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Dehydrochlorination study of plasticized poly(vinyl chloride) containing modified titanium dioxide, cerium stearate, organotin and \( \beta \)-diketone complex after long-term storage

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Abstract

Understanding the influence of additives on the dehydrochlorination of plasticized poly(vinyl chloride) (PVC) from the source and long-term storage is an attractive topic. In this work, the effects of folic acid modified nano titanium dioxide (FANT), cerium stearate, organotin and \( \beta \)-diketone compound additives on the dehydrochlorination of plasticized PVC and long-term storage were investigated using conductivity measurements. The results showed that the induction time of hydrogen chloride removal of plasticized PVC (C-1) containing composite stabilizer at 200 °C were 243% higher than those of the control (S1). After storage, the heat stability of the control decreased significantly. Instead, the induction time and stability time of plasticized PVC containing FANT, cerium stearate, organotin and \( \beta \)-diketone composites were significantly enhanced at 200 °C. The thermal stability sequence from difficult to easy for removal of hydrogen chloride was: 3.0 phr (1.90% wt) (C2) > 1.0 phr (0.64% wt) (C1) > 5.0 phr (3.17% wt) (C3) with FANT. It is inferred that this is due to the FANT’s hydrogen bonding van der Waals force and the complexation reaction of variable valence metal \( \text{Ce}^{+3}/\text{Ce}^{+4} \) with C-Cl bond in PVC polymer molecule. The induction time (min) of hydrogen chloride removal at 200 °C before and after storage is as follows: C-20 (71.9) > C-10 (70.6) > C-1 (60.7) > C-3 (57.2) > C-30 (52.7) > C-2 (49.9) > S1 (25.3) > S10 (19.7). The critical temperature for hydrogen chloride removal by the composite film is around 210 °C. If the content of FANT increased to 3.17%, the intermolecular force and repulsive force in PVC system offset each other, indicating that the increase of FANT content will lead to the increase of repulsive force with PVC. A certain amount of FANT, cerium stearate, organotin and \( \beta \)-diketone composites has a significant synergistic effect on the thermal stability of PVC.

1. Introduction

Polyvinyl chloride (PVC) has the advantages of low price, excellent acid and alkali resistance, chemical corrosion resistance and flame retardancy, it is also an important separation membrane material. In 2020, the output of polyvinyl chloride (PVC) in China was 20.74 million tons, with a year-on-year increase of 3.1%; The apparent consumption of polyvinyl chloride (PVC) in China was 21.07 million tons, a year-on-year increase of 3.9%. As the world’s largest general-purpose plastic, PVC is widely used. It is widely used in building materials, industrial products, daily necessities, floor leather, floor tiles, artificial leather, pipes, wires and cables, packaging film, bottles, foaming materials, sealing materials, fibers and so on. Common bulk heat stabilizer products for PVC include organic tin, calcium zinc metal soap, rare earth metal soap, organic compounds and lead salts. Although there are many reports on the role of different stabilizers, the durability of PVC has not been solved. In the presence of external factors such as folic acid modified titanium dioxide, cerium stearate, organotin and \( \beta \)
-diketone complex, little is known about the changes in the molecular structure of PVC materials that produce hydrogen bonding and van der Waals forces when doped with folic acid, or REDOX capacity when doped with variable-valence metals such as Ce$^{3+}$ and Ce$^{4+}$.

As we all know, when polyvinyl chloride (PVC) is stimulated by heat, oxygen and light in the environment, due to its internal unstable structures[1], degradation processes will occur. The initiation stage of degradation is closely related to structural defects such as tertiary chlorine, allyl chloride and carbonyl allyl. The common degradation processes include thermal degradation (it leads to the fracture of C-Cl bond, since the bond energy is 243 kJ mol$^{-1}$), thermal oxygen degradation (in addition to thermal action, it also produces ROOH, OH, OOH and H radicals), photo-degradation and autocatalytic degradation, according to the free radical process or autocatalytic mechanism [2]. The effects of heat, oxygen, light and catalyst will lead to the production of chlorine free radicals, which are transferred through the chain to capture the hydrogen atoms in PVC molecules and remove hydrogen chloride to form a conjugated polyene carbon chain [3]. The conjugated polyene undergoes polymerization, aromatization, etc. Cyclization and polymerization generate aromatics, polycyclic aromatic hydrocarbons [4, 5].

To this end, methods to improve the thermal stability of plasticized PVC include organotin, calcium zinc metal soap, rare earth earth soap, organic compounds and lead salt stabilizers are used for the following occasions: (1) adsorption of HCl obtained from PVC decomposition to delay PVC decomposition, such as the use of calcium carbonate, nano calcium carbonate and nano titanium dioxide particles; (2) inhibition of the generation of HCl by replacing the chlorine atoms in the PVC molecular chain to generate a stable structure and to avoid the formation of a conjugated double bond structure; and (3) the use of an addition reaction, that is, an unsaturated double-bond reaction with the PVC structure, destroying the unstable structure of PVC to enhance the stability [6]. In fact, due to the influence of some uncertain factors, such as different light intensities and the presence of plasticizer, heat stabilizer and reinforcing agent, PVC still experience degradation [7–9].

There are literature reports, stabilizers such as tin and zinc [10], nano-reinforcing agents [11, 12] including nano-titanium dioxide, etc [13] were used in plasticized PVC to inhibit the removal of hydrogen chloride. Or both improve PVC heat resistance, and promote the degradation of waste plastics. Such as nano-titanium dioxide is an efficient, environmentally protective, nontoxic photodegradation catalyst that can block hydrogen chloride formation and can also react with hydrogen chloride. Other examples include improvement of the photodegradation performance of titanium dioxide by VC [14], ultrafiltration membranes made from Chlorinated poly(vinyl) chloride) EPVC/TiO$_2$ nanocomposite [15], the effect of UV light on the mechanical properties of PVC/TiO$_2$ nanocomposites [16], co-doping of nano-graphite and TiO$_2$ to enhance the photodegradation of PVC films [17], the effect of titanium dioxide particles on the mechanical properties of QUV accelerated aging PVC composites [18], application of polymer–supported titanium dioxide photo-catalyst in environmental remediation [19], the influence of TiO$_2$ on the thermal behavior of PVC composites [20], elimination of degradability of plasticized polyvinyl chloride by an oxygen control tube [21], dehydrochlorination of PVC materials at high temperature [22], flame retardant modification of plasticized PVC without heavy metal stabilizer [23], degradation kinetics of polyvinyl chloride containing Ca and Sn at low temperature [24], effects of titanium dioxide on chemical and molecular changes of QUV accelerated aging PVC wall panels [25]. When using nano-titanium dioxide, folic acid can improve its poor compatibility with PVC [26]. Molecular structure of folic acid is shown in figure 1.

Folic acid is nontoxic and harmless and contains carboxyl, hydroxyl and amide groups. It can form hydrogen bonds with hydroxyl groups on the surface of titanium dioxide. Thus, it can decrease the high surface energy of nanotitanium dioxide particles and the repulsion force between them and PVC molecules and improve the affinity and compatibility between them and PVC. In addition, folic acid-modified titanium dioxide can not only improve the heat resistance of PVC composites but also serve as a potential photocatalyst for the degradation of waste PVC [27]. The photodegradation of waste PVC can be promoted from the source (for
example, nano titanium dioxide is pre-doped as catalyst)\cite{28} to avoid harm to the environment caused by PAHs and dioxins produced by incineration of waste PVC.

In view of folic acid modified nano titanium dioxide and its cerium stearate, organotin and β-diketone complex has convenient source, non-toxicity and environmental protection. Its single component is widely used in industry. Therefore, understanding the mechanism of its interaction with PVC plays a guiding role in improving the long-term stability of PVC.

In the preliminary work, the synthesis, characterization and thermal behavior of folic acid-modified nano-titanium dioxide (FANT), cerium stearate and organotin doped PVC films were investigated using XRD, TG, XPS and TG-IR techniques\cite{29}. In this work, after long-term storage the stability of plasticized PVC containing FANT, cerium stearate, organotin and β-diketone was investigated by conductivity method. The similarity is that the composite stabilizer contains FANT, cerium stearate and organotin, but the difference is that β-diketone is added to the latter. Besides, the latter investigation content is the phenomenon of improved thermal stability of PVC film containing composite stabilizer after storage. FANT, cerium stearate, organotin and β-diketone compound stabilizers for PVC durability have never been reported in the literature.

The effects of pyrolysis temperature, FANT content and long-term storage on the dehydrochlorination of plasticized PVC were investigated using conductivity measurements. The results of dehydrochlorination of PVC-doped FANT, cerium stearate, organotin and β-diketone complex showed that the stability of PVC composite film was not decreased after storage, but the heat resistance was improved. In this work, the possible mechanism of long-term storage dehydrochlorination stability not decreasing, but improving under the action of composite stabilizer was investigated. On the other hand, the composite stabilizer has a significant synergistic effect on improving the heat resistance of PVC film.

2. Experimental part

2.1. Materials

\begin{table}
\centering
\caption{Composition of PVC films.}
\begin{tabular}{cccccccc}
\hline
Sample & PVC/phrs & DOTP/phrs & OT/phrs & CeSt3/phrs & FANT/phrs (wt%) & β-diketone/phrs \\
\hline
S1 & 100 & 50 & 1.0 & & & \\
C-1 & 100 & 50 & 0.5 & 5.0 & 1.0 (0.64) & 1.0 \\
C-2 & 100 & 50 & 0.5 & 5.0 & 3.0 (1.90) & 1.0 \\
C-3 & 100 & 50 & 0.5 & 5.0 & 5.0 (3.17) & 1.0 \\
\hline
\end{tabular}
\end{table}

(Note: The content of FA in FANT was 5 wt%, and S1 is the control sample).

A polyvinyl chloride resin that is consistent with the Q/NPVC01-2016 standard, namely, S-65 (mean degree of polymerization 1000-1100, apparent density 0.50–0.56 g ml\(^{-1}\)), was obtained from the Formosa Plastics Industry Co. (Ningbo, China). The plasticizer dioctyl terephthalate (DOTP), purity 99% (chroma platinum cobalt <50, acid value <0.03 mg KOH g, moisture <0.05%), was obtained from Bluesail Chemical Co. (Zibo, China). Methyl tin mercaptan (OT) was obtained from the Quzhou Jianhua Dongxu Additives Co., Ltd (Quzhou, China). For CAS: 57583-35-4, structural formula (I) contains 75% OT and structural formula (II) contains 25% OT. Cerium stearate (CeSt3) [\(\text{Ce}^{3+}\text{[}\text{C}_{17}\text{H}_{35}\text{COO}^-\text{]}\)]Ce^{3+} (purity 99%, cerium metal 11.0%, melting point 105 °C) was obtained from Luchuan Rubber and Plastic Additives Co. (Zibo, China). Analytically pure folic acid was obtained from Aladdin Biochemical Technology Co. (Shanghai, China). Nanotitanium dioxide (NT) (AEROXIDE TiO\(_2\) P25, titanium dioxide >99.6%, anatase type, medium particle size 20 nm, BET specific surface area 50m\(^2\) / g) was obtained from Degussa AG. β-Diketone (stearoyl benzoyl methane, CAS:58446-52-9, referred to as SMB)(III) purity 99.5% was obtained from Fuxinyuan Technology Co., Ltd (Wuhan, China).

2.2. Preparation of PVC films

First, the plasticizer (DOTP), stabilizer (OT), organic component (β-diketone), costabilizer (CeSt3), and reinforcing agent (FANT) were weighed in proportion, combined at 80 °C and ultrasonicated for 30 min to fully mix the materials and form a uniform calculus liquid. With a high-speed dispersion machine (FS-400) at 2800 rpm, the material temperature was raised from room temperature to 130 °C, and the fluid was stirred for 30 min. Then, the speed was reduced to 600 rpm, the temperature was decreased to 40 °C, and the fluid was stirred for 10 min and discharged. The fluid was added to a mixer (SU-70A) and mixed at 170 °C–175 °C with the screw
speed set at 40 rpm. When the torque increased and then decreased, the refinement continued for 5 min, and the PVC discharge was removed. A flat vulcanizing machine was used to compress the PVC at 100 °C to a thickness of 1.0 mm, and a PVC sheet was obtained. The composition is shown in table 1. Storage conditions of different PVC films are shown in table 2.

2.3. Preparation of the control sample for long-term storage
After sample S1 was stored indoors at 25 °C for 450 days, sample S10 was obtained to represent long-term storage.

2.4. Preparation of PVC containing FANT composite or long-term storage
After storing C-1, C-2 and C-3 indoors at 25 °C for 180 days, composite films C-10, C-20 and C-30, respectively, were obtained to represent long-term storage samples.

2.5. Dehydrochlorination test
A conductivity meter (Shanghai Sanxin Instrument Factory, model SX-731) was used to measure the conductivity of hydrogen chloride-containing aqueous solution at pyrolysis temperatures of 200 and 210 °C according to the BS EN ISO 182-3:2000 standard [30]. The PVC sample particles were exposed in the container, and the induction time and stability time of hydrogen chloride released from PVC were determined at high temperature. The stability time is determined by the length of time required for the conductivity to reach 50 μS·cm⁻¹, which indicates that the removal of hydrogen chloride is basically complete.

2.6. Conversion between conductivity and concentration of dehydrochlorination
The test of PVC thermal stability by the conductivity method requires the release of HCl by continuous heating of PVC, introduction of HCl gas into the absorption tank containing deionized water by a constant flow of N₂, and then measurement of the amount of HCl removed from PVC at each moment by measuring the conductivity change of the absorption solution. Therefore, this method can characterize the entire thermal degradation process of PVC. According to the formula of [HCl], equation (1) can be obtained from reference [31]:

Table 2. Storage conditions of different PVC films.

| Sample no | Raw material No | Temperature/°C | Time/day |
|-----------|----------------|----------------|----------|
| S10       | S1             | 25             | 450      |
| C-10      | C-1            | 25             | 180      |
| C-20      | C-2            | 25             | 180      |
| C-30      | C-3            | 25             | 180      |

(In indoor and air atmosphere).

Figure 2. SEM-EDX analysis of FANT (100 μm).
Here, \(c\) is the concentration of hydrogen chloride in \(\text{mg} \text{l}^{-1}\) and \(k\) is the measured conductivity in \(\mu \text{S cm}^{-1}\). It is known that the absorbed water volume is 60 ml and that the absorbed hydrogen chloride concentration is \(c/16.7\).

### 3. Results and discussion

#### 3.1. Composition of FANT

Figure 2 shows the SEM-EDX analysis of FANT. EDX analysis was performed at two points in the 100 \(\mu\text{m}\) SEM image of FANT NPs. As shown in table 3, the Ti content is the largest, followed by the O content, and the C content is the smallest. Since the content of TiO\(_2\) in this complex is 95%, the higher Ti and O contents and the lower C content are due to the 5% folic acid content. When the added amount of C-1 was 1.0 g, the theoretical calculated values in FA were 51.65 wt% C, 4.3 wt% H, 22.2 wt% N and 21.75 wt% O. The calculated values (in wt%) were 2.58 wt% C, 39.1 wt% O, 56.9 wt% Ti, 1.09 wt% N, and 0.22 wt% H. The mean values measured by EDX were 4.65 wt% C, 38.05 wt% O, 57.3 wt% Ti. The standard deviation (\(\sigma\)) was small (0.1–0.3), showing the credibility of the test results.

| Element | Mean Wt % | \(\sigma\) |
|---------|-----------|-----------|
| C       | 4.40      | 0.3       |
| O       | 38.7      | 0.3       |
| Ti      | 56.9      | 0.1       |

(Note: \(\sigma\) is the standard deviation).

#### 3.2. Composition of stabilized plasticized PVC film

Figure 3 shows the SEM-EDX analysis of the C-1 thin film (20 \(\mu\text{m}\)). Pure PVC resin [-CH\(_2\)-CHCl-]n theoretically contains 38.4 wt% carbon, 4.80 wt% hydrogen and 56.8 wt% chlorine, according to the feed ratio (PVC /DOTP /OT /Ce\(\text{St}_3\) /FANT /\(\beta\)-diketone = 100/50/0.5/5.0/1.0/1.0 phr). The calculated values of each element in the C-1 film were 50.5 wt% C, 36.1 wt% Cl, 5.85 wt% O, 6.57 wt% H, 0.45 wt% Ce, and 0.36 wt% Ti. The elemental analysis values from EDX were 61.9 wt% C, 33.4 wt% Cl and 4.70 wt% O. As shown in table 4, the standard deviation (\(\sigma\)) was small (0.1–0.3), showing the credibility of the test results.

| Element | Wt % | \(\sigma\) |
|---------|------|-----------|
| C       | 61.9 | 0.2       |
| Cl      | 33.4 | 0.2       |
| O       | 4.70 | 0.1       |

(Note: \(\sigma\) is the standard deviation).

\[
\log(c) = -1.05786 + 1.9882 \times \log(k) + 0.003988 \times [\log(k)]^2
\]

Here, \(c\) is the concentration of hydrogen chloride in \(\text{mg} \text{l}^{-1}\) and \(k\) is the measured conductivity in \(\mu \text{S cm}^{-1}\). It is known that the absorbed water volume is 60 ml and that the absorbed hydrogen chloride concentration is \(c/16.7\).
deviation $\sigma$ ranged from 0.1 to 0.2, indicating that the calculated values of C, Cl and O were close to the analyzed values, and the test results were relatively accurate.

3.3. Effect of long-term storage on the dehydrochlorination of S1

The rate of dehydrochlorination of PVC depends on the concentration of potential double bonds that can be generated or on the concentration of unreacted hydrogen chloride.

3.3.1. Effect of long-term storage on the dehydrochlorination concentration of S1

Figure 4 shows the conductivity and concentration curves of hydrogen chloride released by the thermal degradation of S1. Substituting conductivity into equation (1), the concentration of hydrogen chloride at different conductivities was calculated, and the concentration curve at different times was drawn. When the conductivity reached 50 $\mu$S/cm, the concentration of hydrogen chloride solution obtained was 0.257 mg l$^{-1}$.

3.3.2. Effect of long-term storage on the conductivity of S1 dehydrochlorination

Figure 5 shows the conductivity curves of dehydrochlorination of S1 and S10 at 200 $^{\circ}$C. As seen from the figure, the induction period of control sample S1 was 25.3 and 19.7 min at 200 $^{\circ}$C before and after storage, respectively. Thus, the induction period after storage was 5.6 min shorter than the period before storage, while the stability
period after storage was 7.8 min shorter than the period before storage. This result indicates that the induction period and stability time of S1 decrease after storage, which may be attributed to the degradation of organotin stabilizers in the plasticized PVC film. Due to the existence of organotin ($≡$Sn–S–R), Sn-S bonds are oxidized and hydrolyzed by oxygen free radicals in air and hydroxyl free radicals in trace water to produce $≡$Sn–O–O–Sn–R and $≡$Sn–OH + HS–R products, respectively, which leads to a decreased organotin stabilization effect. Scheme 1 shows the effect of oxygen and water in air on Organotin molecules.

At the $200^\circ$C pyrolysis temperature, the induction time and stabilization time of C-1 and C-2 are shifted to the right compared with those of C-10 and C-20. These results indicate that the additives FANT (0.64 wt% and 1.90 wt%) and CeSt$_3$, OT and $\beta$-diketone interact strongly with the PVC polar group (C-Cl bond) during storage. When the FANT content reached 3.17 wt%, the induction time and stabilization time of C-3 both shifted to the left compared with those of C-30. This result indicates that if the content of FANT continues to increase to 3.17 wt%, when the amount exceeds 1.27 wt%, the intermolecular interaction between PVC and FANT, CeSt$_3$, OT and $\beta$-

### Table 5. Induction time and stabilization time of S1 and S10 measured by standard methods at $200^\circ$C.

| Material | Induction time/min | Stability time/min | Material | Induction time/min | Stability time/min |
|----------|-------------------|--------------------|----------|-------------------|--------------------|
| S1       | 25.3              | 33.2               | S10      | 19.7              | 25.4               |

### Table 6. The induction time and stabilization time of PVC doped with FANT determined by the standard method at $200^\circ$C.

| Material/wt% | Induction time/min | Stability time/min | Material/wt% | Induction time/min | Stability time/min |
|--------------|--------------------|--------------------|--------------|--------------------|--------------------|
| C-1/0.64     | 60.7               | 70.6               | C-10/0.64    | 70.6               | 81.8               |
| C-2/1.90     | 49.9               | 67.6               | C-20/1.90    | 71.9               | 84.0               |
| C-3/3.17     | 57.2               | 68.8               | C-30/3.17    | 52.7               | 63.0               |

3.4. Effect of long-term storage on dehydrochlorination of PVC with different FANT contents

Figure 6 shows the dehydrochlorination test results of plasticized PVC-doped FANT at $200^\circ$C after long-term storage. The figure shows that both the induction time and stability time of C-1 and C-2 are shifted to the right compared with those of C-10 and C-20. These results indicate that the additives FANT (0.64 wt% and 1.90 wt%) and CeSt$_3$, OT and $\beta$-diketone interact strongly with the PVC polar group (C-Cl bond) during storage. When the FANT content reached 3.17 wt%, the induction time and stabilization time of C-3 both shifted to the left compared with those of C-30. This result indicates that if the content of FANT continues to increase to 3.17 wt%, when the amount exceeds 1.27 wt%, the intermolecular interaction between PVC and FANT, CeSt$_3$, OT and $\beta$-
Diketone is weakened, indicating that when the content of FANT exceeds 1.9 wt% to 3.17 wt%, the PVC is unstable due to the insolubility of FANT nanoparticles in the polymer.

Table 6 shows the induction time and stabilization time of PVC-doped FANT measured by standard methods at 200 °C after long-term storage. As shown in the table, when the FANT content was 0.64 wt%, the corresponding induction times for C-1 and C-10 at 200 °C were 60.7 and 70.6 min, respectively, and the corresponding stabilization times for C-1 and C-10 were 70.6 and 81.8 min, respectively. After long-term storage, the induction time and stabilization time increased by 9.9 min and 11.2 min, respectively. Similarly, when the FANT content was 1.90 wt%, the induction time and stabilization time of C-20 were 22.0 min and 16.4 min higher, respectively, than those of C-2 after storage. This result indicates that if the content of FANT increases to 1.90 wt%, the force between PVC and additive molecules is attractive (van der Waals force, hydrogen bonding and electrostatic attraction). However if the content of FANT is 3.17 wt%, after storage, C-30 shows better performance than C-3. After storage, the induction time and stabilization time decreased by 4.5 min and 5.8 min, respectively. This finding indicates that with the increase in FANT content to 3.17 wt%, the net force between PVC and additive molecules becomes repulsive, which indicates that plasticized PVC does not improve linearly with the increase in FANT content, and there is an optimal value of FANT.

FANT composite contains FANT, CeSt3O, and β-diketone. OT is the stabilizer, β-diketone is an assistant agent. In addition to FANT, the component cerium stearate has the function of adsorbing and neutralizing hydrogen chloride and capturing free radicals. Besides, cerium is a widely investigated rare earth metal due to its high tolerance, low cost and inherent Ce⁴⁺/Ce³⁺ cycling [32]. Literature reports, cerium based UIO-66 metal–organic frameworks explored as effective redox catalysts, titanium incorporation and generation of ambient oxygen vacancies [33]. The stabilizing effect of Ce atom comes from: Soft and hard acid-base (cerium element belongs to hard acid and tends to form chemical bonds with strong base atoms. A cerium atom (Ce³⁺) has strong coordination ability with unstable chlorine atom (Cl⁺) on PVC molecular chain, and a Ce³⁺ can coordinate with multiple Cl⁺, forming complex bonds to stabilize PVC molecular chain. In addition, cerium atom can also adsorb several HCl molecules, which greatly reduces the concentration of hydrogen chloride as a catalyst for PVC thermal degradation and effectively slows down the degradation of PVC molecular chain; It has electron gain and loss in the variable valence process, combines with the broken chain free radical and the lone electron of the free radical generated in the dechlorination process to eliminate the free radical, or has an addition reaction with the free radical generated by the unsaturated bond to eliminate the unsaturated bond. Or free radical substitution reaction with unstable allyl chloride to eliminate unstable factors; For ion coordination, cerium has two common oxidation values and is easy to convert to each other. It not only has strong coordination effect, but also can capture free radicals to terminate the chain reaction, so the stabilization effect is the best. Peripheral electron arrangement: after 4f⁵d⁶s² forms ions, 5d¹ and 6s² electrons in the outer layer lose, exposing unfilled 4f electron orbitals and 5D orbitals with small energy level difference, It has strong coordination ability. The exposed 4f electrons are also prone to transition and have strong coordination ability. Ce²⁺ can form a stable CeCl₆⁻ coordination compound, Ce²⁺ (and its derivatives) has a large volume, and the spatial effect is also conducive to hinder Cl⁺ to H⁺ close to reduce the probability of HCl production. In
**Figure 8.** Dehydrochlorination test of S1 at 200 °C and 210 °C.

**Table 7.** Induction time and stabilization time of S1 determined by the standard method at 200 °C and 210 °C.

| T/°C | Induction time min⁻¹ | Stabilization time min⁻¹ | T/°C | Induction time min⁻¹ | Stabilization time min⁻¹ |
|------|-----------------------|--------------------------|------|-----------------------|--------------------------|
| 200  | 25.5                  | 33.1                     | 210  | 15.5                  | 19.6                     |

**Figure 9.** Dehydrochlorination test of C-1, C-2 and C-3 at 200 °C and 210 °C.

**Table 8.** Induction time and stability time of PVC doped with FANT determined by the standard method at 200 °C and 210 °C.

| T/°C | Material/ wt% | Induction time min⁻¹ | Stabilization time min⁻¹ | T/°C | Material/ wt% | Induction time min⁻¹ | Stabilization time min⁻¹ |
|------|---------------|----------------------|--------------------------|------|---------------|----------------------|--------------------------|
| 200  | C-1/0.64      | 59.6                 | 70.6                     | 210  | C-1/0.64      | 33.2                 | 39.7                     |
|      | C-2/1.90      | 53.2                 | 67.7                     |      | C-2/1.90      | 33.0                 | 39.3                     |
|      | C-3/3.17      | 58.2                 | 68.8                     |      | C-3/3.17      | 30.5                 | 37.7                     |
addition to acids, the free radicals, $O_2$ and $O_3$ of organic compounds will lead to the degradation of polymers. Many empty orbits of rare earth ions can capture unstable free radicals and make them inactive, which is conducive to thermal stability.

After long-term storage, the possible mechanism of plasticized PVC-doped FANT, CeSt$_3$, OT and $\beta$-diketone composite is shown in figure 7. Before the reaction, the hydroxyl groups on the surface of TiO$_2$ nanoparticles form intramolecular hydrogen bonds with the amino and carboxyl groups in FA to form the FANT complex. After storage at room temperature, under the action of intermolecular forces between PVC and FANT, the C-Cl with FANT’s OH form hydrogen bonds. In addition, DOTP, CeSt$_3$, OT and $\beta$-diketone participate in the interaction with PVC, when electrons are lost in response to oxygen in the air, REDOX reaction occurs: $\text{Ce}^{3+} - e \rightarrow \text{Ce}^{4+}$. $\text{Ce}^{3+}$ and $\text{Ce}^{4+}$ both have a greater force on the C-Cl bond with PVC molecular chain, and form a relatively stable complex. If the amount of FANT reaches 3.17 wt%, the heat resistance of the PVC system decreases due to the incompatibility between FANT and PVC molecules.

3.5. Effect of different temperatures on the dehydrochlorination of S1

Figure 8 shows the dehydrochlorination test of S1 at 200°C and at 210°C. It can be observed from the figure that when the heating temperature rises from 200°C to 210°C, the induction time and stability time of S1 shift to the left. As shown in table 7, the conductivity increases from 200°C to 210°C. When the conductivity reaches 50 $\mu$S/cm, the concentration of hydrogen chloride is $257 \times 10^{-3}$ mg l$^{-1}$. The stability time of the S1 film decreased by 40.8% with the increased temperature; similarly, when no hydrogen chloride concentration was released, i.e., when the concentration was 0 mg l$^{-1}$, the induction time decreased by 39.2%.

3.6. Effect of different temperatures on the dehydrochlorination of C-1, C-2 and C-3

Figure 9 shows the dehydrochlorination test of C-1 (0.64 wt%), C-2 (1.90 wt%) and C-3 (3.17 wt%) at 200°C and 210°C. It can be observed from the figure that if the temperature increases from 200°C to 210°C, the hydrogen chloride concentration curves of C-1, C-2 and C-3 will shift to the left. As shown in table 8, if the temperature is increased by 10°C, the induction time (HCl concentration is 0 mg l$^{-1}$) and stability time (conductivity is 50 $\mu$S/cm and the concentration of hydrogen chloride is $257 \times 10^{-3}$ mg l$^{-1}$) of C-1 will be reduced to 44.3% and 43.8%, respectively, which shows that the time of removing hydrogen chloride is shortened and accelerated. Similarly, the induction time and stabilization time of C-2 decreased by 38.0% and 41.9%, respectively. Correspondingly, the induction time and stabilization time of C-3 were reduced by 47.6% and 45.2%, respectively.

3.7. Effect of FANT on dehydrochlorination

Figure 10 shows the dehydrochlorination test of C-1 and S1 at 200°C. At 200°C, the induction time and stability time of C-1 (with 0.32 wt% OT, 3.17 wt% CeSt$_3$, 0.64 wt% FANT and 0.64 wt% $\beta$-diketone) increased by 243%.
and 223%, respectively, compared with the control sample (S1). The results show that additives can improve the induction period and thermal stability of PVC, as shown in table 9.

4. Conclusion

By doping FANT, cerium stearate, organotin and β-diketone into PVC plasticized film and removing hydrogen chloride after long-term storage, the following valuable results are obtained:

1. After storage, at 200 °C the induction time and stability time decreased significantly from S1 to S10, indicating that the storage stability of single component S1 showed a downward trend at room temperature.

2. Accordingly, the induction time and stabilization time of C-1 (0.64 wt%) increased by 16.3% and 15.9% respectively, the induction and stabilization time of C-2 (1.9 wt%) increased by 44.1% and 24.3% respectively, and the induction and stabilization time of C-3 (3.17 wt%) decreased by 7.87% and 8.43% respectively. It shows that the stability of C-1 and C-2 films is significantly improved after storage. It is speculated that the system of FANT generates intermolecular hydrogen bonds with PVC, and Ce$^{3+}$ and Ce$^{4+}$ in variable valence metal cerium react with C-Cl bond on the PVC molecular chain to form complexes, so that PVC is free from the invasion of oxygen or moisture in the air. With the increase of FANT content from 0.64 wt% to 1.90 wt%, C-1 and C-2 promote the hydrogen bond and electrostatic attraction between PVC polymer molecules and additives through van der Waals force.

3. Meanwhile, the storage stability of C-3 films decreased. If the content of FANT continues to increase from 1.90 wt% to 3.17%, the electrostatic attraction of FANT, cerium stearate, organotin and β-diketone composite system to the C-Cl bond on the PVC molecular chain is offset and weakened due to the decrease of compatibility between FANT and PVC, which indicates that the content of FANT near 1.90% is best.

4. Before and after storage, the induction time (min) of hydrogen chloride removal from different films at 200 °C is as follows: C-20 (71.9) > C-10 (70.6) > C-1 (60.7) > C-3 (57.2) > C-20 (52.7) > C-2 (49.9) > S1 (25.3) > S10 (19.7). Accordingly, the induction time (min) of hydrogen chloride removal from different films at 210 °C is as follows: C-20 (34.9) > C-1 (33.0) > C-10 (32.2) > C-3 (32.0) > C-2 (31.9) > C-30 (29.0) > S1 (15.2) > S10 (11.9). The induction time reflects the ability of chain initiation. The shorter the induction period, the easier the chain initiation, and the longer the induction period, the harder the chain initiation. It can be observed that 210 °C is the critical temperature for hydrogen chloride removal by the composite film, and the induction period of hydrogen chloride removal decreases by 50%, it shows that the temperature is easy to lead to chain initiation and free radical formation.

5. Compared with the control sample S1, the induction and stability time of hydrogen chloride removal reaction of C-1 (0.64 wt% FANT) at 200 °C increased by 243% and 223% respectively. This also shows that the composite system of FANT, cerium stearate, organotin and β-diketone has a significant synergistic effect on enhancing the thermal stability of PVC.

6. The next step is to investigate the thermal life equation, non-isothermal thermal degradation kinetics such as activation energy, pre-exponential factor and mechanism function of PVC composite doped with folic acid modified nano titanium dioxide and its cerium stearate, organotin and β-diketone complex from the perspective of kinetics.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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