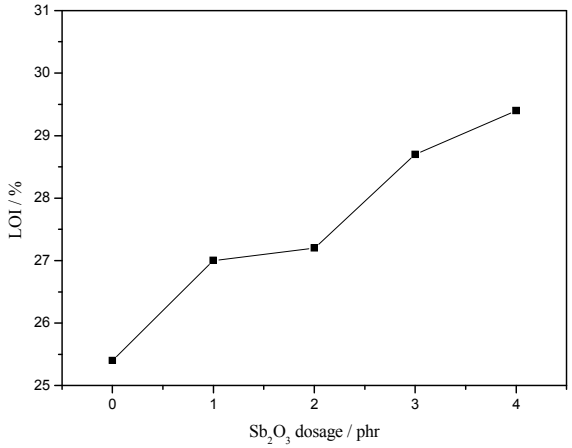

Fig 1. *Curve of the PVCs' LOI values changing with the flame retardants contents.*

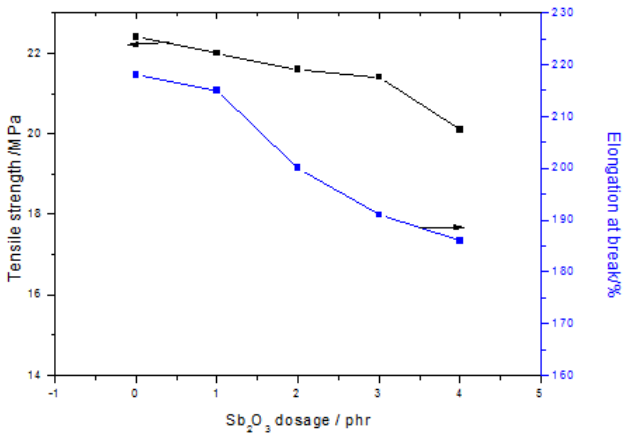

Fig 2. *Mechanical properties of PVCs with different Sb_2O_3 dosage.*

3.1.2. Aluminum Hydroxide

In Figure 3, it can be seen that the PVC samples containing ATH enhance the LOI when incorporated at levels of 5 to 20 parts into the PVC compound. When the additive level is at 20 parts, the LOI can increase by 3%， compared with pure PVC. The higher LOI value represents the better flame retardancy.

ATH decomposes into water and metal oxide during combustion. The release of water while PVC burning offers obvious benefits by helping to displace the oxygen needed to keep the fire burning [5]. The release of water is endothermic.

The effects of ATH on mechanical properties of PVC composites are given in Figure 4. ATH is an inorganic flame retardant, which is essentially nontoxic and relatively inexpensive. The high levels required for adequate flame retardancy [6] often lead to a marked deterioration in mechanical properties.

3.1.3. Conclusion

Comparing Figure1 with Figure 2, Sb_2O_3 has a higher efficiency as flame retardant for PVC than that of ATH. The LOI of PVC with 2phr Sb_2O_3 has reached to 27.2% ,while the LOI of PVC with 20phr ATH is only 26.1%.

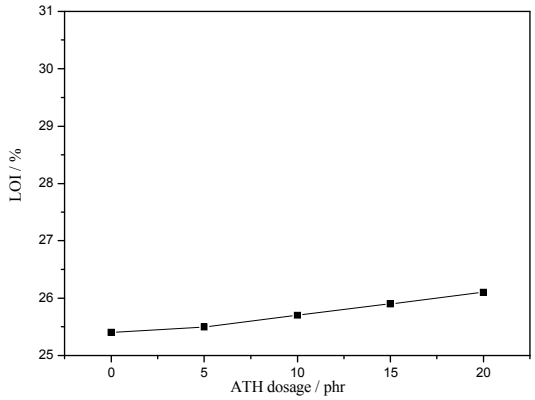

Fig 3. *Curve of the PVCs' LOI values changing with the flame retardants contents.*

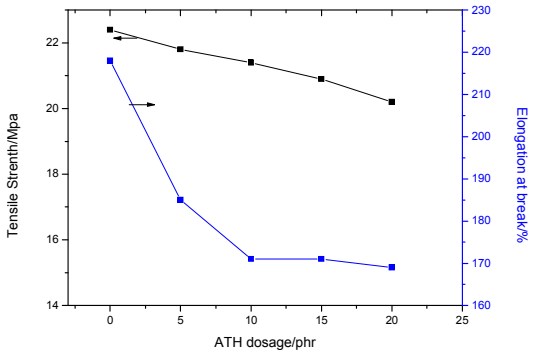

Fig 4. *Mechanical properties of PVCs with different ATH dosage.*

3.2. Two components Systems

3.2.1. Antimony–Aluminum Hydroxide

Figure 5 shows a combination of 3phr antimony oxide with Al (OH) $_3$ irradiated at different doses. It can be seen that the PVC samples containing only Al (OH) $_3$ had marginally increased LOI values, whereas the formulations containing Al (OH) $_3$ combined with a small amount of Sb_2O_3 had significantly more enhanced LOI values. When the additive level of Al (OH) $_3$ was at 20phr, the LOI increased from 25.4 % to 26.1 %, but when 3phr $Sb_2O_3$was also incorporated, the LOI reached 30.3%.

Antimony trioxide reacts with halogen to inhibit the flame reactions. Meanwhile aluminum hydroxide releases crystalliferous water when heated, having a further cooling effect on the polymer, which indicates that Sb_2O_3 and ATH have a good synergistic effect on the flame retardancy of flexible PVC [7].

The smoke density rating (SDR) results about the filled and unfilled PVC are shown in Figure 6. The smoke density decreases with increasing ATH dosage compared

with neat PVC. This indicates this system Antimony–Aluminum Hydroxide has smoke suppression performance. The figure also shows that PVC with ATH alone performs slightly better than PVC filled with 3phr Sb_2O_3 and different ATH dosage. Because Sb_2O_3 reacts with halogen for flame-retardancy, resulting in more release of HCL.

Mechanical properties of PVCs with 3phr Sb_2O_3 and different ATH dosage are shown in Figure 7，in which it can be observed that the tensile strength and elongation of the PVC composites decreased as ATH content increased, but the decrease was not so significant because of the acceptable range of ATH. Many studies [4,6] show that addition of aluminum hydroxide can reach as many as 60phr in order to have a good flame-retardant effect on PVC.

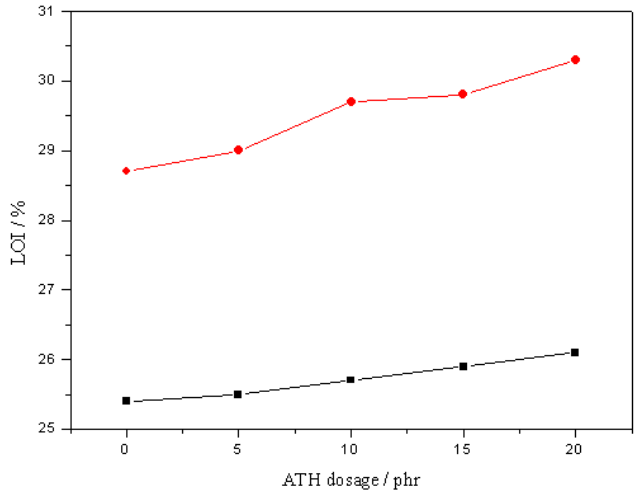

Fig 5. *Curves of the PVCs' LOI values changing with different ATH dosages.*

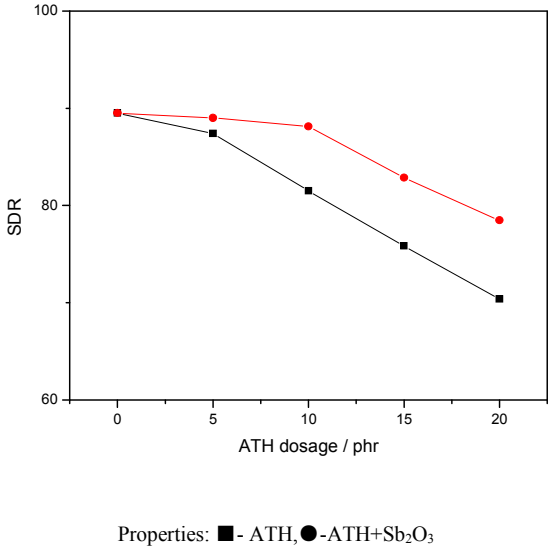

Fig6. *Curves of the PVCs' SDR values changing with the flame retardants contents*

3.2.2. Zinc Borate - Aluminum Hydroxide

Figure 8 indicated that zinc borate addition into the PVC improved the composites. The LOI of PVC containing ATH/ZB are higher than containing Al $(OH)_3$ alone. Compared with adding only ATH, the LOI increased by 5% via adding 3 phr ZB into PVC with the additive level of 20 phr Al $(OH)_3$. In the compound system, the amount of ZB in the compound is fixed to 3phr. The effect of flame retardancy of aluminum hydroxide - zinc borate is due to doubly evaporation of crystal water [8]and zinc borate can also boron oxide that forms a strong protective layer against oxygen[9~10]. The smoke density rating (SDR) results of PVCs are shown in Figure 9. In comparison with PVC with ATH alone, we know that PVC filled with 3phr ZB and different ATH dosage had significantly effects on the smoke density rating (SDR) properties. The SDR of PVC filled with 3phr ZB and 20phr ATH can decrease to 66.98, however the SDR of neat PVC is 89.5. Because both ZB and ATH can decrease the smoke density, as they both evaporate water to dilute the gases when polymer burns. Mechanical properties of PVCs with 3phr ZB and different ATH dosage are also presented in Figure10.

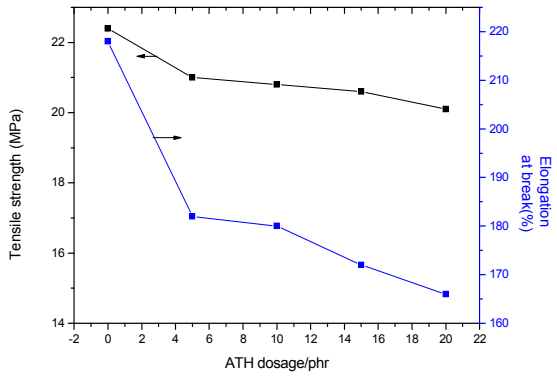

Fig 7. *Mechanical properties of PVCs with 3phr Sb_2O_3 and different ATH dosage.*

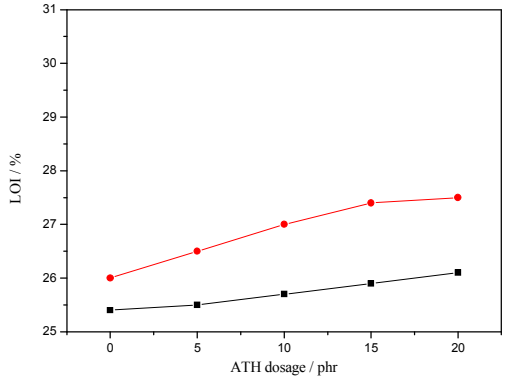

Fig 8 *Curves of the PVCs' LOI values changing with different ATH dosages.*

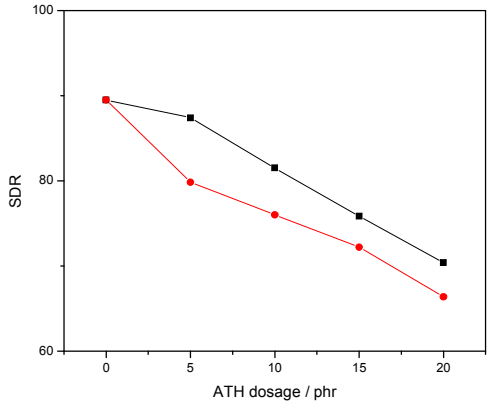

Fig 9. *Curves of the PVCs' SDR values changing with the flame retardants contents*

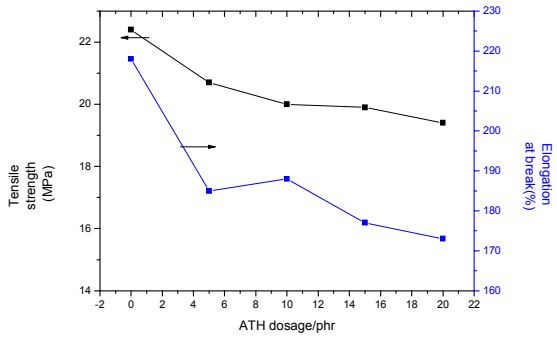

Fig 10. *Mechanical properties of PVCs with 3phr ZB and different ATH dosage.*

3.2.3. SEM

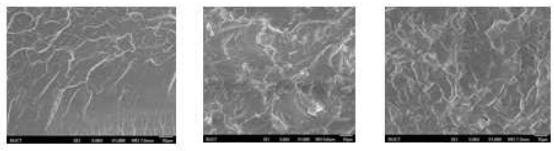

Fig 11. *SEM micrographs of the fracture surface.* （a）*pure PVC*（b）*PVC/ ATH/* Sb_2O_3*=100/20/3*（c）*PVC/ ATH/ ZB=100/20/3.*

PVC is a polymer, when it is damaged, the fracture surface of the samples shows a tough rupture. However, adding an excessive dose of inorganic flame retardants may lead to brittle fracture, which may cause a reduction of the mechanical properties of materials. It can be seen from Figure 11, the three pictures all exhibit ductile fracture with rough fracture surface and white slender line.

3.2.4. Conclusion

The compounded systems as aluminum hydroxide - antimony trioxide (Sb_2O_3-ATH) and zinc - aluminum hydroxide (ZB-ATH) on the flame retardant properties were studied in comparison with PVC with ATH alone.

The LOI can be as high as 30.3 when the amount of ATH is 20 phr and Sb_2O_3 is 3phr. Moreover, the LOI increased by 5% via adding 3 phr ZB into PVC with the additive level of 20 phr ATH. Both of compounded systems' LOI values are higher than containing ATH alone, which demonstrated that either Sb_2O_3 or ZB has a good synergistic effect with ATH.

From the results, it is clearly observed that ZB performs much better than Sb_2O_3 in smoke density. The SDR of PVC filled with 3phr ZB and 20phr ATH can decrease to 66.98

4. Conclusions

In this paper, we prepared flexible PVC with Sb_2O_3、ATH and the compounded systems as Sb_2O_3-ATH, ZB-ATH. From the results of LOI, the filled PVC shows better flame retardation over pure PVC, which means the flame retardant property is improved. Sb_2O_3 has higher LOI value than ATH filled PVC, which is more effective as flame retardant. There existed a synergistic effect between binary system, aluminum hydroxide - antimony trioxide and zinc - aluminum hydroxide, which can improve the flame retardancy. Sb_2O_3 performs much better than ZB in limiting oxygen index. ZB performs much better than Sb_2O_3 in smoke density.

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