Synthesis of Pentaerythritol Adipate Ester-Based Zinc Alkoxide and its Thermal Stability on PVC

Abstract
A new pentaerythritol adipate ester-based zinc alkoxide (PAE-Zn) was synthesized through an alcohol-exchange reaction. The thermal stability of PAE-Zn in PVC (poly vinyl chloride) was examined by conductivity and thermal aging tests. The results showed that the PVC stabilized with PAE-Zn has a good initial color and excellent long-term thermal stability. A synergistic effect of PAE-Zn with calcium stearate (CaSt) and zinc stearate (ZnSt) on PVC thermal stability was also been tested. It showed that the complex of PAE-Zn/CaSt/ZnSt had a better integrated effect on inhibiting the color change of PVC.

Keywords: PVC; Pentaerythritol adipate ester-based zinc alkoxide; Thermal stabilizer

Introduction
Because of the excellent corrosion resistance, antiflaming and electrical insulation, PVC (poly vinyl chloride) has become one of the five commonly used plastics in the world [1,2]. However, PVC has significant defects due to its quick decomposition at temperature higher than 130°C [3-5]. This process results in a significant change in color, reducing the mechanical properties and the generated HCl exacerbates the decomposition of PVC, so the usage of PVC thermal stabilizers is inevitable [4,6]. Our group had synthesized pentaerythritol-based zinc alkoxide (PE-Zn) as a thermal stabilizer [7]. PE-Zn has outstanding performances in terms of color stability and long-term stability of rigid PVC. However, most of the alkoxide have high melting point and poor compatibility with PVC, which significantly restrict their wide applications. In order to decrease the melting point of polyols-based metal alkoxide, an ester group, such as stearic acid, was grafted onto the polyols to obtain pentaerythritol stearate ester-based zinc alkoxide [8].

In this study, a new ester-based metal alkoxide, pentaerythritol adipate ester-based zinc alkoxide (PAE-Zn) was synthesized, which had low melting point and good compatibility with PVC. The thermal stabilizing tests showed that PAE-Zn stabilized PVC had both a good initial color and an excellent long-term thermal stability.

Experimental
Materials
Zinc acetate, ethanol, adipic acid, pentaerythritol, phosphoric acid, cyclohexane, calcium stearate and zinc stearate were all analytical reagents. PVC resin (type 5G-5, average degree of polymerization is 1005 and viscosity number is 6.7) was obtained from China Petrochemical Qilu Limited Co., Zibo, China. Other thermal additives were kindly supplied by Shandong Huike Additives Co.Ltd., Zibo, China.

Preparation of PAE-Zn
Adipic acid and pentaerythritol in a molar ratio of 1:2 were added into a mixer and stirred for 5 min, and then the mixture was placed in a three-necked flask equipped with a condenser-Allihn type and a water separator. The appropriate amount of phosphoric acid was added into the flask as a catalyst and cyclohexane as a wetting agent. The esterification reaction temperature was kept at 170°C until there was no water generated (about 4 h). The pentaerythritol adipate ester (PAE) was obtained after the residual cyclohexane was removed by vacuum distillation.

PAE and zinc acetate in a molar ratio of 2:1 were added into a three-necked flask. Excess ethanol was added and the flask was heated to 160°C for reaction of 4 h. After the ethanol was fully evaporated, PAE-Zn was obtained.

FTIR analysis
PAE-Zn was characterized by FTIR spectroscopy using the KBr disc method. The range of the spectrum wavelength was 400-4000 cm⁻¹ with a scanning rate of 120 min⁻¹ and a resolution of 4 cm⁻¹.

Elemental analysis
Elemental analysis (Vario ELcube) was used to determine, hydrogen, and oxygen contents of the PAE-Zn samples.

Thermal aging test
The PVC blends were prepared by intensively mixing 100.0 phr of PVC, 2.0 phr of acrylic copolymer (ACR), 1.6 phr of stearic acid, 10.0 phr of CaCO₃, 4.0 phr of TiO₂, 8.0 phr of DOP, and 0 phr or 4...
phr of thermal stabilizers in a high-speed stirring for about 3 min. The PVC blends were milled using an open twin roller at 180°C for 5 min. The thickness of the drawn-out sheets was controlled at 1.0±0.1 mm. Thermal aging test: The PVC sheets were cut into small pieces (10 mm × 10 mm). These small sheets were subjected to static thermal aging test according to the ISO standard [8]. The temperature of the thermal aging test box was kept at 180±1°C.

Conductivity test

The PVC sheets were cut into small flakelets with a total weight of 2 g, and then they were put into home-made reaction vessels at N₂ atmosphere. A 60 mL deionized water containing dissolved HCl originated from the decomposition of PVC, was conducted the conductivity measurement.

Results and Discussion

Figure 1 shows the FTIR spectra of PAE-Zn. The strong peak at 3405 cm⁻¹ is the characteristic absorbance of -OH, which suggests plenty of hydroxyl group in PAE-Zn. The peak at 1720 cm⁻¹ is referring to ester carbonyl structure C=O stretching vibration. The peak at 669 cm⁻¹ is ascribed to the Zn-O bond [9] in PAE-Zn.

Table 1 lists the contents of the C, H, O and Zn elements. According to the theoretical basis and experimental results, the structure of PAE-Zn can be inferred and shown in Figure 2. When the PVC is heated to a high temperature, the unstable chloride atom will be removed together with the adjacent hydrogen, and the conjugated double bonds are generated. With the duration of the heating time, the number of conjugated double bonds increases. Meantime, the PVC turned gradually from white to brown, and at the end, it becomes black. The change in PVC color can indicate the degradation of PVC. Figure 3 illustrates the images of PVC samples heated at 180°C for different periods of time. The initial color of pure PVC is light brown, and the color turns to brown after 10 min. The initial color of the PVC sheets containing 2 phr CaSt₂ and 2 phr ZnSt₂ (the commercial used thermal stabilizer of PVC) was almost white and began to change at 20 min, and turned into dark brown quickly at 30 min. It suggests that CaSt₂/ZnSt₂ is an excellent thermal stabilizer for PVC, which has excellent initial thermal stability. But it is a quite short thermal stability, because of the generation of zinc dichloride (ZnCl₂) during the stabilizing process of ZnSt₂, ZnCl₂ is a strong Lewis acid, which can catalyze the dehydrochlorination of the PVC and make the PVC turn into black quickly [10-14]. This phenomenon is called the "zinc burning".

Table 1: The element content of PAE-Zn.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical value</td>
<td>42.74%</td>
<td>6.33%</td>
<td>33.77%</td>
<td>17.16%</td>
</tr>
<tr>
<td>Elemental analysis date</td>
<td>42.41%</td>
<td>6.22%</td>
<td>33.83%</td>
<td>17.54%</td>
</tr>
</tbody>
</table>

The PVC with 4 phr PAE-Zn doesn't turn into complete black until 120 min, indicating that PAE-Zn is a highly efficient thermal stabilizer in inhibiting the degradation of PVC. The adipic acid ester based functional groups would possibly make the PAE-Zn have a good compatibility with PVC and can greatly improve the stability of PVC. However, the initial color of PVC stabilized with PAE-Zn is not as white as that of CaSt₂/ZnSt₂. Meanwhile the synergistic effect of PAE-Zn and CaSt₂/ZnSt₂ was also investigated. It can be seen from Figure 3 that the color of the PVC containing 1 phr ZnSt₂ + 1 phr CaSt₂ + 2 phr PAE-Zn not only presents a quite white in initial color, but also has an excellent long-term stability. This indicated that PAE-Zn and CaSt₂/ZnSt₂ mixture had a pronounced synergetic effect on the stability of PVC. Figure 3 shows that there is no “zinc-burning” phenomenon for the PVC stabilized with the mixture of PAE-Zn and CaSt₂/ZnSt₂. A reasonable explanation is that ZnCl₂ generated during the process of ZnSt₂ replacing the active chloride atom of PVC or neutralizing HCl might be cheated by –OH of PAE-Zn. In conclusion, PAE-Zn is an excellent thermal stabilizer for PVC.

Figure 4 shows curves of conductivity vs. time for different PVC samples. The stability time (Tₚ) of pure PVC is only 20 min, which demonstrates the poor thermal stability of pure PVC. The addition of Ca/ZnSt₂ extends the Tₚ of PVC to 32 min. The Tₚ of PVC stabilized with PAE-Zn is 52 min, the biggest among the four PVC samples, which shows that the addition of PAE-Zn can prolong the long-term thermal stability of PVC obviously. However, the conductivity
of PVC stabilized with PAE-Zn increases a little when the PVC was heated for about 20 min. The increasing conductivity reveals the fact that the PVC begins to decompose. The results agree with that of thermal aging test, demonstrating that PVC stabilized with PAE-Zn has long-term thermal stability, but has common initial color stability. In order to improve the initial color, PAE-Zn was used together with Ca/ZnSt, demonstrate excellent initial color. Figure 4 shows that the PVC stabilized with the mixture of PAE-Zn and CaSt/ZnSt has proper long-term thermal stability (43 min) and excellent initial color.

Figure 4: Change of conductivity of aqueous solution with respect to time at 180°C for PVC without or with different additives. a: Pure PVC, b: Ca/ZnSt2, c: Ca/ZnSt2 + PAE-Zn, d: PAE-Zn

Conclusion

In this paper, PAE-Zn was synthesized and its performance as PVC thermal stabilizers was tested through thermal aging and conductivity tests. Furthermore, the synergistic effect of PAE-Zn and PAE-Zn/(Ca/ZnSt) as PVC thermal stabilizers was also studied. The results showed that PVC stabilized with PAE-Zn had remarkable long-term thermal stability. The PVC stabilized with the mixture of PAE-Zn and Ca/ZnSt had excellent initial color and long-term stability, which could be attributed to the strong synergism between PAE-Zn and ZnSt, due to the hydroxyl groups. PAE-Zn could chelate ZnCl2 to restrain “zinc-burning”.

Acknowledgement

The authors gratefully acknowledge the support of the University Research Program of Shandong Provincial Department of Education (No. J16LC24), SDUT & Zibo City Integration Development Project (NO. 2016ZBXC057), and the National Natural Science Foundation of China (NO. 51574160, NO. 21506118).

References


Conflict of Interest

None.