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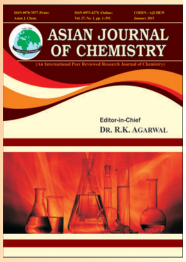

Study of Novel Low Surface Energy Antifouling Coating Prepared with Silicon-Modified Acrylic Resin and Nano-TiO_2

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In this paper, a novel low surface energy antifouling coating was prepared by applying a synthesized silicon-modified acrylic resin and being modified with nano-TiO_2. According to the IR spectrum of the synthesized resin, it was suggested that the polymerization reacted completely between organic silicon and acrylate. The GPC analysis showed the molecular weight was moderate and its distribution was narrow. Low surface energy antifouling coating was prepared by spreading nano-TiO_2, ferric oxide and talcum powder into this resin. The results exhibited that this coating had remarkable low surface energy property with a contact angle > 105°. The seawater exposure test (3 month) by applying this coating also gave very good results.

Keywords: Antifouling, Low surface energy, Nano-TiO_2, Silicon-modified acrylic resin.

INTRODUCTION

Biological fouling of surfaces exposed to the aquatic environment such as ship hulls and offshore marine structures is a serious problem due to the biofouling on ship hulls reducing ship speed, maneuverability and range[1,2]. Meanwhile, fouling increase fuel consumption by as much as 30-40 % and necessitates extensive maintenance, which raises the overall costs of operation[3]. Thus, antifouling coatings for ship hulls are a very important topic in coating research. Traditional marine antifouling coatings had organotin in them. However, the working principle of most of the paint systems applied is based on slow release of toxins in time (self-polishing coatings) which are harmful to marine environment and human health because of their toxicity[4]. So a kind of non-toxic and efficient antifouling coating is needed urgently in modern ship industry. Thus, the low surface energy antifouling coating was proposed in this work.

Low surface energy antifouling coating has been developed in the past decade, which can protect against fouling settlement as the ship moves through the water shear forces on the hull allow[5]. Furthermore, this kind of coating is non-toxic. The most common fouling release coatings are based on highly fluorinated polymers[6] or polyurethane[7]. Although these coatings can provide fouling-release, their inadequate adhesion to the substrate, low durability and high-cost has limited their application[8]. Generally speaking, to prepare low surface energy antifouling coating, the resin with low surface energy and suitable surface microstructure of film is the basic conditions. In this paper, we tried to use nano-TiO_2 to modify the surface property of coating and also applied a new silicon-modified acrylic resin to decrease the surface energy of film. We hoped to prepare a low surface energy antifouling coating with excellent adhesion, stability, water resistance and antifouling property.

EXPERIMENTAL

Methyl methacrylate, butyl acrylate, acrylic acid, butyl acetate, butyl alcohol were all purchased from Shenyang Research Institute of Chemical Industry. Xylene, vinyl triethoxy silane (VTES), benzoyl peroxide, iron oxide red, calcium carbonate, talcum powder and nano-TiO_2 (10-20 nm) were purchased from Changzhou Maideng Rubber Plastics Chemical Co., LTD (Changzhou, China).

Synthesis of silicon-modified acrylic resin: Methyl methacrylate, butyl acrylate, acrylic acid, butyl acetate, butyl alcohol and xylene were put into four-neck flask with a dropping funnel, a condenser pipe a thermometer and a N_2 protect apparatus. Then the flask was heated up to 105 °C. Benzoyl peroxide was added stepwise within 2.5 h. The flask was heated up to 115 °C for 2-3 h. The last benzoyl peroxide was added stepwise into the flask within 1 h. Then it was put at 100 °C for heat preservation for 1 h to get a transparent viscous fluid.

Preparation of low surface energy antifouling coating: Low surface energy antifouling coating was prepared by spreading proper amount of nano-TiO_2, 4 wt % ferric oxide and 3 wt % talcum powder into the silicon-modified acrylic resin.

Analytical techniques: Infrared spectra were recorded on Nicolet 5700. The molecular weight of resin was measured by model GPC-3060D Agilent.

The examination of the contact angle between film and water was measured on model Cam200, KSV. The water drop diameter was 1.25 mm. The examination was carried on within 30 s after the water dropped onto the film surface. The final result is the average of 10 results.

The coating was applied by means of air spray to the board and dried for 72 h. Then the board was put into the water and weighted every other day. The water absorption was calculated by the following eqn. 9:

$$\text{Water absorption } (\%) = \left\{ \frac{m_{(\text{film+board})a} - m_{(\text{film+board})b}}{m_{(\text{film+board})b} - m_{(\text{board})}} \right\} \quad (1)$$

where m_a was the weight before the board was put into water, m_b was the weight after the board was put into water.

RESULTS AND DISCUSSION

Characterization of synthesized silicon-modified acrylic resin: The infrared spectrum of the silicon-modified acrylic resin (Fig. 1) showed a series of sharp peaks around 1110-1050 cm^{-1} confirmed the presence of -Si-O- group in the resin. This means that the organic silicon monomer took part in polymerization. Two broad band appearing at wave number 2900 cm^{-1}, 1733.7 cm^{-1} were the indicative of the presence of structural C-H, C=O, respectively, which proved the acrylate also took part in polymerization. The bands at 3640-3300 and 1500-1300 cm^{-1} were due to the acrylic acid part existing in the resin. In this spectrum, we could not find peaks at either 1695-1540 or 3125-3030 cm^{-1} region, which confirmed the elimination of C=C and its C-H. This result indicated that all the monomers took part in the polymerization and reacted completely. The above-mentioned results can be concluded that the polymerization reacted completely between organic silicon and acrylate as expected. The silicon-modified acrylic resin was prepared successfully.

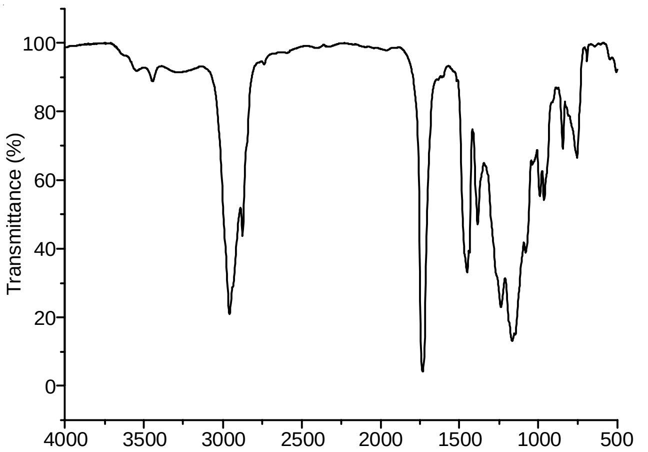

Fig. 1. Infrared spectrum of silicon-modified acrylic resin

To get a coating with good physical performance, not only the resin shall be thermoplastic, but also the molecular weight of the resin should be relatively high. However, if the molecular weight is too high, the mass fraction of solid will be too low and the mass fraction of solvent will rise sharply. So the recommended molecular weight of thermoplastic resin[9] should be in between 75000 and 120000. And, the distribution of the molecular weight must be narrow. Thus, high molecular weight affects performance of the film, while low molecular weight affects performance of spreading. To study the effect of the molecular weight clearly, a parameter named PD is employed to judge the distribution of the molecular weight[9]. It was calculated by the following eqn.:

$$PD = M_w/M_n \quad (2)$$

where M_w is weight average molecular, M_n is number average molecular.

Higher PD led to more widely molecular spread, compared with that the lower PD result in more narrowly molecular spread. If PD value of a resin ≥ 4-5, it will not be suitable to apply as a film forming material[10].

GPC analysis of this synthesized resin was summarized in Fig. 2 and it can be seen that M_w = 78296 and PD = 2.5166. Thus, the molecular weight of our resin can meet the requirement of a thermoplastic film material. On the other hand, the distribution of the molecular weight was prefer narrow. This result will makes sure the stabilization of the film matter.

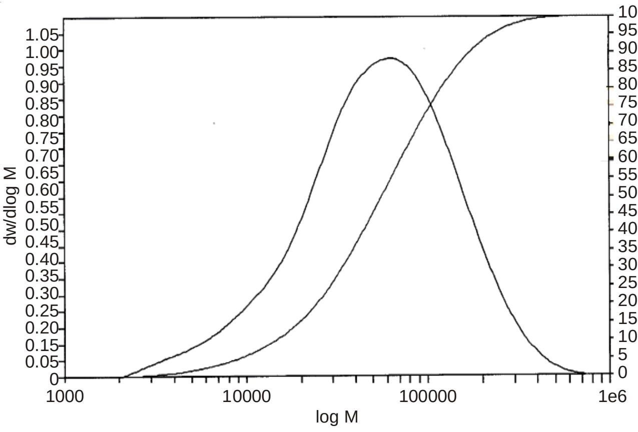

Fig. 2. GPC results of the molecular weight distribution of the resin

Effect of mass fraction of nano-TiO_2 on the low surface energy property of the coating: Low surface energy antifouling coating restrains marine organisms from attaching to the hull by its low surface energy. In this paper, we tried to use nano-TiO_2 to modify the surface of the antifouling coating and imitate the lotus effect, which may decrease the surface energy of the antifouling coating. To measure the surface energy, contact angle is considered as a useful parameter, which can be detected easily. It is well known that the higher contact angle between film and water is, the lower surface energy of film is. The effect of the addition of nano-TiO_2 on the contact angle was studied and the results were shown in Fig. 3.

It could be seen that the mass fraction of nano-TiO_2 had important effect on the surface energy of the coating film. At first, the contact angle between film and water increased with

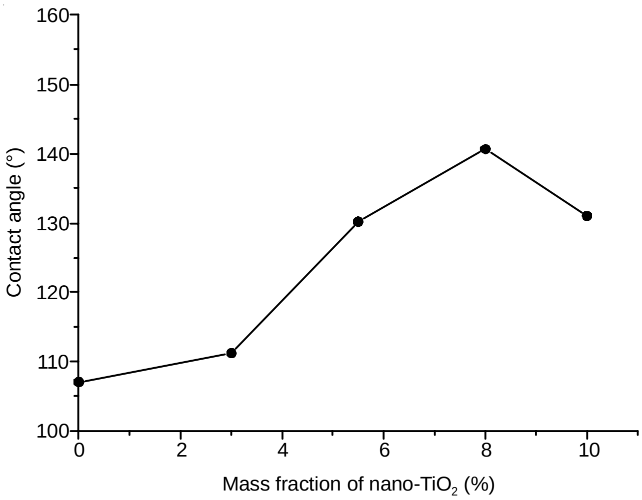

Fig. 3. Effect of mass fraction of nano-TiO_2 on contact angle between paint and water

increasing addition of nano-TiO_2 and got the biggest angle 140.6° when the mass fraction of nano-TiO_2 was 8 %. This result suggested that the addition of nano-TiO_2 could improve micro-nano surface structure of the film and thus provided low surface energy and good hydrophobic property. This biggest angle also indicated that this coating showed remarkable low surface energy property. Comparatively, the contact angle decreased when the addition of nano-TiO_2 increased to 10 %. This was probably because of the destroy of the micro-nano structure, the excess TiO_2 will decrease the roughness of the film surface.

Effect of nano-TiO_2 on the water absorption of coating film: Water absorption of film reflects surface microstructure and is an important parameter to assess the physical properties of coating film[10]. The permeability resistance of film will be improved when the micro-holes in film surface changed small and few. Meanwhile, the water resistance and antifouling property will also enhance. By contrast, if there was so much absorbed water in the film, the hardness of the film will be decreased, film will be destroyed meanwhile the antifouling performance will decline.

Fig. 4 present that the water absorption of the film was obviously decreased when nano-TiO_2 was put into coating. According to the results, the water absorption increased as the addition of nano-TiO_2 was lower or higher than 5.5 %. When the nano-TiO_2 was added into silicon-modified acrylic-resin would result in the micro-holes on the material surface becoming smaller and fewer and changing them to be nano-holes. Thus, the water resistance and antifouling capacity of film were enhanced obviously. However, with the increase of nano-TiO_2, the resin could not cover all the fillers which may lead to some filler solve in water. Consequently, there will be many large holes appeared on the film surface and finally decrease the water absorption property.

Seawater immersion test of this novel antifouling coating: In order to illustrate the antifouling performance of this novel coating, panels coated with this coating (nano-TiO_2, 5.5 %) was immersed in seawater for 3 months. It can be seen clearly that panel with this coating showed nearly no biofouling which indicated very good antifouling performance.

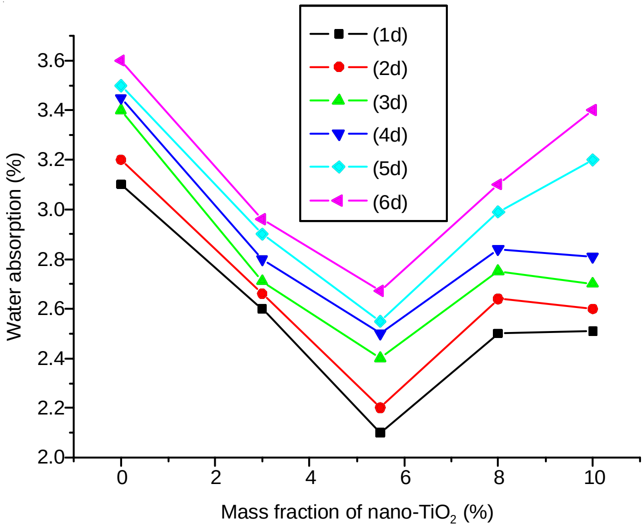

Fig. 4. Effect of nano-TiO_2 mass fraction on water absorption of the coating film

Conclusions

- The silicon-modified acrylic resin was synthesized and the IR analysis showed that the polymerization reacted completely between organic silicon and acrylate as expected. Meanwhile, the molecular weight was moderate and its distribution was narrow. This resin was suitable to be applied in antifouling coating.
- The addition of the nano-TiO_2 could not only decrease the surface energy of the coating film, but also improve the water absorption property. According to the results, the optimal addition of nano-TiO_2 should be in the range of 5.5 %. At such conditions, the contact angle was 131°, while the water absorption was lowest. The seawater immersion test also proved that the coating prepared at such conditions showed very good antifouling performance in 3 months.

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