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Improve surface levelling of powder coating with semi-crystalline polyester resin

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ABSTRACT

The levelling performance of polyester powder coating is not as well as liquid coating due to its matrix polyester resin. 1,6-hexanediol (HDO), neopentyl glycol (NPG), terephthalic acid (PTA), isophthalic acid (IPA) were used to synthesize semi-crystalline polyester resin (HDO, PTA and IPA) and amorphous polyester resin (NPG, PTA and IPA). The semi-crystalline polyester resin was introduced to powder coating for further use. The structure of semi-crystalline polyester resin was characterized by 1H-nuclear magnetic resonance (1H NMR) and X-ray powder diffraction (XRD). The viscosity of the polyester resins were investigated by cone-and-plate viscometer (CPV). The reactivity of the coatings was characterized by differential scanning calorimetry (DSC). The levelling performance was studied by flow, cone-and-plate viscometer (CPV), atomic force microscope (AFM) and scanning electron microscope (SEM). The results showed that the semi-crystalline polyester powder coating had higher reactivity and better levelling performance than that of amorphous polyester powder coating.

1. Introduction

Powder coatings have the advantages of no solvent emission, which represents one of the trends in the coating market [1,2]. There are four systems of powder coatings: polyester/TGIC (Triglycidyl Isocyanurate), polyester/HAA (β-hydroxy alkylamide), polyester/Isocyanate and polyester/Hybrid. The systems based on carboxyl-terminated polyester crosslinked by TGIC, HAA and Isocyanate show good durability and adequate mechanical property as well as other properties, which mainly for outdoor use. Conversely, the system based on carboxyl-terminated polyester crosslinked by epoxy resin shows excellent levelling performance and decorative performance, which mainly for indoor use.

Thermoset powder coatings are mainly made up of reactive polyester resin, curing agent, fillers and pigments. Among all of the raw materials, the polyester resin and curing agent determine the properties of the powder coating and the film. Particularly, the levelling performance of the coating are affected by the viscosity of the polyester resin and curing reactivity [3]. As showed in Fig. 1, the film forming behavior during curing process can be divided into three stages [4]. Firstly, the viscosity of coating increases when the powders start to melt. Secondly, the powder coating starts to flow and the viscosity decreases. Thirdly, the viscosity increases rapidly when the powder coating crosslink together. According to the curing mechanism of powder coating, the levelling performance of the film is determined by the rheological behavior in the second and third stage.

Linear molecular chain help to reduce viscosity and improve levelling performance [5], however, linear structure will reduce Tg, which is bad for storage stability. Meanwhile, lower reactivity also help to improve levelling performance [6], and what is worse, the coating may not be well cured and weaken film properties. Thus it is a difficult point to improve levelling performance. The levelling performance will be easily improved when the semi-crystalline polyester resin is introduced into the powder coating. Different from amorphous polyester resin, the semi-crystalline polyester resin have rapid drop in viscosity when it reach the melting point, which help to improve levelling performance [7]. Compared with linear amorphous polyester resin (lower Tg), by crystal structure design can adjust Tg, which may settle storage stability.

The synthesis of semi-crystalline polyester resin [8–12], the effect of crystallization, the characterization [12,13] and application [14–16] of semi-crystalline polyester resin were widely discussed. However, few studies are focused on the effect of semi-crystalline polyester resin on levelling performance. The aims

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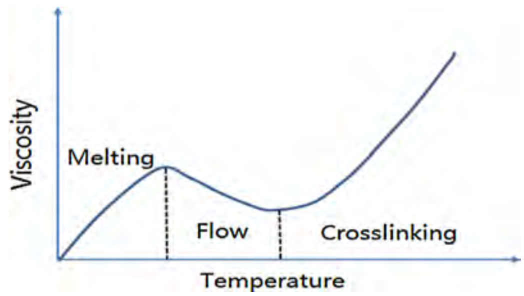

Fig. 1. Film forming behavior during curing process.

of this study is to improve levelling performance with semi-crystalline polyester resin.

The semi-crystalline and amorphous polyester resins were synthesized to prepare powder coatings in this paper. The structure of polyester resin was characterized by 1H NMR and XRD. The viscosity of polyester resin was studied by CPV. The reactivity of powder coating was determined by DSC. The levelling performance were studied by CPV, AFM and SEM. The results showed that the semi-crystalline polyester powder coating had higher reactivity, better levelling performance than that of amorphous polyester powder coating.

2. Experiment

2.1. Materials

The neopentyl glycol (NPG) was purchased from Basf, Jilin, China. The 1,6-hexanediol (HDO) was purchased from Eastman, USA. The terephthalic acid (PTA) was purchased from BP, Zhuhai, China. The isophthalic acid (IPA) was purchased from AGIC, Japan. The monobutyltin oxide (MBTO) was purchased from Arekma, France. The triglycidyl isocyanurate (TGIC) was supplied by Niutang Chemical, China. The titanium dioxide (TiO_2) was supplied by Shandong Doguide Group Co., Ltd, China (pigment grade, rutile phase, coated with SiO_2, 0.2–0.4 μm). The barium sulfate ($BaSO_4$) prepared by grinding method with particle size 1–3 μm was supplied by Guizhou Hongkai Chemical Co., Ltd. The acrylics levelling agent (PV88) was purchased from Worlee, German. The benzoin was purchased from Ningbo Zhihua Chemical Co., Ltd, China. The brightener was purchased from Ningbo South-Sea Chemical Co., Ltd, China. All the materials were commercial products and used without further purification.

2.2. Experimental

The PTA (20 mol), HDO (22 mol) (or NPG) and MBTO (0.024 mol) were firstly added into the 8 L reaction vessel with stirrer and distillation bridge. Then the temperature was programmatically (10 °C/h) increased to 235 °C in a nitrogen atmosphere. The IPA(3.1 mol) was added into the vessel for the acidolysis and terminating at an acid value of 8–15 mg KOH/g. Condensation was performed in vacuum environment(−0.094 MPa) at an acid value of 45–50 mg KOH/g and the vacuum environment was removed until the acid value reached 32–34 mg KOH/g. The amorphous polyester resin was synthesized by NPG, PTA and IPA, and the semi-crystalline polyester resin was synthesized by HDO, PTA and IPA. The properties of the synthesized polyester resins are listed in Table 1.

The powder coating was prepared according to the formula showed in Table 2 by a twin screw extruder at an extrusion temperature of about 100 °C. Subsequently the powder was sieved to obtain a particle size between 40 and 50 μm. The powder thus obtained was deposited on cold rolled steel with a thickness of 80 μm by electrostatic spraying. The panels were transferred to an air ventilated oven, where was cured for 10 min at a temperature of 200 °C. Finally, the powder coating and film properties were characterized. Generally, semi-crystalline and amorphous polyester were blended use because of the ductibility of the semi-crystalline polyester resin, which was likely to make the powder coating hard to extrude and crush if the semi-crystalline polyester resin used only. The semi-crystalline powder coating in the paper was prepared with a ratio of 75:125 between semi-crystalline and amorphous polyester specifically.

Table 1
Properties of polyester resin.

Properties	Amorphous	Semi-crystalline
AV/(mgKOH/g)	33.25	32.81
Viscosity/(Pa.s/200 °C)	45.3	16.7
Reactivity(time/s, 180 °C)	232	251
Tg/(°C)	63	58.5
Mn	4018	3435
Mw	5766	4925
Molecular weight distribution	1.435	1.434

2.3. Characterization

The nuclear magnetic resonance (NMR) spectra were recorded with a AVANCE AV (Bruker Co., Zurich, Switzerland) instrument using $CDCl_3$ as solvent and TMS as internal standard, the pulse repetition time and the polarization angle was 10 s and 60° respectively.

The X Ray Diffraction (XRD) was carried out on a TD-3500 (China) instrument with a voltage of 35 kV and a current of 25 mA. The diffraction patterns were determined over a range of diffraction angle $2\theta = 10 - 60°$ and the scanning rate was 0.04°/s.

The Cone-and-Plate Viscometer (CPV) analysis was obtained with a D16HT instrument (REL, England) at a rotation speed of 750 r/min with a rotor diameter of 19.1 mm.

The differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC204 instrument in nitrogen atmosphere at 200 °C.

The atomic force microscope (AFM) was performed on a CSPM5500 (Primitive Nano Instruments Co.) instrument and scanning electron microscope (SEM) was determined on a JSM-6701(JEOL Co., Japan) instrument.

The Laser particle size analyzer was determined on Malvern Mastersizer 2000 instrument.

The glossiness of the film were examined by XGP portable mirror gloss meter according to GB/T9754-2007 method. The flow of the powder coating were tested according to GB/T9754-2007 and GB/T21782-2010 method.

3. Results and discussion

3.1. Structure of polyester resin

The 1H NMR spectrum of polyester resin is showed in Fig. 2. The peaks (labeled a, b and c) in the region were assigned to the hydrogen atoms of HDO, while the peaks (labeled k and j) in the region were assigned to the hydrogen atoms of NPG. The peak (labeled d) in the region between 8.0 and 8.2 ppm was assigned to the hydrogen atoms of PTA. The peak (labeled e) at 8.67 ppm was also shifted to high wave number due to esterification between IPA and pre-polymer (—OH group), which were assigned to the hydrogen atoms of IPA. The results confirmed that both of the two polyester resins were IPA terminated [14].

Crystallization of polyester resin can be investigated by XRD. Fig. 3 presents the XRD spectrum of the synthetic polyester resin samples with different crystalline degree respectively. The

Table 2
Formulation of powder coating.

Raw material	Semi-crystalline powder coatings(g)	Amorphous powder coatings(g)
Semi-crystalline resin	75	0
Amorphous resin	125	200
TGIC	15	15
Titanium Dioxide	80	80
Barium Sulfate	60	60
Leveling Agent	2.4	2.4
Benzoin	1.2	1.2
Brightener	1.5	1.5

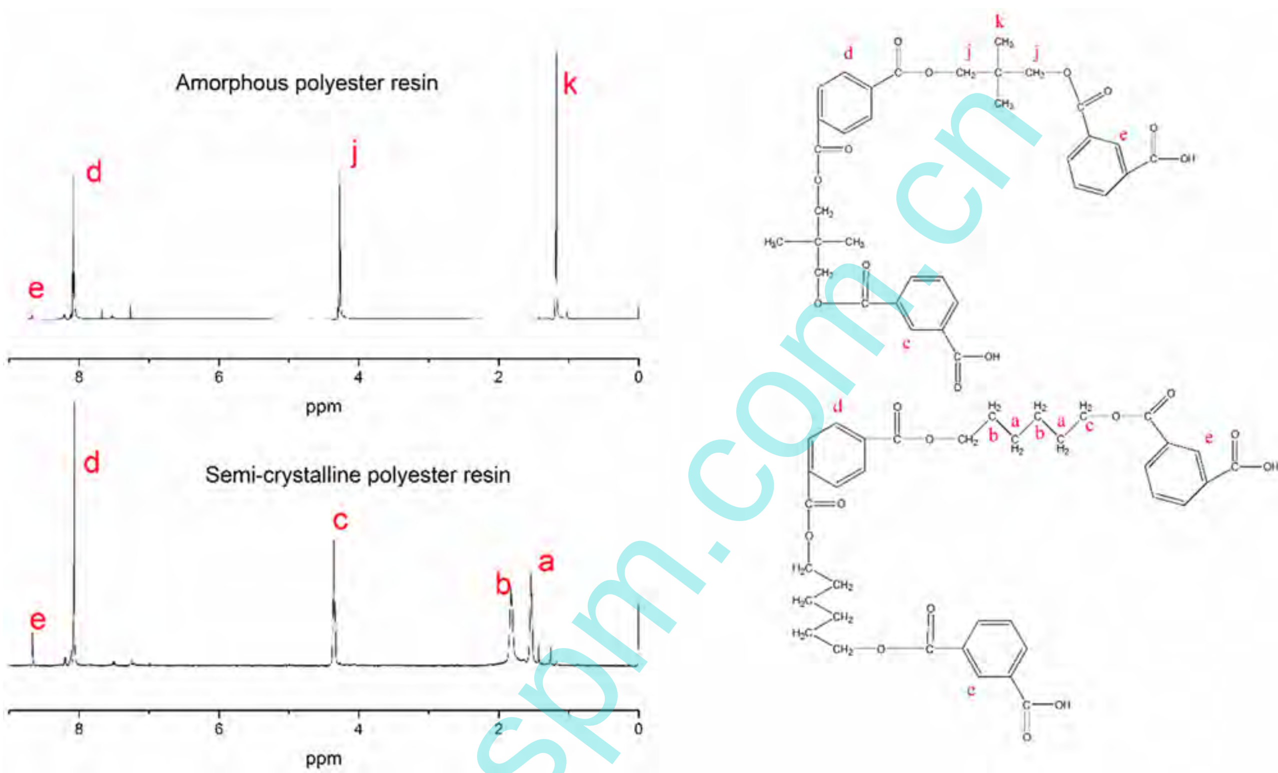

Fig. 2. 1H NMR spectrum of polyester resin.

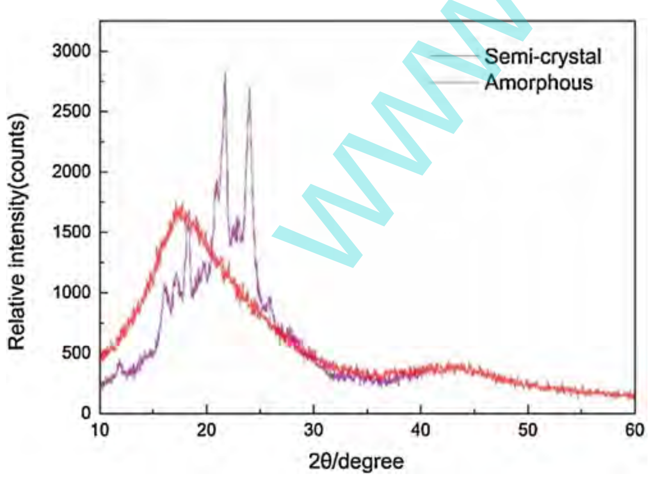

Fig. 3. XRD spectrum of the polyester resin.

broad base line of spectrum implied the existence of amorphous polyester resin in the sample synthesized by NPG, PTA and IPA, but there might be crystal nucleus in the amorphous structure. Narrow diffraction peaks and relative intensities indicated the three-dimensional sequential crystallization structure in the sample consist of HDO, PTA and IPA, which might have a 38.5% crystallization degree after Peakfit analysis [15]. As a raw material with unbranched structure in the synthesis, HDO has the advantage of regularity and flexibility in the molecular chain compared with NPG, which contributes to form the crystallized polyester resin easily.

3.2. *Viscosity of the two resins*

The rheological curve of semi-crystalline polyester resin and amorphous polyester resin is showed in Fig. 4. As showed in Fig. 4, the viscosity of the two resins had a drop when temperature increased. The viscosity of semi-crystalline polyester resin was lower than that of amorphous polyester resin at the same temperature, which will help to improve the levelling performance of the powder coating prepared with semi-crystalline polyester resin. Compared with amorphous polyester resin, lower viscosity of semi-crystalline polyester resin was affected by crystal structure and Mw, especially the crystallinity.

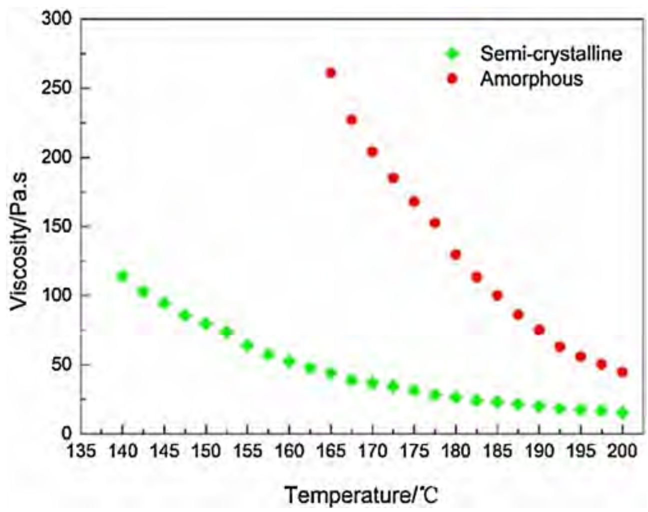

Fig. 4. Viscosity of the two resins.

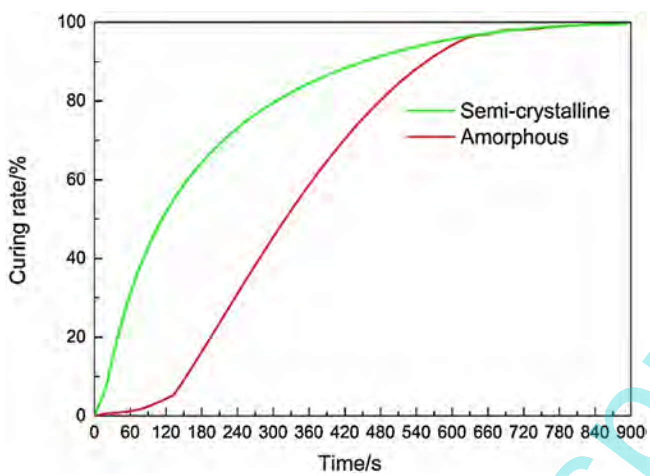

Fig. 5. The reactivity of the two coatings.

3.3. Reactivity

The curing reaction of the powder coatings can be measured by DSC [16,17].The relationship between curing degree of the powder coatings and time at isothermal curing reaction of 200 °C is showed in Fig. 5. As Fig. 5 shows, the curing degree curve of semi-crystalline polyester powder coatings was above the amorphous polyester powder coating curve in the beginning of curing, which showed that the semi-crystalline polyester powder coatings had a higher reactivity than that of amorphous polyester powder coating. The two curves became closer when time increased. The curing degree of the two polyester powder coatings were substantially at the same conversion over 90% after curing 10 min, which indicated that the powder coatings were substantially cured under the curing condition of 200 °C/600 s.

3.4. Levelling performance

The flow (including horizontal flow and inclined-plane flow) is applied to characterize the levelling performance of the coating. As showed in Fig. 6 (horizontal flow) and Fig. 7 (inclined-plane flow), the horizontal flow of semi-crystalline polyester powder coating was 31 mm, while the amorphous polyester powder coating was 27 mm. Meanwhile, the inclined-plane flow of semi-crystalline polyester powder coating was 83 mm, while the amorphous polyester powder coating was 52 mmThe results showed that the levelling performance of the semi-crystalline polyester powder coating was superior to that of amorphous polyester powder coating.

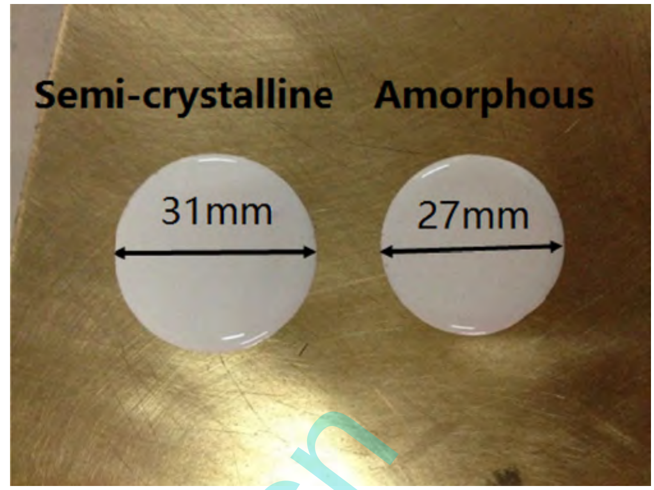

Fig. 6. The horizontal flow of the two coatings.

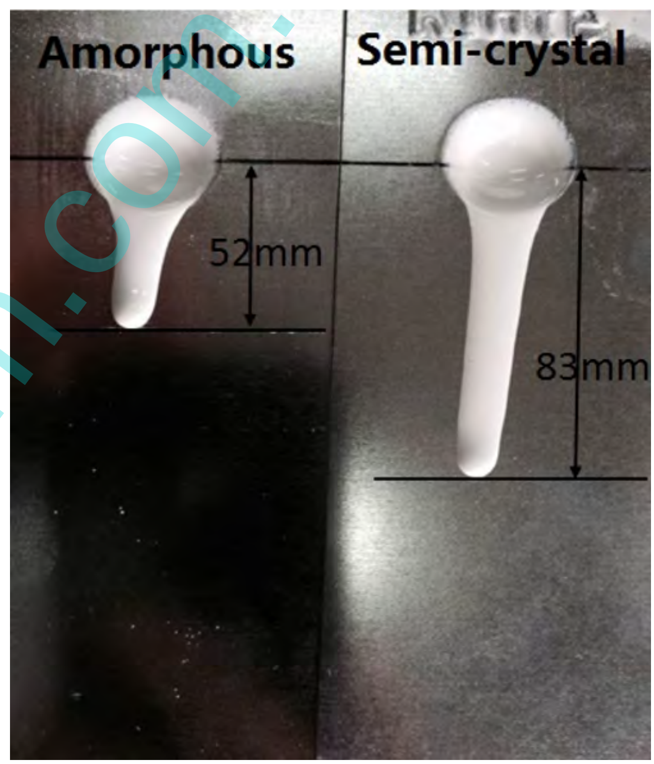

Fig. 7. The inclined-plane flow of the two coatings.

The levelling performance was affected by the particle size of the coating and the increasing rate of viscosity during curing process [18,19].The particle size and its distribution of the two coating(Fig. 8) was mainly the same, hence the particle size had less effect on levelling performance herein. Furthermore, the rheological curves of the powder coating in the film forming process is showed in Fig. 9. As showed in Fig. 9, the trends of the two curves were approximately the same. The rheological curve of semi-crystalline polyester powder coating was below the amorphous polyester powder coating curve in the film forming process of curing. At the same curing time, the viscosity of powder coating

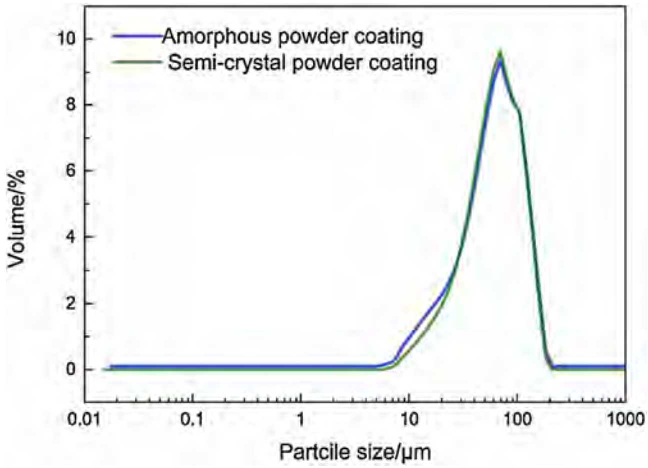

Fig. 8. The particle size of the two coatings.

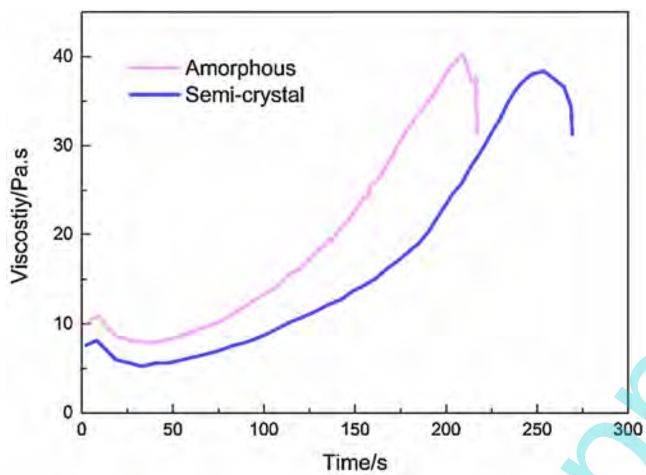

Fig. 9. Rheological curves during film forming process.

prepared with semi-crystalline polyester resin was lower than that of amorphous in the curing process, that dued to the low viscosity (Fig. 4) and crystal structure of the semi-crystalline polyester resin, and which help to improve levelling performance.

3.5. Film morphology

The film surface is showed in Fig. 10, the film of semi-crystalline polyester powder coating was smoother, less orange peel and

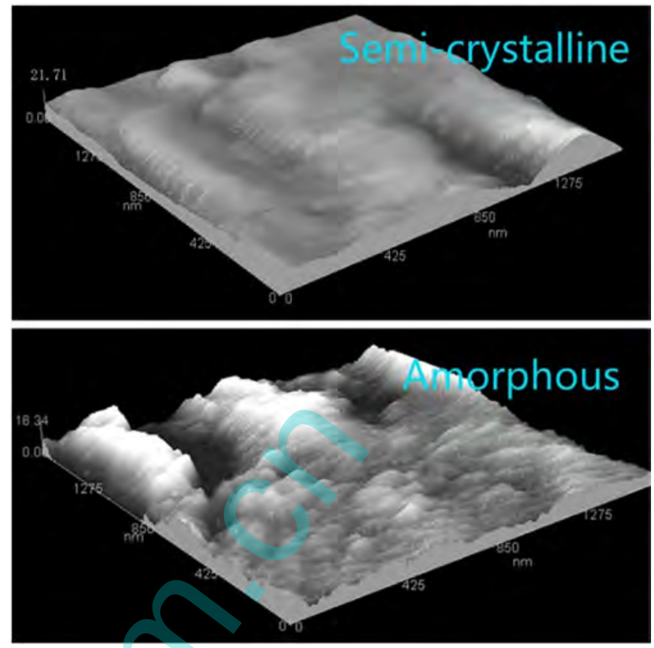

Fig. 11. AFM images of the two coatings.

higher gloss. The AFM is applied to study the surface evenness of the two coating. Fig. 11 is the AFM images of the two coatings. The average roughness (Ra) and root mean square roughness (Sa) of semi-crystalline polyester powder coating were 3.51 nm and 4.51 nm, while the amorphous polyester powder coating were 4.23 nm and 5.30 nm. The results confirmed that the film of semi-crystalline polyester powder coating was smoother than that of amorphous polyester powder coating. The surface evenness is affected by the dispersion of filler in the coating and the wetting properties of the resin [20–22]. Fig. 12 is the SEM micrographs of semi-crystalline and amorphous polyester powder coatings, as illustrated in Fig. 12, the filler was fully dispersed in the semi-crystalline polyester powder coating, and lower viscosity help to improve wetting properties [23,24]. All the results showed that the levelling performance of amorphous polyester powder coating was inferior to that of semi-crystalline polyester powder coating.

4. Conclusions

The semi-crystalline polyester resin was synthesized by PTA, HDO and IPA, and the amorphous polyester resin was synthesized by NPG, PTA and IPA. The crystal structure of semi-crystalline

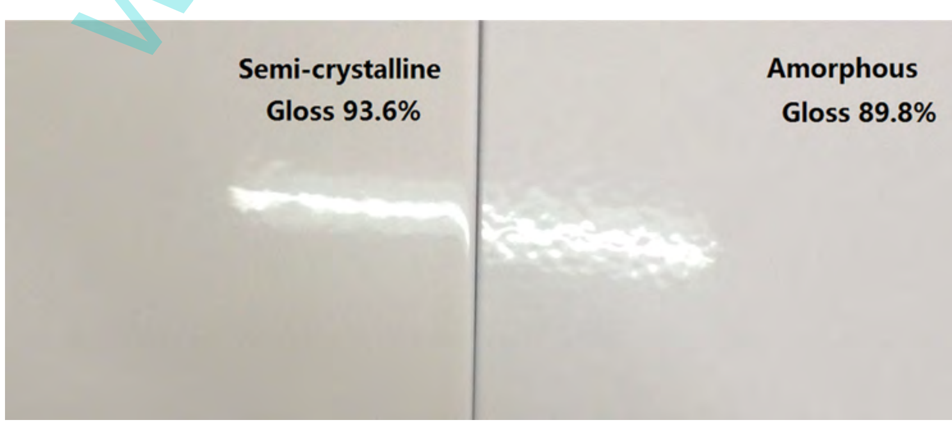

Fig. 10. Film morphology.

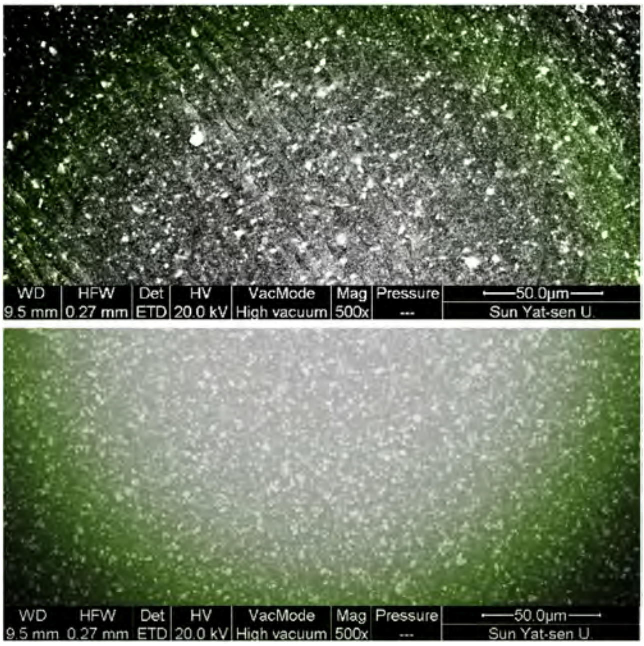

Fig. 12. SEM micrographs of the two coatings.

polyester resin was HDO and PTA. A series of experiments were carried out to test the levelling performance of the semi-crystalline polyester powder coating and amorphous polyester powder coating. All the results showed that the semi-crystalline polyester coating exhibited excellent levelling performance and higher reactivity.

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