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Influence of soy protein isolate on the thermal stability of poly(vinyl chloride) in the presence or absence of calcium and zinc stearates

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ABSTRACT

The influence of soy protein isolate (SPI) and its mixture with calcium stearate ($CaSt_2$), and zinc stearate ($ZnSt_2$) with various ratios on the processing thermal stability of poly (vinyl chloride) (PVC) was investigated by measuring dehydrochlorination rate of PVC (DHC), visual color comparison, and thermogravimetric analysis (TGA). The results suggested that SPI acted as a long-term thermal stabilizer like $CaSt_2$ to absorb HCl released from PVC, which is due to the primary amine (-NH_2) and polyols containing hydroxyl groups in SPI. Moreover, SPI improved the stabilization effect of the traditional $CaSt_2/ZnSt_2$ stabilizer, and the combination of SPI and $CaSt_2/ZnSt_2$ at certain ratios exhibited desirable stabilization efficiency in prolonging the discoloration time.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most important commercial polymer materials and is widely used due to its good performance in respect of mechanical behavior as well as low price [1]. However, PVC suffers from poor thermal stability; it undergoes extensive autocatalytic dehydrochlorination with formation of conjugated double bonds in polymer chains which results in severe discoloration and loss of mechanical properties [2–4]. Therefore, thermal stabilizers are necessarily added to protect it from thermal degradation during its processing and applications [2]. Some conventional thermal stabilizers, such as basic lead salts [5], can react with the evolved hydrogen chloride gas, thus retarding the further catalytic action of the eliminated hydrogen chloride [6,7]. The other ones, metallic soaps [8–12] and esters or mercaptides of dialkyltin [13–16], can exchange the labile chlorine in the backbone chains for other more stable complex derived from the stabilizer.

However, the application of lead salts and organic tin stabilizers are limited due to their toxicity, even though they are quite efficient. On the other hand, Ca/Zn stabilizers have not got wide industrial application because of their low efficiency. Moreover, zinc chlorides are strong catalysts for the dehydrochlorination process and easy to cause sudden severity of discoloration of certain formulations [12]. Many researchers have focused on nontoxic complex stabilizers with high efficiency for PVC processing, such as (natural) polyols [17], saturated polyesters [18], ester thiols [19,20], and intercalated hydrotalcite-like materials [21]. Nevertheless, the high costs limit their applications. The interests for low cost and environment-friendly stabilizer used in the processing of PVC have increased widely in recent years.

As natural biopolymer, soy protein isolate (SPI) has been extensively studied due to its low cost, availability and biodegradability. It is obtained from soybean seeds by a separation method based on chemical reactivity and solubility [22]. The application of SPI include adhesives, plastics, films, coatings, glazing agents and emulsifiers in food chemistry, therapeutics, agricultural equipment, automobiles, marine infrastructure and civil engineering [23]. SPI contains more protein than any other soy protein products, and possesses many side reactive groups such as $-NH_2$, $-OH$, and $-CN$. These basic groups are facile to absorb hydrogen chloride, which implies that SPI can be used as thermal stabilizer for PVC. In this paper, the thermal stability of PVC with varied ratios of $ZnSt_2$/SPI, $CaSt_2$/SPI as well as Zn–Ca/SPI as thermal stabilizer is assessed by measurement of dehydrochlorination (DHC) rates, color and TGA analysis. The influence of SPI on the thermal stability of PVC in presence or absence of calcium and zinc stearates is investigated.

2. Experimental

2.1. Materials

The PVC (SG-5) was purchased from Weiye Plastics Corporation, Ningbo, China (K-Fikenstcher value of 68). DOP (purity of 99.5%,

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Sinopec Jinling Petrochemical Corporation, Nanjing, China) was used as plasticizer. SPI was supplied by Tianjiu Biotechnology Corporation, Heze, China. $ZnSt_2$, $CaSt_2$ and Zn–Ca stabilizer (the weight ratio of zinc to calcium salt was 1:2.5), were produced by Jialong Chemical Corporation, Shenzheng, China. All materials were used without any treatment.

2.2. Preparation of PVC films

PVC (100 phr) and DOP (40 phr) with various amounts of stabilizers (Table 1) were melt blended by using a two-roll mills (the roll with the length of 35.0 cm and the diameter of 16.0 cm; rotation speeds of front and back roll are 24 and 30 rpm respectively) at the temperature of 160 °C ± 2 °C for 5 min. The PVC material was compression molded under a pressure of 10 MPa at 180 °C for 2 min, then cold molded under 2 MPa at 30 °C for 10 min to form 1-mm-thick plaque test samples.

2.3. Method of measurement

2.3.1. Dehydrochlorination rate of PVC (DHC)

Dehydrochlorination of PVC plaques at 180 °C was determined by continuous potentiometric method [24]. The PVC plaques with the size of 2 mm × 2 mm were placed in the reaction vessel. The gaseous HCl released from the degradation of PVC samples was transported by nitrogen gas (120 ml/min). The efficiency of thermal stabilizers was evaluated by measurement of stabilization and induction time using the method illustrated in Fig. 1.

2.3.2. Color measurements

To carry out the static thermal aging tests via observing the color change of the samples, the PVC plaques with the size of 5 cm × 5 cm were put into an air circulation oven at 180 °C. Plaques were taken out for measurement for each 20 min (or 10 min). The efficiency of stabilizers was evaluated by comparing the visual color differences of heated PVC plaques.

2.3.3. Thermogravimetric analysis (TGA)

Thermal degradation of PVC was evaluated by thermogravimetric analyzer (SDTA851e, METTLER TOLEDO, Switzerland) from 50 to 600 °C at a heating rate of 20 °C/min with the protection of nitrogen.

Table 1
The compositions of stabilizer in PVC samples.

Samples	SPI (phr)	$ZnSt_2$ (phr)	$CaSt_2$ (phr)	Ca–Zn stabilizer ($ZnSt_2/CaSt_2$ = 1/2.5, wt)
1	4	0	0	0
2	3	1	0	0
3	2	2	0	0
4	1	3	0	0
5	0	4	0	0
6	3	0	1	0
7	2	0	2	0
8	1	0	3	0
9	0	0	4	0
10	3	0	0	1
11	2	0	0	2
12	1	0	0	3
13	0	0	0	4
14	4	0	0	4
15	6	0	0	4
16	8	0	0	4
17	10	0	0	4

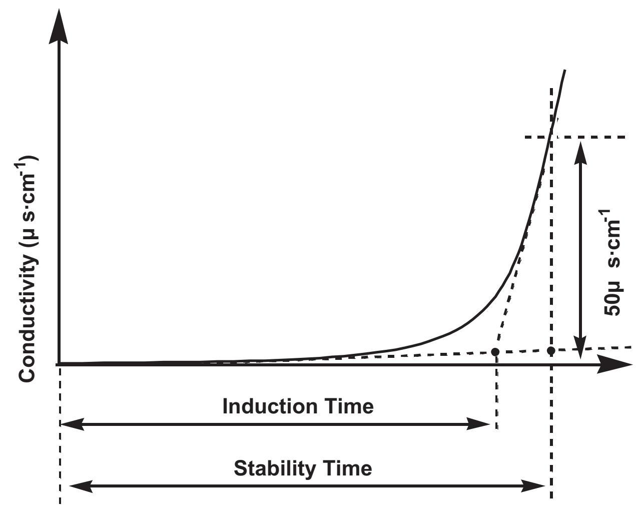

Fig. 1. Scheme of determination of stability time and induction time.

3. Results and discussion

3.1. Formulations stabilized with $ZnSt_2$/SPI

Fig. 2 and Table 2 showed the results of dehydrochlorination of PVC formulations stabilized with SPI in presence of $ZnSt_2$, thermally degraded at 180 °C in air. The results represented the average of three parallel experiments. As is well known, $ZnSt_2$ is able to scavenge HCl due to its stronger Lewis acidity and react with labile chlorine atoms. HCl is eliminated from regions poor of $ZnSt_2$ and accelerates the dehydrochlorination of PVC, and further react with $ZnSt_2$ to form $ZnCl_2$. Thus the amount of Lewis acid ($ZnCl_2$) increases simultaneously. In this case, auto-acceleration of dehydrochlorination occurred. According to the results, the formulation stabilized with $ZnSt_2$ released HCl quickly with a sudden dehydrochlorination at only 6.5 min from the beginning. Compared with PVC/$ZnSt_2$ samples, there is a very slight retardance of dehydrochlorination occurred on the PVC/$ZnSt_2$/SPI samples, which suggests the $ZnSt_2$/SPI has a better stabilization effect than $ZnSt_2$ for PVC stabilization.

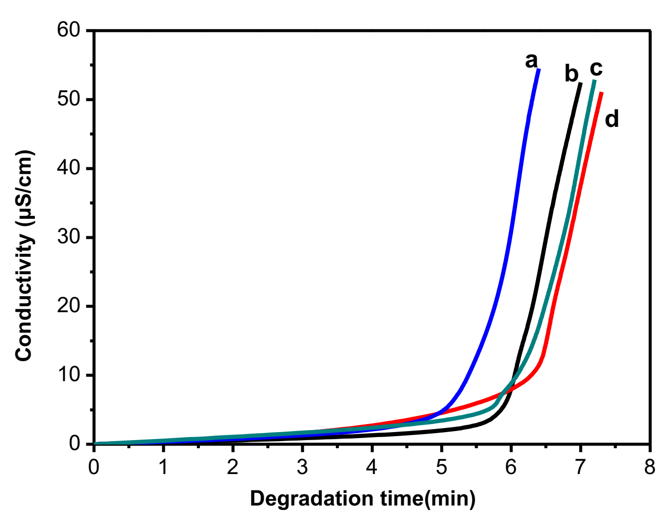

Fig. 2. HCl evolution curves, as a function of time, for formulations stabilized with $ZnSt_2$/SPI in different ratios (a) 4.0:0.0, (b) 3.0:1.0, (c) 2.0:2.0, (d) 1.0:3.0.