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Preparation and Surface Properties of Fluorinated Epoxy Acrylic Cathodic Electrodeposition Coatings

LIJUN CHEN[1,*], YIJIANG SHAO[2] and JIANWEI HUI[2]

[1]School of Chemical Engineering and Materials Science, Zhejiang University of Technology, No. 18 Chaowang Road, Hangzhou, Zhejiang Province, P.R. China
[2]Wanguo Coatings Co. Ltd., Huzhou 310052, P.R. China

*Corresponding author: Tel: +86 18968048502; E-mail: chenlj@zjut.edu.cn

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The fluorinated epoxy acrylic cathodic electrodeposition (CED) coatings were prepared by mixing blocked polyisocyanate and cationic resin. The cationic resin was prepared *via* copolymerizing hexafluorobutyl acrylate (HFBA), methyl methacrylate (MMA), butyl acrylate (BA) and glycidyl methacrylate (GMA) and opening loop and acidizing the prepared terpolymer. The particle size of resultant cathodic electrodeposition coatings water suspension was 28.62 nm. Zeta potential of cathodic electrodeposition coatings was 41.84 mV, which indicated the stability of cathodic electrodeposition coating water suspension is high. The water-resistance and chemical resistance of cathodic electrodeposition coatings are improved.

Key Words: Fluorinated monomer, Acrylic cationic resin, Epoxy, Cathodic electrodeposition coatings.

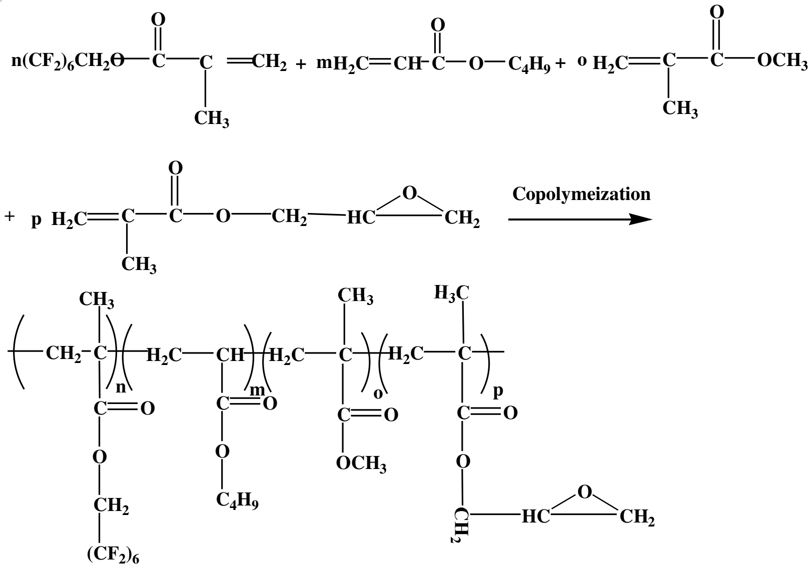
INTRODUCTION

Cathodic electrodeposition coatings are widely used in the ground coating of the automotive industry because of their low content of volatile organic compound, high degree of automation and usage[1]. Presently, cathodic electrodeposition coatings have a tendency to finishing coating[2]. Cathodic electrodeposition coatings are mainly composed of the epoxy or acrylic cationic resin and the blocked polyisocyanate[3]. The acrylic cationic resin has many merits such as good weather resistance and decoration and high glossiness. However, the drawbacks of the acrylic cationic resin in cathodic electrodeposition coatings such as poor water resistance and hydrophobic property are strongly neglected. Therefore, the application of cathodic electrodeposition coatings in the hardware such as outdoor light fitting and bathroom fittings is restricted further. Fortunately, the fluorinated resin has been proved to have excellent hydrophobic property and low surface energy[4,5]. At present, the fluorinated modification of epoxy acrylic cationic resin has not been reported. In this communication, we would like to introduce the fluorine carbon chain into epoxy acrylic cationic resin and prepare cathodic electrodeposition coatings to improve their water resistance or hydrophobic properties. The pathway to preparing cathodic electrodeposition coatings is given in **Scheme-I**.

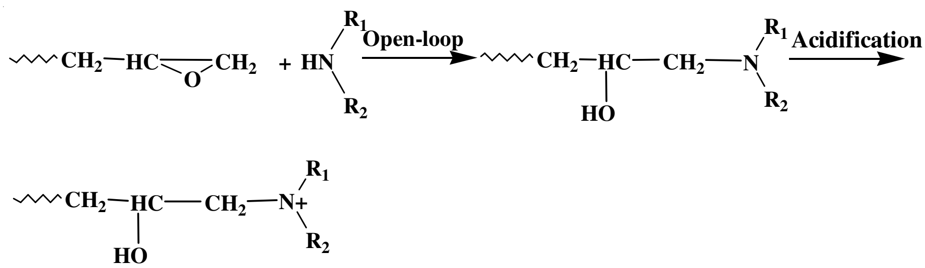
EXPERIMENTAL

Butyl acrylate (BA) and methyl methacrylate (MMA) were distilled under reduced pressure prior to polymerization. Glycidyl methacrylate (GMA) was industrial grade and purchased from Tianjin Chemical Reagent Institute. Hexafluorobutyl acrylate (HFBA) was industrial grade and purchased from Harbin Xeogia Fluorine-silicon Material Co. LTD. Propylene glycol monomethyl ether acetate (PMA), whose content was 99 %, was bought from Aladdin reagents. Benzoyl peroxide (BPO) was chemically pure grade and obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Diethanolamine and acetic acid, which were analytically pure grade, were used as received. The blocked polyisocyanate was industrial grade and a gift from Wanguo Coatings Co. Ltd. The water used in this experiment was distilled followed by deionization.

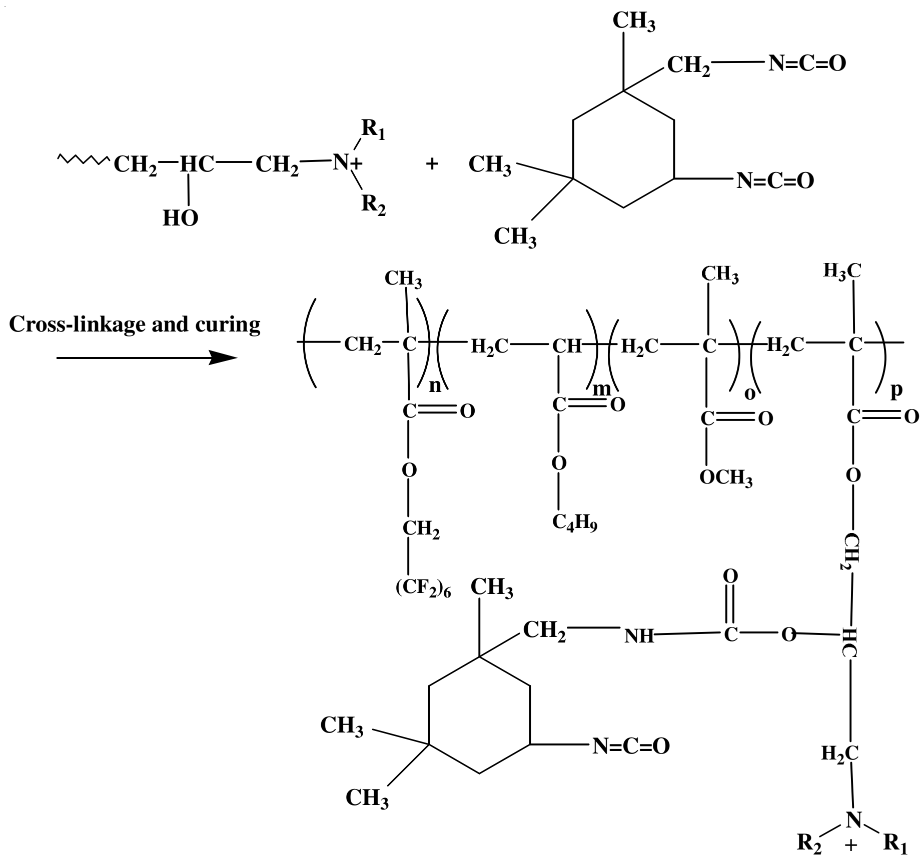
Preparation of fluorinated epoxy acrylic cationic resin: Propylene glycol monomethyl ether acetate (PMA) was charged into a 250 mL three-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel and heated to 80 ºC with the water bath under the moderate agitation. Then the mixed solution composed with MMA, BA, GMA, HFBA and BPO was dripped into the flask within 3 h through the dropping funnel. And the reaction continued for 2 h after the mixed solution was dripped completely. Then diethanolamine



(I) Copolymerization



(II) Open-loop and acidification



(III) Cross-linkage and curing

Scheme-I: Pathway to preparing cathodic electrodeposition coatings was added into the flask and the temperature was kept for another 2 h. Finally, acetic acid was added and agitated for 0.5 h. Thus, the fluorinated epoxy acrylic cationic resin was obtained. In the experiment, the stirring speed was maintained at 200 rpm throughout the runs.

Preparing film of cathodic electrodeposition coatings: The blocked polyisocyanate and the fluorinated epoxy acrylic cationic resin was added into a 100 mL three-neck flask. Then the moderate amount of de-ionized water was dripped into the three-neck flask within 0.5 h through dropping funnel under the moderate agitation. Thus, cathodic electrodeposition coatings were obtained. cathodic electrodeposition coatings were placed for 24 h at room temperature. The film of cathodic electrodeposition coatings was obtained from spreading the coatings on the clean glass uniformly and curing at 150 ºC for 2 h in the bake oven.

Characterization: The particle size and zeta potential of cathodic electrodeposition coatings were tested by zetatrac dynamic light scattering detector (Microtrac Limited Corporation, USA) at 25 ºC. The power and the wavelength of the diode laser used in the dynamic light scattering measures were 3 mW and 780 nm, respectively. The contact angle between film and water was determined with the Data Physics contact angle meter (OCA-20, Germany) at room temperature.

RESULTS AND DISCUSSION

Particle size and zeta potential of cathodic electrodeposition coatings: The appearance of the prepared cathodic electrodeposition coatings is translucent and accompanied with blue-fluorescence. Fig. 1 showed the particle size of the prepared cathodic electrodeposition coatings. Fig. 1 indicates that the particle size of cathodic electrodeposition coatings is unimodal distribution. From Fig. 1, it is found that the particle size of the cathodic electrodeposition coatings is 28.62 nm. It is well know that the stability of oil/water emulsion can be judged from the value of zeta potential. Usually, larger the absolute value of zeta potential is and higher the stability of oil/water emulsion is. In this study, zeta potential of cathodic electrodeposition coatings is 41.84 mV, which indicates that the stability of cathodic electrodeposition coating water suspension is high.

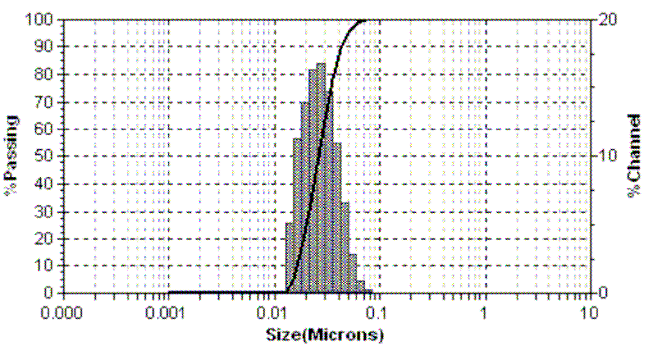
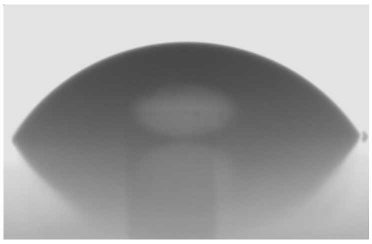
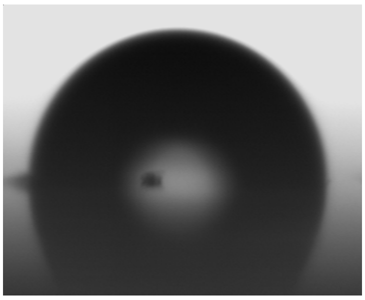


Fig. 1. Particle size and its distribution of cathodic electrodeposition coatings (Mv = 28.62 nm, F = 1.09)

Contact angle: Contact angle is a typical property to understand the surface energy of materials. The surface energy of a polymeric material can be estimated in terms of contact angle measurement by depositing a water drop on the surface of film and the value of contact angle depends on the chemical compositions of film surface[6,7]. The contact angles of cathodic electrodeposition coatings with and without fluorinated monomers are shown in Fig. 2. Fig. 2 indicates that the contact angle of the film of fluorinated cathodic electrodeposition coatings is increased obviously in comparison with the one of cathodic electrodeposition coatings without fluorinated monomer. The obvious increase of the contact angle is caused by the fact that more fluorine atom is introduced into a single polymer and fluorine atom tends to locate on the film surface during the film formation to minimize the interfacial energy, which can increase the hydrophobic property of polymer. The lower the surface energy is, the larger the contact angle. Therefore, it is expected that introducing fluorinated monomer with more fluorine atom into a single polymer can increase the hydrophobic property of polymer.



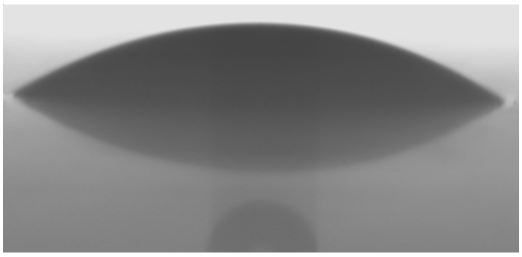
(a) 60.0º



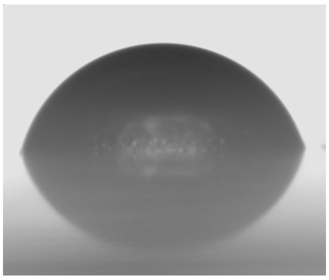
(b) 93.3º

Fig. 2. Contact angle of film of cathodic electrodeposition coatings (a) cathodic electrodeposition coatings without fluorinated monomer; (b) cathodic electrodeposition coatings with 10 % fluorinated monomer)

Chemical resistance: The glass slides coated with fluorinated cathodic electrodeposition coatings were immersed into a solution of 5 % (wt %) H_2SO_4 at room temperature for 24 h. Then, the glass slides were washed with distilled water and dried at 100 ºC. The contact angle of polymer film was examined and shown in Fig. 3. In comparison with Fig. 2, results indicate that the reducing degree of the contact angle is decreased when the fluorinated monomer is introduced, implying the increased chemical resistance of polymer film. The increased chemical resistance is attributed to more fluorine atoms in the molecule of the latex. The long side chain of C-F bond makes the fluorinated moieties accede to the outermost layer because of its low surface energy. The fundamental chain of C-C is mostly enclosed with fluorine atom intensively and the closer spiral structure is formed to protect C-C against impacting when more fluorine atoms are combined with the fundamental chain of C-C in the molecule.



(a) 33.9º



(b) 81.9º

Fig. 3. Contact angle of film of cathodic electrodeposition coatings (a) cathodic electrodeposition coatings without fluorinated monomer; (b) cathodic electrodeposition coatings with 10 % fluorinated monomer)

Conclusion

The fluorinated epoxy acrylic cathodic electrodeposition coatings were prepared by mixing blocked polyisocyanate and cationic resin. The cationic resin was prepared *via* copolymerizing of hexafluorobutyl acrylate, methyl methacrylate, butyl acrylate and glycidyl methacrylate and opening loop and acidizing the prepared terpolymer. The appearance of the prepared cathodic electrodeposition coatings is translucent and accompanied with blue-fluorescence. The stability of cathodic electrodeposition coating water suspension is high. The water-resistance and chemical resistance of cathodic electrodeposition coatings are improved.

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