Stabilizing effects of estertins mercaptide (methyl acrylate) for PVC degradation

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Abstract. The thermal and UV light (ultraviolet light) stability of PVC films with estertins mercaptide (methyl acrylate), methyltins mercaptide and the compound consisted of estertins mercaptide (methyl acrylate) and hydrotalcite (2:2.5) were investigated by ageing in a circulation oven at 190 °C and irradiating with 72W UV light for 96h, respectively, and then the yellowness and transmission rate were tested by Color Quest XE. Hydrotalcite was proved to have good synergies with estertins mercaptide (methyl acrylate) on improving the thermal stability and UV light stability. The retarding effects of the heat stabilizers to PVC degradation were tested by TGA from 50 °C to 600 °C. The results show that temperature of HCl evolution from PVC film was improved obviously by compounding with estertins mercaptide(methyl acrylate) and hydrotalcite and estertins mercaptide(methyl acrylate) was found to have a better long term stability. Sn⁴⁺ consistence of water and seawater in which films before and after UV light irradiation were soaked for 60 days was analyzed by ICP; the results indicate that the Sn⁴⁺ consistence from the films with estertins mercaptide(methyl acrylate) as thermal stabilizer was lower than that from the film with methyltins mercaptide. The crosslink moderately by UV irradiation for PVC films can hold back the dissolution of organotin heat stabilizers from PVC products into water and seawater.

1. Introduction
Organotin has been used for pesticides, wood preservatives and heat stabilizers for polyvinyl chloride (PVC) and antifouulant for several decades [1]. They are mainly classified into two categories, estertins and alkyltins. Dimethyltins bis-(isoctyl thioglycollate)( methyltins mercaptide) are widely used as thermal stabilizer in the production of sheets, profiles, general purpose and potable water pipes, sidings, films, foils, bottles and articles meant for paper packaging [2,3]. However, the byproducts with which they react such as labile chlorine atoms or HCl exhibit greater toxicity [4-8], and cause a serious pollution to the water when they are used as the stabilizer in PVC water pipe [9-11]. According to the literature [12], estertins, such as di-β-carboxalkoxyethyltins bis (isoctyl thioglycollate) [estertins mercaptide (methyl acrylate)] are lower toxic, cheaper and safer than alkyltins, and the byproducts of the reaction between estertins mercaptide (methyl acrylate) and the polymeric chains, mainly accumulated are much lower toxic than those of methyltins mercaptide[13], but preliminary researches showed that the retarding effects to PVC degradation at early stage were not so effective as methyltins mercaptide.

Hydrotalcite [Mg₆Al₂(OH)₁₆CO₃·4H₂O] which has been known for an extended period of time has good synergies with many kinds of stabilizers such as Ca/Zn compounds and lead salts [13].
objective of the present study is to investigate the retarding effects of estertins mercaptide (methyl acrylate) mercaptide (methyl acrylate) and hydrotalcite(2:2.5) on degradation of PVC.

2. Experimental

2.1 Materials, equipments and samples preparation

PVC paste resin (P440) from Shanghai Chlor-Alkali Chemical Co., Ltd., dioctyl phthalate (DOP) and stearic acid from Shanghai Sinopharm Chemical Reagent Co., Ltd., hydrotalcite from Xiamen Xindakang Inorganic Materials Co., Ltd., methyltins mercaptide from Shanghai Zhiqiang Plastic Auxiliary Co., Ltd., and estertins mercaptide (methyl acrylate) made according to the literature [14], seawater was from Yellow Sea located in Fengxian District of Shanghai, circulating water was from laboratory. Films(about 30mm diameter×1.5mm thickness) were prepared from PVC (100phr), DOP (60phr), stearic acid(1phr) and heat stabilizer(2phr) by mixing at 25º C and gelating at 170º C for 15 min. The thermal stability, the UV light stability and the stability in water and seawater of three film samples were tested. The films 1#, 2# and 3# are compounded with different thermal stabilizers, namely estertins mercaptide (methyl acrylate), methyltins mercaptide and estertins mercaptide (methyl acrylate)/ hydrotalcite (2:2.5), respectively.

2.2 Test methods

Each film sample was cut into nine circular specimens (30mm diameter×1.5mm thickness) for testing thermal stability for 45 minutes in a forced air convection oven, and took out one piece every 5 minutes. The thermal stability of film samples was investigated both by comparing the color changes of every specimen aged for 5 min, 10 min, 15min, …, 45 minutes directly and by measuring yellowness and transmission rate of the specimens by a Color Quest XE from American Hunterlab Company. Mass loss during heating of the film samples was measured by thermogravimetry using a Germany Linseis Thermogravimetric Analyzer (TGA) with heating at a rate of 10°C min⁻¹ from 50°C to 600°C under nitrogen at 40 cm³ min⁻¹.

The film samples were irradiated during 96 h at room temperature, using 72W, T8 G13, 365nm, UV lamps and the effect was measured by yellowness before and after UV aging.

About 0.5g films 1#-3# before and after UV aging were cut into 2mm ×2mm size particles and immersed into 150mL water or seawater for 60 days at room temperature. Sn⁺⁺⁺⁺ consistency of the filtered water and seawater was analyzed by means of VARIAN inductively coupled plasma atomic emission spectrometer (ICP OMS) to determine the stability of three kinds of stabilizers both in water and seawater.

3. Results and discussions

3.1 Thermal stability and transparency of the film samples

The air oven ageing results of the samples were shown in figure 1.

When PVC is under heating, HCl which is evolved as a result of PVC degradation induces the formation of conjugated double bonds. The stability of the samples can be characterized by yellowness because the colors of PVC films turn from yellow to black as conjugated structures increase.

The experimental results from Fig.1 showed that significant difference wasn’t observed of all the film samples within 25 minutes at 190°C, the colors of film 1# and 2# became brown in 30 minutes and 40 minutes, respectively, and turned to dark brown in 45minutes. However, film 3# sample was still light brown till 45minutes. The results above indicated that the thermal stability of methyltins mercaptide was better than that of estertins mercaptide (methyl acrylate), and that is the compound of estertin mercaptide (methyl acrylate) and hydrotalcite that shows the best stability under thermal aging.
The yellowness from films 1\textdegree{}-3\textdegree{} given in figure 2 increased from 2.22, 1.99 and 3.24 to 6.85, 4.02 and 9.52 within 25 minutes, respectively. The films 1\textdegree{} and 2\textdegree{} were over 40 after 45 minutes, while film 3\textdegree{} attain only 16.57 after the same time of aging. The results told that hydrotalcite shows synergistic effects with estertins mercaptide (methyl acrylate).

Figure 3 shows the light transmission rate difference of film 1\textdegree{}-3\textdegree{}. The films 1\textdegree{} and 2\textdegree{} increased from 84.26\% and 85.60 to 89.97\% and 87.74\%, respectively within 25 minutes, and film 1\textdegree{} had excellent transparence, probably because the ester group in estertins mercaptide (methyl acrylate) had good plasticizing action, but the transparence decreased quickly with the increase of conjugated structures after 25 minutes. The results that the light transmission rate of film 3\textdegree{} increased from 82.77\% to 89.16\% in the first 25 minutes and stayed at 82.45\% till 45 minutes indicating the hydrotalcite could be well dispersed in PVC under the action of the plasticizer.

3.2 Analysis to UV light irradiation

The yellowness and the light transmission rates of films which were irradiated by 72 KWh UV light for 96h were reported in table 1 giving the quantitative information about the resistance to UV light aging of the samples.
Table 1. Test results of UV light irradiation.

| Characteristic parameters | Experimental samples |
|---------------------------|-----------------------|
|                           | film 1\(^a\) | film 2\(^b\) | film 3\(^c\) |
| Before aging:             |           |           |           |
| Yellowness                | 4.52      | 5.02      | 3.19      |
| Transmission rate (\%)    | 89.97     | 87.74     | 89.16     |
| After aging:              |           |           |           |
| Yellowness                | 7.45      | 6.78      | 3.65      |
| Transmission rate (\%)    | 88.29     | 87.22     | 88.24     |

It was observed from table 1, before UV light irradiation, the transparence and yellowness of film 2\(^b\) is not so good as film 1\(^a\), however, the transparence of the film 3\(^c\) with 2.5phr hydrotalcite is 89.16, which proves hydrotalicates can enhance the thermal stability to PVC. Comparing the results of before and after UV irradiation, the transparence of the film 1\(^a\) decreases for 1.87\%, film 2\(^b\) for 0.59\% and film 3\(^c\) for 1.03\%, which indicates methyltins mercaptide can keep the film better transparence after UV irradiation. The yellowness of film 1\(^a\) increases for 65\%, film 2\(^b\) for 35\% and film 3\(^c\) for 14\%. The yellowness of film 3\(^c\) changes less, which proves that the compound of estertins mercaptide (methyl acrylate) and hydrotalcite can increase the UV irradiation stability of PVC film.

3.3 PVC degradation analysis

When PVC was heated, DOP evaporated from the surface and HCl evolved from thermal degradation released from film as gaseous products [5]. The mass loss caused by DOP evaporation was neglected because its content in the three film samples were the same. TGA curves presented in figure 4 and the respective results presented in table 2 indicate that when the remaining mass rate was 99\%, the temperatures were 138.1\(^0\)C, 163.2\(^0\)C, and 156.4\(^0\)C from films 1\(^a\), 2\(^b\) and 3\(^c\), respectively. At the remaining mass rate was 95\%, the temperatures were 198.1\(^0\)C, 204.2\(^0\)C, and 200.5\(^0\)C, respectively. This result proves film 2\(^b\) is more stable than the other two films at the initial stage of PVC degradation, which means methyltins mercaptide gives the better stability to PVC. However, with the increase of temperature, films 2\(^b\) and 3\(^c\) are more stable indicates estertins mercaptide (methyl acrylate) and the compound stabilizer have the better stability for PVC at higher temperature.

![Figure 4. TG curves](image1.png)  
![Figure 5. DTG curves](image2.png)
DTG curves in figure 5 showed that the degradation speed and the mass loss rate from film 2 was the biggest confirming that the results in table 2 furthermore. The degradation speed of film 3 as shown in figure 5 was faster than that of film 1 because the crystalwater, OH\(-\) and CO\(_3\)\(^{2-}\) also evaporated from the layers of hydrotalcite accompanied with the increasing of temperature. But OH\(-\) and CO\(_3\)\(^{2-}\) can react with HCl, so it has the best thermal stability even if the degradation speed is bigger when the temperature is over 200\(\degree\)C [15].

**Table 2.** TGA analysis of thermal degradation.

| Characteristic parameters | Temperature at different stage (\(\degree\)C) |
|---------------------------|-------------------------------------------|
|                           | film\(1^g\) | film\(2^g\) | film\(3^g\) |
| \(T_{1%}\)             | 138.1       | 163.2       | 156.4       |
| \(T_{5%}\)             | 198.1       | 204.2       | 200.5       |
| \(T_{10%}\)            | 230.1       | 231.1       | 227.2       |
| \(T_{16%}\)            | 248.6       | 248.4       | 242.7       |
| \(T_{20%}\)            | 257.3       | 255.3       | 249.4       |
| \(\Delta m_1/\%\)      | 79.47       | 81.20       | 76.80       |

note: \(T_{m%}\) is temperature at \(m%\) remaining mass rate; \(\Delta m_1\) is the rate of mass loss from 50 to 400\(\degree\)C.

3.4 Analysis of \(Sn^{4+}\) consistence in water

Table 3 gave the \(Sn^{4+}\) consistence of the water in which films \(1^g\)-\(3^g\) before and after UV irradiation had been soaked for 60 days was analyzed by means of ICP. At first, The standard liquid is prepared with 20mg/L \(Sn^{4+}\) consistence. The \(Sn^{4+}\) consistence of fresh water and seawater is analyzed by ICP, in fresh water no \(Sn^{4+}\) trace is found and \(Sn^{4+}\) consistence of seawater is 0.0722mg/L.

**Table 3.** The analysis results of ICP test.

| Samples       | \(Sn^{4+}\) consistence of Water (mg/L) | \(Sn^{4+}\) consistence of Seawater (mg/L) |
|---------------|----------------------------------------|-------------------------------------------|
| film \(1^g\)  | 0.823                                  | 0.954                                     |
| \(1^g\) UV aging | 0.383                                  | 0.416                                     |
| film \(2^g\)  | 1.066                                  | 1.930                                     |
| \(2^g\) UV aging | 0.482                                  | 0.779                                     |
| film \(3^g\)  | 2.568                                  | 4.029                                     |
| \(3^g\) UV aging | 1.348                                  | 1.547                                     |

Organotins and organotins chlorides produced by organotin reacting with HCl or liable chloride atoms are digested during the analysis by ICP and exist in the form of \(Sn^{4+}\) in freshwater, so organotin’s consistence dissolved into the water from PVC film samples can be characterized by means of detecting \(Sn^{4+}\) consistence of the freshwater. The results from table 3 indicated that \(Sn^{4+}\) consistence from film \(1^g\) was lower than those from film \(2^g\) both in water and seawater, it meant estertins mercaptide (methyl acrylate) were more stable. It is interesting to find that \(Sn^{4+}\) consistence
from film 3\# was far higher than those from film 1\# and 2\# assigned to organotin hydroxides and organotin carbonate compounds formed by OH\(^-\) and CO\(_3^{2-}\) evaporated from the interlayers of hydrotalcite reacted with organotin chlorides dissolved in water, but the effects of these byproducts to the freshwater need to be investigated furthermore [16]. We also find that Sn\(^{4+}\) consistency of every film after UV irradiation was higher than that of before UV irradiation, proves UV irradiation accelerates the solution of organotin from PVC film into water.

The information that Sn\(^{4+}\) consistency in seawater was more than those in water showed salt compounds and microorganisms in seawater can accelerate the solution of organotin from PVC films. It’s interesting to find Sn\(^{4+}\) consistency of the water and seawater which films after UV irradiation soaked were lower than that without being irradiated. This result showed that the crosslink moderately by UV irradiation for PVC films can hold back the dissolution of organotin heat stabilizers from PVC products into water and seawater.

4. Conclusions

The thermal stability of PVC films with estertins mercaptide (methyl acrylate), methytlins mercaptide and estertins mercaptide (methyl acrylate)/ hydrotalcite (2:2.5) compound was tested by air oven aging and TGA, respectively. The results showed that the property of inhibiting to PVC degradation under heating and UV light irradiation of estertins mercaptide (methyl acrylate) which didn’t retard HCl evolution as well as methytlins mercaptide is improved by compounding with hydrotalcite [Mg\(_6\)Al\(_2\)(OH)\(_{16}\)CO\(_3\)·4H\(_2\)O]. Compared to methytlins mercaptide, estertins mercaptide (methyl acrylate) kept a better stability both in water and seawater. The crosslink moderately by UV irradiation for PVC films can hold back the dissolution of organotin heat stabilizers from PVC products into water and seawater.

Acknowledgments

The work financially supported by science and technology development project of Yanbian state (2015-GX11) and university students’ research and innovation project of Shanghai (Nos. cs1504007).

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