Curing of polyester powder coating modified with rutile nano-sized titanium dioxide studied by DSC and real-time FT-IR

Qiwu Shi · Wanxia Huang · Yubo Zhang · Yang Zhang · Yuanjie Xu · Gang Guo

Abstract Polyester powder coating modified with 2 mass% of rutile nano-sized titanium dioxide (nano-TiO$_2$) was prepared by melt-blend extrusion method. The nano-TiO$_2$ dispersion state in the powder coating matrix was analyzed by field emission scanning electron microscopy (FE-SEM), which presented a well dispersion of modified nano-TiO$_2$ in the polyester powder coating. The effect of nano-TiO$_2$ on the curing of polyester powder coating was investigated by differential scanning calorimeter (DSC). Kissinger and Crane methods were used to study the activation energy (E) and reaction order (n) of the coating. The results indicated that 2 mass% of nano-TiO$_2$ additive played a prompting role in the curing of polyester powder coatings, due to the hydroxyl functional groups existed on the surface of nano-TiO$_2$. Furthermore, real-time Fourier transform infrared (FT-IR) spectroscopy with a heating cell was also employed to record the curing actions, of which results were consistent with the DSC experiments.

Keywords Polyester powder coating · Rutile nano-sized titanium dioxide · Curing · DSC · Real-time FT-IR

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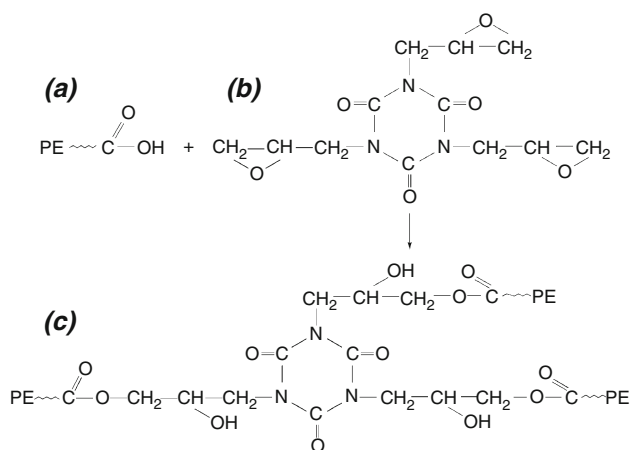
Introduction

Powder coatings are widely used in household appliances, automobiles, office accommodations, steels and architecture fields, due to their excellent advantages such as no volatile organic content, energy savings and high utilization rates. As a solid powder environmental-friendly coating, powder coatings have attracted many ongoing researches. Powder coatings attain their maximum properties through a curing reaction involving melting, flow and cure completion [1, 2]. In general polyester powder coating is a physical blend of lightly branched carboxyl-terminated polyester and triglycidyl isocyanurate (TGIC) and the curing take place through the reaction between hydroxyl of COOH and epoxy groups, which could be schematically explained by Fig. 1. The curing process determines physical and chemical properties of coating films, such as hardness, adhesion, gloss, chemical resistance, weather resistance, and so on [3, 4]. In order to investigate the curing dynamics of powder coatings, DSC is used as the common methods to obtain the kinetics of curing actions [5–8]. Furthermore, a novel and powerful FT-IR spectroscopy equipped with a heating cell has been used to simultaneously investigate the correlation between the thermal behaviors and the structure changes of polymer composites, such as epoxy resin, asphalt, acrylic/methacrylic sacrificial copolymers and cumene hydroperoxide [9–13]. It is also a potential method to study the thermal properties of powder coatings.

With the progress of technology and market demand, powder coatings are demanded for excellent properties of coating films, which promotes new methods including synthesis and modification of based resin, selection of curing system and curing agent and introduction of suitable functional additives [14–17]. The introduction of functional additives could affect many physical and chemical

Fig. 1 Schematic representation for the curing reaction of polyester powder coating between carboxyl-terminated polyester and TGIC. Chemical structures of (*a*) carboxyl-terminated polyester, (*b*) TGIC, (*c*) product of the reaction

properties of the coating films effectively through simple process. Wherein, rutile nano-TiO_2 is a new and effective additive for the anti-ageing function [18, 19]. But the effects of nano-TiO_2 on the curing properties of powder coating have not been revealed in articles.

In this work, polyester powder coating and the sample modified with 2 mass% of rutile nano-TiO_2 were prepared by melt-blend extrusion method. To investigate the curing properties of samples, non-isothermal dynamic DSC and real-time FT-IR with a heating cell were both used to observe curing action of the samples. The effect of nano-TiO_2 on the curing properties of polyester powder coatings was discussed. We found that 2 mass% amount of nano-TiO_2 addition played a prompting role in the curing of polyester powder coatings. But the nano-TiO_2 did not affect curing reaction order of powder coating.

Experimental

Materials

Saturate polyester resin and triglycidyl isocyanurate (TGIC) were directly purchased from the Cytec Surface Specialties Inc., and the polyester resin has a curing temperature of 190 °C. Rutile nano-TiO_2 was purchased from Panzhihua Iron & Steel Research Institute in China, with grain size range from 30–50 nm. Aluminate coupling agent was purchased from Chongqing Jiashitai Chemical Co., China.

The nano-TiO_2 particles were modified with aluminate coupling agent according to a dry coating method [20] as described below: the nano-TiO_2 particles were put into a high-speed mixer (Dachen Machinery Manufacturing Co.

China, SHR-10A) with a rotate speed of 2000 rpm, and subjected to high impaction and dispersion due to collisions with stirring blade at 130 °C. 1.5 mass% of aluminate coupling agent was then added into the powder and stirring for 20 min. The resulting mixtures were centrifuged and washed with fresh ethanol to remove unattached coupling agent. Finally, the modified particles were dried at 60 °C for 2 h.

Preparation of polyester powder coatings modified with nano-TiO_2

The powder coatings studied were prepared according to the following process: polyester and TGIC were blended physically with a mass proportion of 93/7, and then rutile nano-TiO_2 was added to modification system. Details of coatings composition were given in Table 1. The system was well-mixed by a high speed premixer with a mixing speed of 2000 rpm, and then melted and extruded in a twin screw extruder. The extrudate was milled and sieved into particle size of less than 100 μm for application.

FT-IR spectroscopy measurements

The surface functional groups of nano-TiO_2 were analyzed by FT-IR spectrometer (Bruker, Tensor 27) to estimate the modification effect. The resolution of detection was set as 4 cm^{-1}. For each sample, the compact sheet of nano-TiO_2/potassium bromide powder mixture (1:100 in mass) was acquired under an oven temperature of 110 °C for 5 min.

The curing actions were recorded by FT-IR spectrometer in real-time using a High Temperature Cell (Harrick Scientific, HTC-3). The temperature was controlled by an Automatic Temperature Controller (Harrick Scientific, ATC-001). Coating powders were dissolved in acetone and then spread on KBr plates, which were then placed in the HTC-3. Dynamic curing was carried out at a rate of 5 °C min^{-1}, from room temperature to 210 °C. The FT-IR spectroscopy was scanned repeatedly.

FE-SEM measurements

Dispersion of nano-TiO_2 in powder coatings were analyzed by FE-SEM (FEI, Inspect F). The testing sheets with 3 mm

Table 1 Composition of powder coatings

Ingredient	Polyester resin/mass%	TGIC/mass%	Rutile nano-TiO_2/mass%
Original system (P0)	93	7	0
Nano-TiO_2 modified system (MP)	91.14	6.86	2

depth were prepared by curing powder coatings in a PTFE mould at 180 °C for 15 min, and undergoing brittle fracture in liquid nitrogen atmosphere. Gold sputter coated fracture sections were then examined with an accelerating voltage of 20 kV. The magnifying power was 40,000×.

DSC measurements

The curing properties were investigated by DSC (SETA-RAM Instruments, DSC 131). About 10 mg of the powder samples were placed in aluminum DSC pans, and dynamic experiments were carried out at rates of 5, 10, 15, 20, and 25 °C min^{-1}, respectively, from room temperature to 260 °C under nitrogen flowing at 10 ml min^{-1}. Based on the results obtained from the DSC scans, starting and peak points on the exothermic regimes were selected for further calculations. The theoretical curing temperatures were obtained by T-β extrapolation method.

To evaluate possible effects of the nano-TiO$_2$ on the curing properties of the polyester powder coatings, the Kissinger's method [21] and Crane's method [22] were performed to calculate kinetic parameters of the curing reaction: activation energy (E) and reaction order (n). Wherein, the E value is applied to represent the difficult degree of curing reaction, and the n value to represent the complexity.

The Kissinger's equation could be expressed in Eq. 1, and the Crane's equation in Eqs. 2 and 3:

$$-\ln\left(\beta/T_P^2\right) = E/RT_P - \ln(AR/E) \quad (1)$$

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}\left(1/T_p\right)} = -\left(\frac{E}{nR} + 2T_p\right) \quad (2)$$

when $E/nR \gg 2T_p$, the Eq. 2 could be approximately simplified as Eq. 3,

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}\left(1/T_p\right)} = -\frac{E}{nR} \quad (3)$$

Where T_p, β, R, A are the exothermic peak temperature, the heating rate, the gas constant, and the impact frequency factor, respectively.

Results and discussion

FT-IR characterization of nano-TiO$_2$

The surface modification with coupling agent could form an organic film covering the nano-TiO$_2$ particle, and transform the initial hydrophilic character to a lipophilic character. In order to elucidate the surface modification effects of nano-TiO$_2$, the analytic results were carried out by FT-IR in Fig. 2. Comparing the FT-IR spectra of unmodified with modified samples, absorbance peaks of −CH$_3$− and −CH$_2$− groups emerge at 2960.5 and 2871.9 cm^{-1}, which are resulted from successful linking of some organic materials to nano-TiO$_2$. Furthermore, the absorbance peaks at 3426.9 and 1626.7 cm^{-1} denote stretching vibration and bending vibration bands of hydroxyl group, respectively. The two hydroxyl characteristic peaks are strengthened largely after modification, indicating that the surface modified nano-TiO$_2$ had greater surface activity.

FE-SEM morphology

In Fig. 3, the dispersion states of nano-TiO$_2$ in the powder coating matrix are shown. As can be seen, the dispersion of modified nano-TiO$_2$ in the polyester powder coating film has been improved largely. Due to the surface effect of nano-sized particle, the unmodified nano-TiO$_2$ particles form aggregation seriously in powder coating system, as can be seen in Fig. 3a. But the nano-TiO$_2$ particles are more dispersed after surface treating with aluminate coupling agent (Fig. 3b). The average size of modified nano-TiO$_2$ particles is reduced from ∼350 to ∼100 nm. Because of the higher specific surface area of nano-particles, they have more contact area with the resin matrix, which will result in the property improvement of the nano-TiO$_2$ modified polyester powder coatings.

Curing temperature of nano-TiO$_2$ modified powder coating detected by DSC

The dynamic experiments were carried out at five different heating rates. Fig. 4a and b show the DSC spectra of the
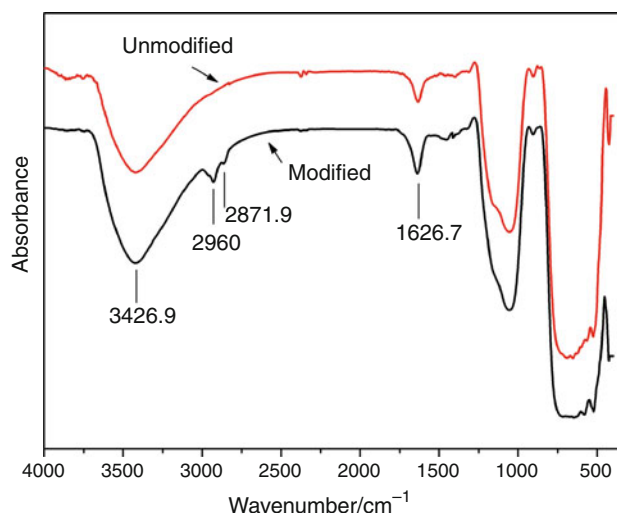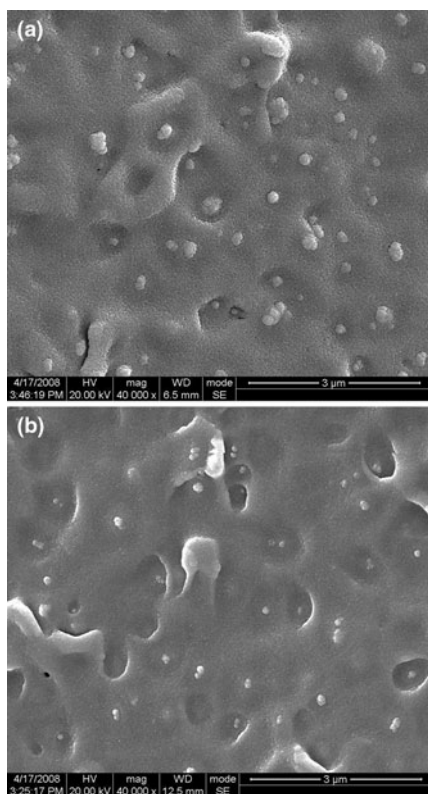

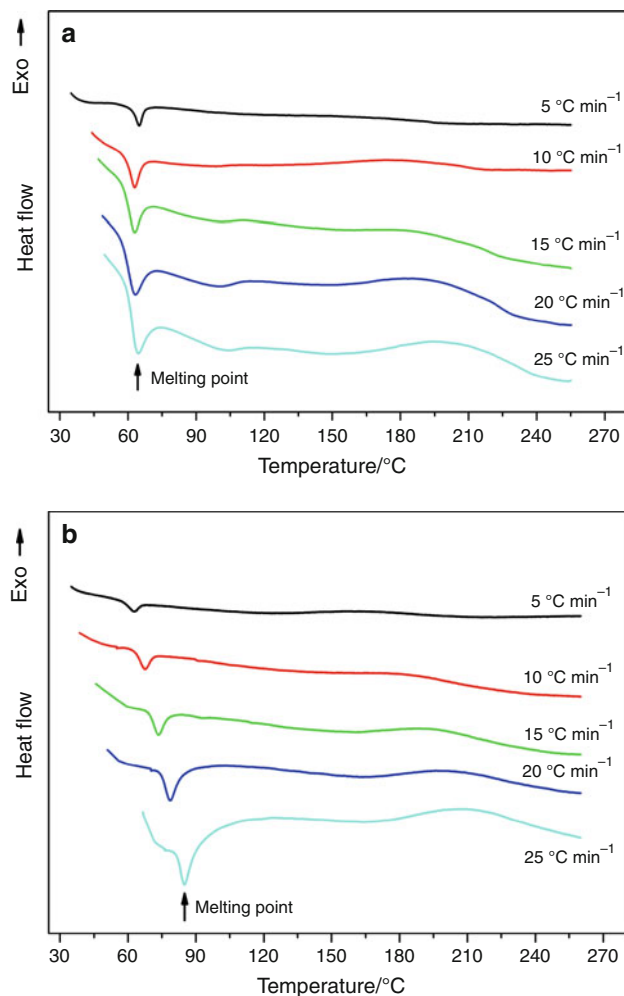**Fig. 2** FT-IR spectrum of unmodified and modified nano-TiO$_2$

Fig. 3 FE-SEM morphology of cross section for **a** original and **b** nano-TiO$_2$ modified polyester powder coating samples

Fig. 4 Non-isothermal DSC spectra of **a** original and **b** nano-TiO$_2$ modified polyester powder coating samples with 5, 10, 15, 20, and 25 °C min^{-1} heating rates

original powder coating samples and the samples modified with nano-TiO$_2$, respectively. From Fig. 4a, an endothermic transition from 50 to 70 °C appears before the exothermic curing process, which is associated with the melting point. On further heating, an evident exothermic occurred at temperatures from 130 to 260 °C.

As can be seen in the Fig. 4b, the addition of nano-TiO$_2$ makes a delay of the melting point. The phenomenon appears more obviously at higher heating rates. Normally the melting point is a thermodynamic phenomenon, not a kinetic phenomenon, so the melting point should not be varied with the heating rate, which would be conflict with our presented result. We conclude the reason that the well dispersion of nano-TiO$_2$ in the powder coating has favored the formation of a nanocomposite system, in which the inorganic nano-TiO$_2$ phase has a function of blocking in the melting process of organic resin phase.

Furthermore, the curing processes of both systems are accompanied by an evident single exothermic peak. It indicates that the curing processes are mainly dependent on the reaction of resin and curing agent. At a higher heating rate, the exothermic peak of curing reaction will shift to higher temperature region, of which reason is that

thermal effect accumulates greater at a higher heating rate.

The characteristic points of the exothermic curing peak of the original and the nano-TiO$_2$ modified polyester powder coating samples at different heating rates are listed in Table 2.

According to Table 2, the temperatures of curing peaks dependent on heating rates are figured in Fig. 5. And then, the starting (T_o) and peak (T_p) temperatures of the curing reaction could be deduced by extrapolating the heating rate to be zero. We observed that T_o and T_p of the curing reaction of the original polyester powder coating sample were 135.48 and 165.97 °C versus 125.88 and 158.89 °C of the nano-TiO$_2$ modified sample. The result shows that the T_o and T_p temperatures of the nano-TiO$_2$ modified system are decreased by 9.60 and 7.08 °C, respectively. It

Table 2 Starting (T_o) and peak (T_p) temperatures of the curing reaction of the polyester powder coating samples at different heating rates

β/°C min^{-1}	P0		MP	
	T_o/°C	T_p/°C	T_o/°C	T_p/°C
5	140.18	172.9	135.01	168.22
10	146.79	179.92	148.49	180.69
15	152.81	188.19	161.65	193.01
20	157.73	194.49	171.17	201.77
25	162.11	201.24	178.95	211.14
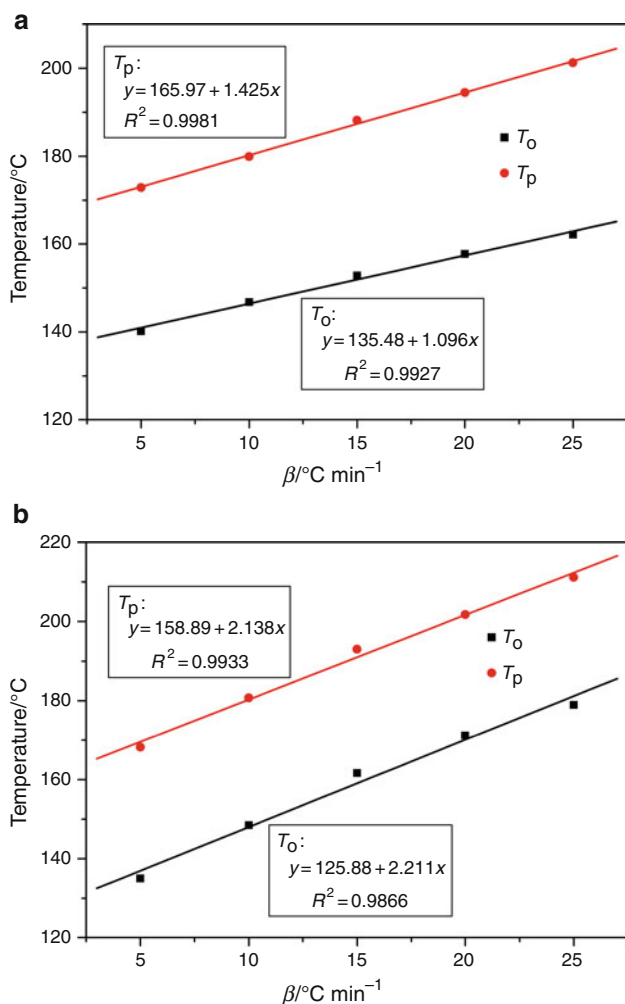
Fig. 5 Starting (T_o) and peak (T_p) temperatures of curing peaks dependent on heating rates for **a** original and **b** nano-TiO$_2$ modified polyester powder coating samples

implies that the curing reaction of the modified system happens earlier, so the modified system could be cured at a lower temperature.

Curing kinetics of nano-TiO$_2$ modified powder coating studied with DSC

In this study, the cure kinetics of the original and nano-TiO$_2$ modified polyester powder coatings were investigated by non-isothermal DSC. The experimental DSC data are displayed in Table 3.

According to the Kissinger's Eq. 1, the E value of curing reaction could be obtained by plotting $-\ln(\beta/T_p^2)$ versus $1/T_p$ (Fig. 6). The two group plots in Fig. 5 were linearly fitted. We deduced slopes of the two curves, which were used to calculate E value of both systems. And then, the n value could be calculated by plotting $\ln \beta$ versus $1/T_p$ (Fig. 7) according to the Crane's equation (3). The results are listed in Table 4.

Table 4 shows that E value of nano-TiO$_2$ modified system is less than the original system largely, which demonstrates that the addition of 2 mass% of nano-TiO$_2$ has a promoting effect on the curing reaction of polyester powder coatings. As mentioned in FT-IR test, the hydroxyl functional groups were found to exist on the surface of nano-TiO$_2$, which may be the reason for a promoting effect on the curing reaction [23]. Furthermore, the modification had a positive influence not only on improving the dispersion of nano-TiO$_2$ in powder coatings, but also on strengthening the hydroxyl functional groups. So, the nano-TiO$_2$ could play the promoting role more greatly. Meanwhile, the reaction orders of both systems are around 0.9, which are less than 1.0. It indicates that the addition of nano-TiO$_2$ does not affect the curing reaction order of polyester powder coatings.

FT-IR spectroscopy analysis of the curing reaction in real-time

In order to illustrate the curing reaction of the original and nano-TiO$_2$ modified polyester powder coatings, the FT-IR spectroscopy was performed in real-time, by monitoring the absorption of specific peaks around 908 and 843 cm^{-1}. These two peaks represent the C–O–C bond typical of the epoxide ring, which are associated with the curing reaction of polyester resin as demonstrated in Fig. 1. With the curing reaction, magnitude of the peaks would decrease gradually. Figure 8 shows FT-IR spectrum at seven different temperatures from 130 to 205 °C, the absorbance peaks around 908 and 843 cm^{-1} of the two systems are both weakened obviously with the temperature increased. It can be related to the ring-opening of epoxy groups induced by the reaction between hydroxyl of COOH and epoxy groups during the curing reaction. Nevertheless, it is clear that the nano-TiO$_2$ modified system shows larger decreasing amplitude of the two peaks in the temperature range from 130 to 205 °C, indicating a faster reaction rate.

Table 3 Characteristic data of the exothermic curing peaks of the polyester powder coating samples at different heating rates

Samples	$\beta/K\ min^{-1}$	$1/T_p/K^{-1}$	$\ln \beta/K\ min^{-1}$	$-\ln(\beta/T_p^2)/K^{-1}\ min^{-1}$
P0	5	2.242×10^{-3}	1.609	10.59
	10	2.207×10^{-3}	2.303	9.93
	15	2.168×10^{-3}	2.708	9.56
	20	2.138×10^{-3}	2.996	9.30
	25	2.108×10^{-3}	3.219	9.11
MP	5	2.286×10^{-3}	1.609	10.55
	10	2.203×10^{-3}	2.303	9.93
	15	2.145×10^{-3}	2.708	9.58
	20	2.106×10^{-3}	2.996	9.33
	25	2.065×10^{-3}	3.219	9.15
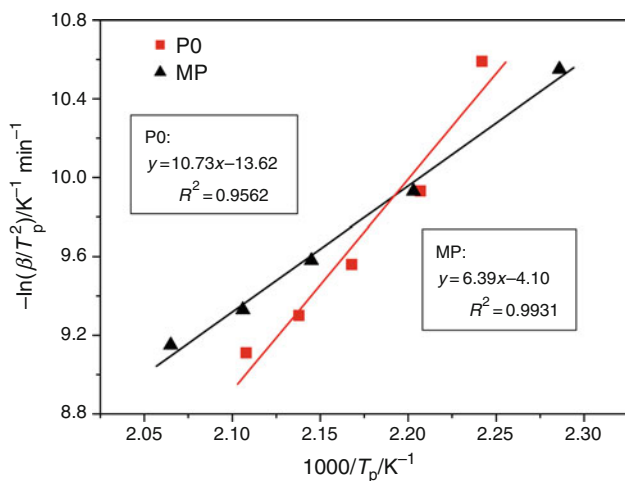
Fig. 6 The $-\ln(\beta/T_p^2)$ versus $1/T_p$ curves according to Kissinger's method
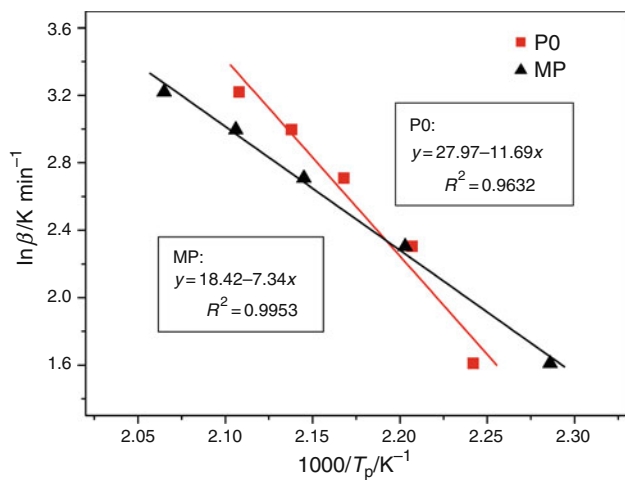
Fig. 7 The $\ln \beta$ versus $1/T_p$ curves according to Crane's method

It may be attributed to the promoting effect of nano-TiO$_2$ on the curing reaction of polyester powder coatings. The results are consistent with the above DSC experiments.

Table 4 E and n values of the curing reaction of original and nano-TiO$_2$ modified polyester powder coating samples

	Activation energy $(E)/KJ\ mol^{-1}$	Reaction order (n)
P0	89.24	0.9181
MP	53.13	0.8710
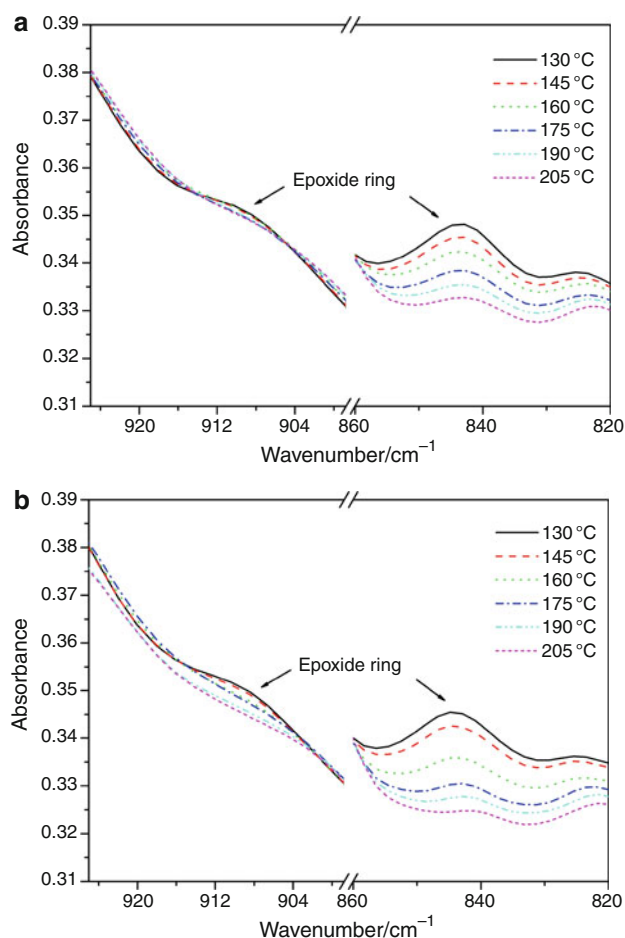
Fig. 8 FI-IR spectroscopy of curing reaction of **a** original and **b** nano-TiO$_2$ modified polyester powder coating samples at seven different temperatures, with 5 °C min^{-1} heating rate

Conclusions

In this study, polyester powder coating was modified by 2 mass% of nano-TiO$_2$. According to FT-IR and FE-SEM, the hydrophobicity of nano-TiO$_2$ modified by F-1 was enhanced, which benefited their dispersion in powder coating.

From a series dynamic DSC experiments carried out at five different heating rates, the effect of nano-TiO$_2$ on the curing of polyester powder coating was investigated. The results revealed that, the addition of nano-TiO$_2$ made a delay of the melting point, and then the starting and peak temperatures of curing reaction of the nano-TiO$_2$ modified system were decreased by 9.60 and 7.08 °C, respectively, which were deduced by extrapolating the heating rate to be zero. Furthermore, the cure kinetic parameters of the original and nano-TiO$_2$-modified polyester powder coatings were calculated according to the Kissinger's method and Crane's method. The activation energy (E) and the reaction order (n) demonstrated that 2 mass% amount of nano-TiO$_2$ addition played a prompting role in the curing of polyester powder coatings. And nano-TiO$_2$ did not affect curing reaction order of powder coating. FT-IR spectroscopy analysis results of the curing reaction in real-time were consistent with the DSC experiments.

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