Synthesis and Characterization of Super-Hydrophobic Coating Materials

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***Abstract*—The hydrophobic properties of lotus have won support among the people. It can not only resistant to the condensation of water, but also has the function of self-cleaning and anti-pollution. Super-hydrophobic coating has a great practical value in real life.The super-hydrophobic coating materials were based on low surface energy base materials pigment, additives and curing agent. Then they were sprayed on the tinplate. The properties of this hydrophobic coating were characterized by fourier transform infrared analysis (FT-IR),hydrophobic angle measuring device, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). The FT-IR results confirmed structure of polymer. And the results also showed that when the ratio of m1(weight of pigment) /m2(weight of base material) was 1/1.26 and SiO2 content was 15%, the hydrophobic angle and rolling angle were 146.43 °and 10°, respectively. The results also implied that the super-hydrophobic coatings had micro/nano structure and good thermal property.**

Keywords-super-hydrophobic; hydrophobic angle; micro/nano structure; thermal property

I. Introduction

With the development of science and technology, people have devoted great attention to study of super-hydrophobic materials and have made significant progress [1]. Studying the surface with special wettability on research and development of functional super-hydrophobic surface are significantly important. Hydrophobic coatings mainly relate to the wettability of coatings, usually characterized by the hydrophobic angle of liquid solid contact plane[2]. Solid surface wetting is one of the most important properties of solid surfaces, and in people's daily life and industrial production also plays an important role[3]. The super-hydrophobic coating refers to the static water contact angle greater than 150 degrees when the water drops onto the clean substrate surface[4]. There are many super-hydrophobic surfaces in nature such as the surface of lotus leaf, the wing of butterflies, the feet of water skippers, and the feather of waterfowls et al[5].These material has water-repellent and low-adhesion. These unique properties have shown wide potential applications, such as self-cleaning, anti-icing, anti-corrosion, anti-fouling et al[6]. According to the super-hydrophobic principle of lotus leaf, the hydrophobic property of the micro/nano structure is a method to maintain the super-hydrophobic property[7]. Thus, in this paper, we reported a simple and efficient method to prepare super-hydrophobic coatings.Super-hydrophobic coating was composed of fluorocarbon resin with low surface energy as the base material and the mixture of aerosil and titanium dioxide as pigment filler. Moreover, the structure and hydrophobic properties of the super-hydrophobic coating were described in detail.

II. Experimental

A. Materials

The raw materials used were fluoroethylene-vinyl ether copolymer (FEVE)(Shanghai Dongfo Chemical Company Limited), isophorone diisocyanate trimers (IPDI-trimer)(Shanghai Dongtu Chemical Import & Export Company Limited), aerosol (Hangzhou Jubang Chemical Company Limited), rutile type titanium dioxide, butyl acetate (Tianjin Yongda Chemical Reagent Company Limited), dispersant agent (AFCONA-4060, Changsha Tianqi Fine Chemical Company. Limited), coupling agent (KH-602 Nanjing Langke Chemical Company Limited), defoaming agent (AFCONA-2022, Changsha Tianqi Fine Chemical Company. Limited) wetting agent (AFCONA-3034 Changsha Tianqi Fine Chemical Company. Limited).

B. Preparation of Super-Hydrophobic Coatings

1) Preparation of Super-Hydrophobic Painting

FEVE were solved in butyl acetate and dimethylbenzene to form uniform solution in four-flask with high speed stirring. Then coupling agent and other additives, including defoaming agent, wetting agent and dispersant agent were added to solution. After stirring the solution for a period of time, an amount of aerosil and rutile type titanium dioxide were added into the system. A certain period of time later, the mixture was ground. Then the super-hydrophobic paintings were obtained.

2) Preparation of Super-Hydrophobic Coating

Coatings of the super-hydrophobic on tinplate were prepared by blending the super-hydrophobic painting with curing agent IPDI-trimer, and sprayed on tinplate by a spray gun. The samples were characterized after drying in an oven. The IPDI-trimer amount was calculated according to the following formulae(NCO/OH=1.1).

$$m_{IPDI-trimer} = \frac{OHV \times 42 \times m_{FEVE} \times NCO/OH}{561 \times NCO}$$

OHV - The hydroxyl value of FEVE

42 - The relative molecular weight of NCO

NCO -The isocyanate value of IPDI-trimer

m_{FEVE} -The pure solid of FEVE

C. *Characterization*

FT-IR spectra were collected on FTS-135 Fourier Transform Infrared. Spectrometer was recorded in the range of 500~4000 cm-1. Hydrophobic angle and rolling angle of the super-hydrophobic coatings were determined by using the hydrophobic angle measuring device(KRUSS DSA 30,Germany). The surface morphology of samples were determined by scanning electron microscopy(SEM, S480021, Japan). Thermal properties of the super-hydrophobic coating w conducted by the Sta449C Netzsch thermal gravimetric analysis(TGA) from room temperature to 600 ℃ at 10℃/min under nitrogen atmosphere.

III. RESULTS AND DISCUSSION

A. *Infrared Analysis of Super-Hydrophobic Coatings*

FT-IR spectra provided a rapid means for the characterization of functional groups of organic molecules. And Figure I showed the FT-IR spectra of super-hydrophobic coating, FEVE,and IPDI-trimer.

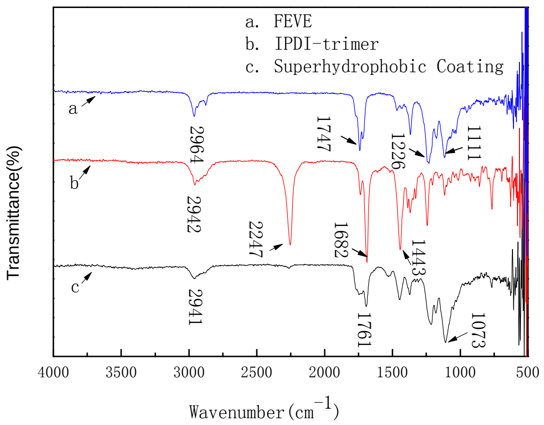


FIGURE I. FT-IR SPCTRA FOR SUPERHYDROPHOBIC COATING, FEVE AND IPDI-TRIMER

As can be seen from Figure I, Spectral line a, b and c represented the FT-IR spectra of FEVE, IPDI-trimer and superhydrophobic coatings, respectively. It was clear that the stretching vibration characteristic absorption peak of-OH groups at about 3000cm-1 was not obvious in spectral line a. In spectral line b, 1443cm-1, 2247cm-1 were the stretching vibration characteristic absorption peak of C-N groups and -NCO groups in the IPDI-trimer, respectively. However, the peak of 2247cm-1 in the spectral line c disappeared substantially, indicating -NCO groups reacted completely. In spectral line a, b and c 2967cm-1 was stretching vibration characteristic absorption peak of the C-H groups, and 1700cm-1 was stretching vibration characteristic absorption peak of the C = O groups. At about 1073 cm-1 of spectral line a and spectral line b have found stretching vibration characteristics absorption peak of the C-F group. It proved that the existence of C-F group in FEVE and C-F group did not participate in the reaction. The results suggested that the peak of –OH group was not obvious but existence in FEVE, and the carbamates were obtained by the reaction of –NCO and –OH groups via gradual polymerization.

B. *Effect of m1(Weight of Pigment) /m2(Weight of Base Material) Value on Hydrophobic Angle and Surface Tension of Super-Hydrophobic Coatings*

Figure II showed the influence of m1(weight of pigment) /m2(weight of base material) value on hydrophobic angle and surface tension of super-hydrophobic coatings. The results showed that the hydrophobic angle increased gradually and the surface tension changed with the increasing of m1(weight of pigment) /m2(weight of base material) value. As can be seen from Figure II, the best ratio was between 1/2 and 1/3. Especially when the ratio was 1/1.26, the hydrophobic angle reached 141°. And the surface tension was relatively small and about 300mN/m. Therefore, the best ratio of m1(weight of pigment) /m2(weight of base material) was 1/1.26.

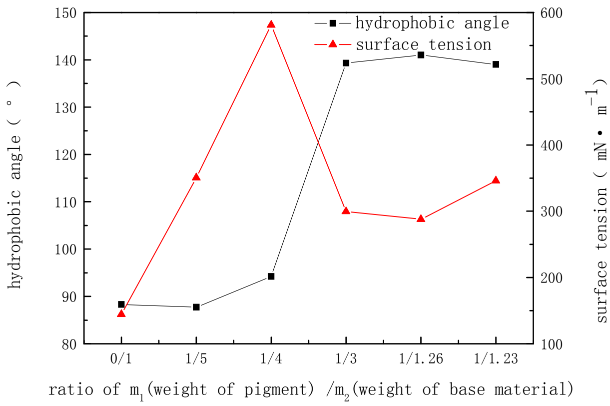


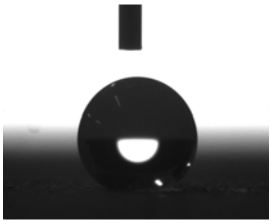
FIGURE II. EFFECT OF M1(WEIGHT OF PIGMENT)/M2(WEIGHT OF BASE MATERIAL) ON HYDROPHOBIC ANGLE AND SURFACE TENSION OF SUPER-HYDROPHOBIC COATINGS

C. *Effect of the SiO2 Content on the Hydrophobic Angle of Super-Hydrophobic Coatings*

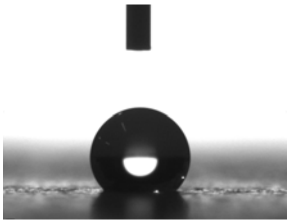
The hydrophobic angle and rolling angle of super-hydrophobic coatings were shown in Figure III. On the premise of m1(weight of pigment) /m2(weight of base material) value with 1/1.26, the hydrophobic angle of super-hydrophobic coatings corresponding to the SiO2 content of 9.4%, 9.56%, 12.48%, 15%, 17.3% were 138.07°, 139.64°, 140.83°, 146.43° and 153.33°, respectively. It can also be seen from Figure III, the rolling angle of super-hydrophobic coatings corresponding to the SiO2 content of 9.4%, 9.56%, 12.48%, 15%, 17.3% are 14.4°, 16.8°, 13.9°, 10°and 11.55°, respectively. The results showed that the SiO2 content was 15%, the hydrophobic angle and rolling angle were 146.43 °and 10°, respectively.

D. *Electron Scanning Microscope (SEM) Analysis of Super-Hydrophobic Coating*

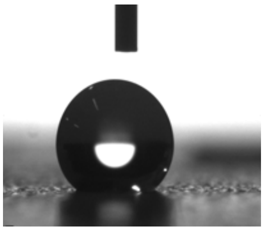
The surface structure of super-hydrophobic coating was characterized by SEM in Figure IV. The SEM picture indicated that the surface of super-hydrophobic coating had the micro/ nano structure, which was one of the important factors for being super-hydrophobic. And the more micro/nano structure, the better hydrophobic properties. The micro/nano structure made a large amount of air exist in the water droplets and structure surface, reducing the interface area between water droplet and solid surface. Therefore the hydrophobic property of super-hydrophobic coating became better.



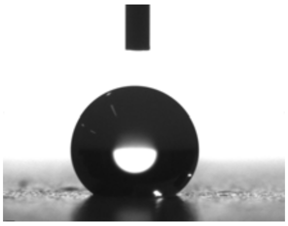
A) THE CONTENT OF SIO2 WAS 9.4%, HYDROPHOBIC ANGLE WAS 138.07°.



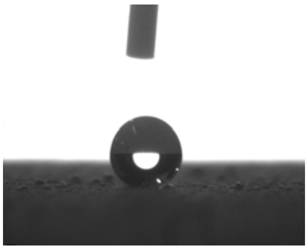
B) THE CONTENT OF SIO2 WAS 9.56%, HYDROPHOBIC ANGLE WAS 139.64°.



C) THE CONTENT OF SIO2 WAS 12.48%, HYDROPHOBIC ANGLE WAS 140.83°.



D) THE CONTENT OF SIO2 WAS 15%, HYDROPHOBIC ANGLE WAS 146.43°.



E) THE CONTENT OF SIO2 WAS 17.3%, HYDROPHOBIC ANGLE WAS 153.33°.

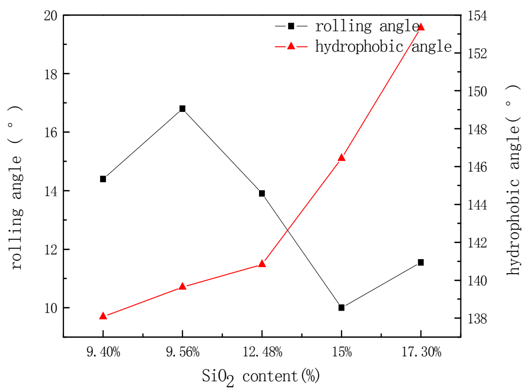


FIGURE III. EFFECT OF THE SIO2 CONTENT ON THE HYDROPHOBIC ANGLE AND ROLLING ANGLE OF SUPERHYDROPHOBIC COATING.

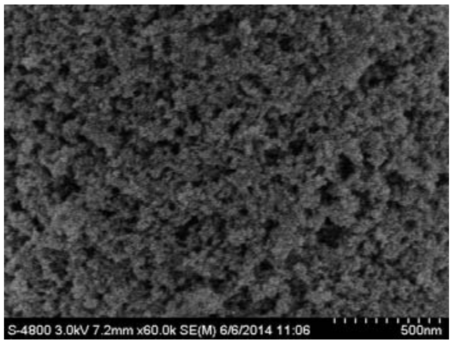


FIGURE IV. SEM OF SUPER-HYDROPHOBIC COATING(SIO2 CONTENT WAS 15%,RADIO OF M1(WEIGHT OF PIGMENT)/M2(WEIGHT OF BASE MATERIAL) WAS 1/1.26).

E. Thermal Gravimetric Analysis of Super-Hydrophobic Coatings

The thermal decomposition temperature of the polymer was an important parameter to describe the thermal properties of the polymer. And it determined the operating temperature of a composite material directly. As shown in Figure V, the super-hydrophobic coating had good thermal stability. It was clear that the initial thermal decomposition temperatures of the coating was up to 300℃, and it had a relatively high thermal stability with a weight loss of 5% about 315℃ and a weight loss of 10% about 350℃. The results showed that the super-hydrophobic coating had good thermal property.

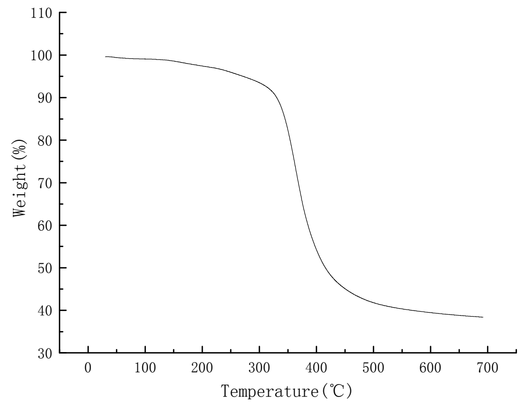


FIGURE V. TGA OF SUPER-HYDROPHOBIC COATING(SIO2 CONTENT WAS 15%,RADIO OF M1(WEIGHT OF PIGMENT)/M2(WEIGHT OF BASE MATERIAL) WAS 1/1.26).

IV. CONCLUSION

In this paper, the super-hydrophobic coatings were composed of FEVE with low surface energy as the base material, the mixture of aerosil and titanium dioxide as pigment filler and IPDI- trimer as curing agent. Then a series of super-hydrophobic coating samples have been prepared via the technology of spraying process successfully. The FT-IR results confirmed structure of polymer.They showed good hydrophobic properties when the ratio of m1(weight of pigment) /m2(weight of base material) was 1/1.26 and SiO2 content was 15% with hydrophobic angle and rolling angle were 146.43 °and 10°, respectively. The result also implied that the super-hydrophobic coating had micro/nano structure and good thermal property.

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