Effect of Oxidized Polyethylene Wax on Curing Process of Powder Coatings

Wenxue Wang, Yujue Wang, Yuying Han, Ziliang Liu, Chuanxing Wang*

College of chemical engineering, Qingdao university of science and technology, Qingdao, China

* Corresponding author e-mail:wangchxstar@163.com.

Abstract: In this paper, differential scanning calorimetry (DSC) was used to analyze the reaction kinetics of powder coatings. The effects of oxidized polyethylene wax (OPEW) on the curing process of powder coatings were investigated by exploring the curing process of OPEW-0wt% and OPEW-8wt% powder coatings. The T_g of OPEW-8wt% powder coating was 57.1 °C, which was greater than the T_g of OPEW-0wt% powder coating, indicating that OPEW increased the storage stability of the system. The apparent activation energy (E_a) of the two powder coatings was investigated by the Kissinger and Doyle-Ozawa equations. The Crane empirical equation was used to calculate the curing reaction order (n) of the two powder coatings, and the curing kinetics was discussed. The E_a of OPEW-0wt% was 64.35 kJ·mol^{-1}, and the E_a of OPEW-8wt% was 60.95 kJ·mol^{-1}, indicating that OPEW could promote the curing reaction.

1. Introduction

The curing process of powder coatings can be divided into three stages, melting, flowing and curing crosslinking [1,2]. The degree of curing crosslinking in production depends on the curing time and curing temperature. Therefore, the performance of the film depends largely on the curing temperature and time [3,4]. DSC technology, with the small amount of sample and the high accuracy of measurement, is widely used in the study of the kinetics of chemical reactions [5].

Although polyester/TGIC powder coatings have a series of advantages, there are still deficiencies, the pigments and fillers are not easily dispersed in the resin system. Therefore, OPEX can be added to improve the dispersibility of pigment and filler. OPEW has the advantages of low viscosity, high softening point and good hardness, and excellent dispersibility for fillers and pigments [6,7]. Therefore, this paper uses Differential Scanning Calorimetry to explore the effect of OPEW on the curing process of powder coatings.
2. Experimental section

2.1 Reagents and Instruments

Electrostatic sprayer (HY-301, Tianjin Hanze in coating product manufacturer), Vacuum drying oven (DZF-6050, a Shanghai constant scientific instrument co., LTD.), Differential scanning calorimeter (204 F1, Germany NETZSCH companies), Polyester powder coating (OPEW-0wt% OPEW-8wt%, Self-synthesized).

2.2 Curing Kinetics and Characterization

The curing reaction rate of the polyester resin system was determined by the apparent activation energy (Ea) of the curing reaction. The apparent Ea could directly determine the degree of difficulty in curing reaction [8,9]. The apparent Ea and the curing reaction order (n) of the polyester resin curing reaction were generally measured by DSC curves at different heating rates [10]. The DSC analysis instrument is the 204 F1 Differential Scanning Calorimeter of NETZSCH Company in Germany. The heating rates of the samples were 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively. The temperature range was 25-300 °C in N2 atmosphere.

3. Results and discussion

3.1 Effect of OPEW on the Curing Process of Powder Coatings

![DSC curve of powder coating](image)

**Figure 1.** DSC curves of powder coating

| Basic feature | OPEW-0wt% | OPEW-8wt% |
|--------------|-----------|-----------|
| Glass transition temperature ($T_g$) /°C | 54.4 | 57.1 |

*Fig. 1 was the DSC curve of OPEW-0wt% and OPEW-8wt% powder coatings. Both powder coatings had significant endothermic transitions as can be seen in Fig. 1, where the temperature of 54.4 °C and 57.1 °C, respectively was the glass transition temperature ($T_g$) of the powder coating. It could be seen that OPEW improved the $T_g$ of powder coatings and increased the storage stability of powder coatings. When the temperature was further increased, the OPEW-8wt% powder coating exhibited a distinct endothermic peak due to the melting of OPEW in the powder coating. The temperature continued to rise and an exothermic peak appeared in both curves, indicating that the powder coating began to solidify at this temperature.*
3.2 Curing Kinetic Parameters of OPEW-0wt% Powder Coating

![Figure 2. Non-isothermal DSC curve of OPEW-0wt% powder coating](image)

It could be seen from Fig. 2 that the curing temperature of the system varied with the heating rates. When the heating rate increased from 5 °C/min to 20 °C/min, peak temperature, termination temperature and exothermic peak position of the OPEW-0wt% powder coating system were shifted to the high temperature direction. At the peak position, the heat flow rate was the highest, and the curing reaction rate was the fastest here. As the heating rate increased, dH/dt (thermal efficiency per unit time) increased, so the thermal inertia became larger and the temperature difference generated was larger.

3.2.1 Curing Temperature

The determination of the curing process parameters generally used the T-β extrapolation method. It could be seen from Fig. 2 that the DSC curves of different heating rates had exothermic peaks at different temperatures. In actual production, it was usually cured at a constant temperature. Therefore, the extrapolation was used to obtain the temperature at β = 0, and then got the best curing temperature range.

Table 2. Curing reaction characteristics of OPEW-0wt% powder coatings at different heating rates

| Powder coating | Heating rate °C/min | Melting point/°C | T₀/°C | Tₚ/°C | Tᵣ/°C | ΔH J/g |
|----------------|---------------------|-----------------|-------|-------|-------|--------|
| OPEW-0wt%      | 5                   | 55              | 123.9 | 146   | 190.7 | 18.33  |
|                | 10                  | 58              | 126.7 | 157   | 206.9 | 18     |
|                | 15                  | 59.5            | 135.1 | 169   | 216.8 | 17.93  |
|                | 20                  | 61.5            | 143.4 | 177   | 226.2 | 18.71  |

Table 2 was curing reaction characteristics of OPEW-0wt% powder coatings at different heating rates. According to the data in Table 2, Taking T (starting temperature T₀, peak temperature Tₚ, and termination temperature Tᵣ) plotted against β, and linearly fit it. By linear fitting, T₀ was 115.5 °C, Tₚ was 136 °C, and Tᵣ was 181.05 °C. They reflect the curing characteristics of the system. The actual curing process factors were very complicated, so the T₀ and Tₚ obtained by fitting could not be directly used for the actual production curing temperature. Generally, the curing temperature at the time of production was higher than the theoretical temperature to increase the curing efficiency and reduce the curing time.
3.2.2 $E_a$ and $n$

Table 3. Curing kinetics parameters of OPEW-0wt% powder coating

| $\beta$/K·min$^{-1}$ | $T_p$/K | $\ln(\beta/T_p^2)$ | $\ln\beta$ | $(1/T_p)\times10^3$/K$^{-1}$ |
|---------------------|---------|----------------|-----------|-----------------------------|
| 5                   | 419.15  | -10.46701979   | 1.609437912 | 2.385780747                |
| 10                  | 430.15  | -9.825682877   | 2.302585093 | 2.324770429                |
| 15                  | 442.15  | -9.475248181   | 2.708050201 | 2.261675902                |
| 20                  | 450.15  | -9.223429448   | 2.995732274 | 2.221481728                |

Note: $\beta$: heating rate, $T_p$: Peak temperature.

Kinetic parameters are usually determined by the DSC curve data using the Kissinger differential equation and the Doyle-Ozawa equation. Their mechanism is to regard the top of the exothermic peak of the DSC curves as the maximum rate at which the curing reaction occurs, assuming that the number of reaction stages $n$ does not change during the reaction.

Kissinger Differential equation:

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = \frac{E_a}{R}$$  \hspace{1cm} (1)

Doyle-Ozawa equation:

$$\frac{d[\ln\beta]}{d(1/T_p)} = -1.052 \frac{E_a}{R}$$  \hspace{1cm} (2)

$\beta=\frac{dT}{dt}$: heating rate, K·min$^{-1}$, $T_p$: peak temperature, °C. $E_a$: apparent activation energy, kJ·mol$^{-1}$. $R$: molar gas constant, 8.314, J·mol$^{-1}$·K$^{-1}$.

Based on the test data of the non-isothermal DSC in Table 3, $-\ln(\beta/T_p^2)$ and $\ln\beta$ were plotted against $1/T_p$, respectively, and the results were shown in Fig. 4. $\ln(\beta/T_p^2)$ and $1/T_p$ equation: $y=7.235-7.3893x$, $\ln\beta$ and $1/T_p$ equation: $y=21.928-8.5109x$. $E_a$ was 64.35 kJ·mol$^{-1}$ by calculation.

Figure 4. Line fitting of $\ln(\beta/T_p^2)$ - $1/T_p$ with $\ln\beta$ - $1/T_p$
The curing reaction series $n$ was calculated by the Crane empirical equation. The Crane equation is as follows:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{(E_a/nR)}{Tp}$$

When $\frac{E_a}{nR} >> 2T_p$, the formula (3) could be reduced to:

$$\frac{d(\ln \beta)}{d(1/T_p)} = \frac{E_a}{nR}$$

The curing reaction series $n$ (0.929) could be obtained by linear regression with $-\ln \beta$ plotting $1/T_p$.

3.3 Curing Kinetic Parameters of OPEW-8wt% Powder Coating

3.3.1 Curing Temperature

According to the data in Table 4, $T_p$ (peak temperature $T_p$, and termination temperature $T_f$) were plotted against $\beta$, and linearly fit it. By linear fitting, $T_p$ was 134.75 °C, and $T_f$ was 190.9 °C.

Table 4. Curing reaction characteristics of OPEW-8wt% powder coatings at different heating rates

| Powder coating | Heating rate °C/min | Melting point/°C | $T_p$/°C | $T_f$/°C | $\Delta H$ J/g |
|----------------|----------------------|------------------|----------|----------|--------------|
| OPEW-8wt%      | 5                    | 54.9             | 145      | 199.8    | 21.12        |
|                | 10                   | 57.1             | 158      | 210.9    | 24.29        |
|                | 15                   | 58.6             | 164.1    | 220.4    | 24.74        |
|                | 20                   | 60.7             | 178.5    | 228.7    | 23.62        |

![Figure 5. Linear fitting of $T_p$ and $T_f$ to temperature rise rate](image)

3.3.2 $E_a$ and $n$

Table 5. Curing kinetics parameters of OPEW-8wt% powder coating

| $\beta$/K min$^{-1}$ | $T_p$/K | $\ln(\beta/T_p^2)$ | $\ln \beta$ | $(1/T_p) \times 10^3$/K$^{-1}$ |
|----------------------|---------|-------------------|-------------|-----------------------------|
| 5                    | 418.15  | -10.46224253      | 1.609437912 | 2.391486309                 |
| 10                   | 431.15  | -9.830327022      | 2.302585093 | 2.319378407                 |
| 15                   | 437.25  | -9.452960027      | 2.708050201 | 2.287021155                 |
| 20                   | 451.65  | -9.230082814      | 2.995732274 | 2.214103841                 |

Based on the test data of the non-isothermal DSC in Table 3, $-\ln(\beta/T_p^2)$ and $\ln \beta$ were plotted against $1/T_p$, respectively, and the results were shown in Fig. 6. $\ln(\beta/T_p^2)$ and $1/T_p$ equation: $y=6.591-7.0930x$, $\ln \beta$ and $1/T_p$ equation: $y=20.7404-7.9620x$. $E_a$ was 60.95 kJ·mol$^{-1}$ by calculation.
The calculation formula is the same as in section 3.2.2. The curing reaction series n (0.92) could be obtained by linear regression with \(-\text{Ln}\beta\) plotting \(1/T_p\).

### 3.4 Effect of OPEW on Curing Kinetic Parameters of Powder Coatings

| samples          | Ea/kJ·mol\(^{-1}\) | Order of reaction n | \(T_p/°C\) | \(T_g/°C\) |
|------------------|---------------------|---------------------|-------------|------------|
| OPEW-0wt%        | 64.35               | 0.92                | 136         | 54.4       |
| OPEW-8wt%        | 60.95               | 0.92                | 134.75      | 57.1       |

It could be seen from Table 6 that after the addition of OPEW, the curing temperature of the powder coating was reduced from 136 °C to 134.75 °C, indicating that OPEW decreased the relevant temperature of the curing process. \(E_a\) refers to the energy required for a molecule to change from a normal state to an active state in which a chemical reaction is likely to occur, directly determining the degree of difficulty in curing reaction. The lower the \(E_a\) of the reaction, the greater the rate of curing reaction. The \(E_a\) of OPEW-0wt% was 64.35 kJ·mol\(^{-1}\), and the \(E_a\) of OPEW-8wt% was 60.95 kJ·mol\(^{-1}\), indicating that OPEW could promote the curing reaction. The \(T_g\) of OPEW-8wt% powder coating was 57.1 °C, which was greater than the \(T_g\) of OPEW-0wt% powder coating, indicating that OPEW increased the storage stability of the system. Since the \(T_g\) of the sample coating film was larger than the storage temperature (25 °C), the segment activity of the polymer was limited, and there was no segment-level or molecular-level diffusion between the different particles, and the system had good chemical stability.

### 4. Conclusions

In this paper, differential scanning calorimetry was used to analyze the reaction kinetics of powder coatings. The \(T_g\) of OPEW-8wt% powder coating was 57.1 °C, which was greater than the \(T_g\) of OPEW-0wt% powder coating, indicating that OPEW increased the storage stability of the system. The \(E_a\) of the two powder coatings was investigated by the Kissinger and Doyle-Ozawa equations. The Crane empirical equation was used to calculate the curing n of the two powder coatings, and the curing kinetics was discussed. The \(E_a\) of OPEW-0wt% was 64.35 kJ·mol\(^{-1}\), and the \(E_a\) of OPEW-8wt% was 60.95 kJ·mol\(^{-1}\), indicating that OPEW could promote the curing reaction. The n of the sample was 0.92, and the n was not an integer, indicating that the curing process was a complex physical and chemical reaction.
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