The effects of thermally reversible agents on PVC stability properties

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Abstract. One kind of thermally reversible cross-linking agents for improving PVC thermally stability was synthesized. The chemical structure and thermally reversible characteristics of cross-linking agents were investigated by FTIR and DSC analysis, respectively. FTIR results confirmed that the cyclopentadienyli barium mercaptides ((CPD-C₂H₄S)₂Ba) were successfully synthesized. DSC results showed it has thermally reversible characteristics and the depolymerization temperature was between 170 °C and 205 °C. The effects of cross-linking reaction time on gel content of Poly(vinyl chloride) compounds was evaluated. The gel content value arrived at 42% after being cross-linked for 25 min at 180 °C. The static thermally stability measurement proved that the thermally stability of PVC compounds was improved.

1. Introduction
Polyvinyl chloride (PVC) is a kind of good comprehensive performance resin. The production is second only to polyethylene resin. It has been used in many fields with its excellent properties [1, 2]. However, since its poor heat resistance (softening point is 80°C), deformation resistance, abrasion resistance, electric breakdown resistance and poor mechanical strength is not enough higher shortcomings, limit its application.

Recently, many researchers have focused on PVC modification through physical (filling, blend) and chemical (copolymerization, grafting and cross-linking) modification methods [3-8]. It is well known that PVC thermal decomposition is from active chlorine structure began to emerge the HCl autocatalytic continuous degradation process, so try to remove or replace the active chlorine can effectively improve the strength of the PVC and heat resistance. The cross-linking of PVC is an effective method to enhance it [9-16]. Moreover, through the thermally reversible cross-linking method for modification of PVC, maybe improve the mechanical properties, environmental stress cracking resistance and reduce the permanent deformation products, moreover, the thermal stability performance of PVC may be enhanced through the introduction of sulphydryl groups [17-19].

One kind of thermally reversible cross-linking agent for improving PVC thermal properties was synthesized in this work. Its chemical structure and thermally reversible characteristics were tested by FTIR and DSC, respectively. The influence of reaction time on gel content of flexible PVC and
amount with cyclopentadienyl barium mercaptides ((CPD-C₂H₄S)₂Ba) on thermal stability of flexible PVC were evaluated.

2. Experimental

2.1. Materials
All the materials used in this work has been described by Wang and Fang[19].

2.2. Synthesis procedure

2.2.1. Synthesis of cyclopentadiene (CPD). Dicyclopentadiene (DCPD) (70 ml) was added in 100 ml three-mouth flask. The whole reaction system was filled with nitrogen gas for protection. Heated the reactants to boiling and then collected the boiling point at 41~42 °C fraction. 60 ml colorless transparent liquid, cyclopentadiene (CPD) was obtained for 2 h and kept in ice water bath during the splitting decomposition process. The anhydrous magnesium sulfate was added in the bottle.

2.2.2. Synthesis of cyclopentadienyl sodium (CPD-Na). NaOH (73 g, 1.8 mol) was separately added in two 250 ml suction flasks connected by Y type three. Then 135 ml THF was slowly added with magnetic stirring. The two suction flasks were placed in ice bath. The newly prepared 60 ml CPD was injected into the two suction flasks. Meanwhile, Y type three ways while the other end was connected to a magnetic rotor 500 ml suction flask, preparing for the next reaction. The purple red liquid, cyclopentadienyl sodium (CPD-Na) was obtained for 17 h. The whole reaction was under ice bath and with nitrogen protection conditions.

2.2.3. Synthesis of cyclopentadienyl ethyl bromide (CPD-C₂H₄Br). 1, 2- dibromoethane (C₂H₄Br₂) (63 ml) was added into a 500 ml suction flask. Then, the obtained CPD-Na was slowly poured into the suction bottle with magnetic stirring. After reacting at the room temperature for 0.5 h, the mixture was heated to 50 °C for 8 h. Then separated the product and washed oily liquid with deionized water for several times. After that added a small amount of ether oil, fractions were collected and then purified the oil liquid.

2.2.4. Synthesis of cyclopentadienyl ethyl mercaptan (CPD-C₂H₄SH). Thiourea (CH₄N₂S) (34 g, 0.45 mol) and Benzyltrim-ethyl-ammonium chloride (C₁₀H₁₆N·Cl) (0.3 g, 0.0016 mol) were dissolved in 140 ml deionized water with heating and stirring. Cooled to 50~60 °C, slowly dripped cyclopentadienyl ethyl bromide (CPD-C₂H₄Br) with stirring. After reacting for 4 h, the compound was cooled and then added NaOH (30%) water solution. The product was washed with deionized water until neutral.

2.2.5. Synthesis of cyclopentadienyl barium mercaptides ((CPD-C₂H₄S)₂Ba). The cyclopentadienyl ethanethiol salt, cyclopentadienyl barium mercaptides ((CPD-C₂H₄S)₂Ba) was prepared as follows: a concentration of barium hydroxide aqueous solution was prepared in advance and then slowly dropped cyclopentadienyl ethyl mercaptan under stirring. Until the PH value was neutral, the final product was filtered off, and then cleaned using deionized water and dried under vacuum at 40 °C to a constant weight.

2.3. PVC compounds specimen preparation
The composition of flexible PVC compound was given in Wang and Fang [19]. It was pointed that there was 1 Phr organic tin in the compositions without thermally reversible cross-linking agents.
2.4. Chemical structure analysis by FTIR
The structure of cross-linking agent and derivatives were measured on a Perkin-Elmer FTIR (coating or KBr) at 4 cm\(^{-1}\) resolution and 32 times scanning.

2.5. Thermally reversible characteristics measured by DSC
DSC test was run on a TA 910 DSC from 23 °C to 300 °C at heating rate with 10 °C /min.

2.6. Gel content testing
The method has been described by Wang and Fang[19].

2.7. Static thermal stability
The Congo red method was used to test PVC thermal stability properties. The method was as follows, the cross-linked PVC composite specimen were cut into small pieces of 2 mm×2 mm at first, and then loaded into the test tube. When the glycerol was heated at 200 °C, put the test tube in the oil bath. The time for the color of Congo red test paper changing to the equivalent of PH of 3 is recorded.

3. Results and discussion

3.1. FTIR

![Diels-Alder reaction](image)

**Figure 1.** Diels-Alder reaction.

![Reaction route](image)

**Figure 2.** The reaction route of CPD-C\(_2\)H\(_4\)S)\(_2\)Ba.
Thermally reversible agents for improving flexible PVC thermal stability, cyclopentadienyl barium mercaptides ((CPD-C\(_2\)H\(_4\)S)\(_2\)Ba) was synthesized in this paper. Figure 1 shows the Diels-Alder reaction between dicyclopentadiene (DCPD) and cyclopentadiene (CPD). Figure 2 shows the synthetic reaction route of CPD-C\(_2\)H\(_4\)S)\(_2\)Ba. The structure of intermediate and target products (I, II, III and IV marked in Figure 2) are characterized by FTIR spectra as shown in Figure 3 (a-d).
From the FTIR spectra, it was found that the absorption peaks at about 3104 cm\(^{-1}\), 2914 cm\(^{-1}\) and 1364 cm\(^{-1}\) in Figure 3(a) were attributed to \(-\text{CH}=\text{CH}-\) bond, \(-\text{CH}_2-\) bond and C-H bond of cyclopentadiene, respectively, which represent the major chemical structure of CPD. As can be seen from Figure 3(b), a new peak at 588 cm\(^{-1}\) which was associated with C-Br bond stretching vibration appeared. The other characteristic peaks of CPD still existed, which showed that CPD-C\(_2\)H\(_4\)Br was obtained. From Figure 3(c), it could be seen that a new peak at 674 cm\(^{-1}\) assigning to C-S bond and another new peak at 2523 cm\(^{-1}\) belonging to S-H bond appeared. It proved that CPD-C\(_2\)H\(_4\)SH was obtained. And these two peaks changed as seen from Figure 3(d), one peak at 2523 cm\(^{-1}\) disappeared and meantime the other peak at 674 cm\(^{-1}\) turned to be blue shift which proved S-Ba is forming. From the above FTIR analysis, it is confirmed that the target product was successfully synthesized.

### 3.2. DSC

Figure 4 illustrates the DSC curves of (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba. The result shows that there exist three endothermic peaks in Figure 4. The peak at 90 °C belongs to the water in (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba. The peak at 137 °C belongs to the melting points of (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba. The endothermic peak between 170 °C and 205 °C is assigned to the depolymerization temperature of (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba.

![Figure 3. FTIR spectra of (a) CPD (b) CPD-C\(_2\)H\(_4\)Br (c) CPD-C\(_2\)H\(_4\)SH (d) (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba.](image)

![Figure 4. DSC curves of cyclopentadienyl barium mercaptides ((CPD-C\(_2\)H\(_4\)S)\(_2\)Ba).](image)

### 3.3. Influence of reaction time on gel content for PVC

Figure 5 illustrates the results of gel content under different cross-linking time for flexible PVC with 3 Phr (CPD-C\(_2\)H\(_4\)S)\(_2\)Ba at 180 °C. It is found that the cross-linking time has obvious influence on gel content of PVC. The value is below 10% for the cross-linking time less than 15 min at this reaction temperature. The gel content value reaches at 15% for 20 min cross-linking reaction and it increases to 42% at maximum for 25 min. However, the gel content decreases for prolonging the reaction time for 35 min.
3.4. Influence of the amount of agents on thermal stability of flexible PVC

It is well known that the static thermal stability time is the reflection of PVC compounds thermal stability. Figure 6 shows the results of stable time of flexible PVC with different agent amount. The result shows that the stable time increases with adding agent amount from 1 Phr to 5 Phr. It is proved that the agent can react with the active chlorine in PVC structure and then enhance the thermal stability of PVC.

4. Conclusions

The cyclopentadiene derivatives, cyclopentadienyl barium mercaptides ((CPD-C₅H₄S)₂Ba) was successfully synthesized. The chemical structure of intermediate and target products were characterized by FTIR. It proved that the target products were obtained. From the DSC analysis, it is found that the cyclopentadiene derivatives have thermally reversible temperature. The gel content value arrived at 42% after being cross-linked for 25 min at 180 °C. The cross-linking agent amount has strong effects on PVC compounds static stability.
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