



Surface properties and self-cleaning ability of the fluorinated acrylate coatings modified with dodecafluoroheptyl methacrylate through two adding ways

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ABSTRACT

The fluorine-modified acrylate resin was synthesized by solution radical polymerization using dodecafluoroheptyl methacrylate (DFMA) and other acrylate monomers. The same weight of DFMA was added into the reaction through two different ways: (1) adding DFMA as bottom monomer (AFBM); (2) adding DFMA drop by drop (AFDD). The different coatings were prepared by blending the fluorine-modified acrylate resin with the curing agent. Compared with AFDD coating, the AFBM coating exhibited better self-cleaning ability which was confirmed by the self-cleaning test through measuring the specular gloss of coatings before contamination and after water droplets flushing. The fluorine content at the surface of AFBM coating increased from 15.1 at.% to 23.1 at.%, while the water contact angles increased by 8° and the sliding angles decreased obviously. Furthermore, the contact angles and self-cleaning ability of the coatings prepared with DFMA through two adding ways both decreased after scrubbing by wet cotton because of the decrease of the surface fluorine atom content. It could be concluded that high contact angles and low sliding angles were advantageous for coatings to obtain excellent self-cleaning ability.

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1. Introduction

The self-cleaning ability of coatings is important to prevent or remove pollution, and is already applied in automobiles, ships, buildings, self-cleaning windows, textiles and solar panels [1–7]. The generalized use of this self-cleaning technology will allow surface to maintain the aesthetic appearance unaltered over time [8] and result in large decreases in maintenance costs at the same time. A number of fluorinated coatings widely used for the self-cleaning ability have been reported due to their extremely low surface energy. Je-lk Moon et al. [9] designed fluorine-modified acrylic resins with different fluorine content, and predicted the polluting-preventive ability as well as the removability of acrylic coatings by using a peel test results. Super hydrophobic self-cleaning cellulose surfaces with multiscale structures were fabricated through the combination of ATRP of glycidyl methacrylate followed by pentadecafluorooctanoyl modification. After contamination of the surface

with carbon black powder, water droplets adsorbed the dirt and rolled off the surface when the substrate was tilted [10]. Xiaofeng Ding et al. prepared a long-term super hydrophobic self-cleaning coating which was fabricated by blending ambient-cured fluorinated polysiloxane binder with TiO₂ nanoparticles. This coating could provide long-term super hydrophobic and photocatalytic self-cleaning properties for practical applications as self-cleaning coatings [11].

Acrylate resin could also be modified with fluorine monomers [12–14] and many articles about fluorine modified acrylate resin were reported. The relationship between surface properties and the fluoromethylene chain length of the R_f groups was discussed. The authors clarified the water-repellent mechanism of the fluoromethylene number of the R_f groups [15,16]. The surface properties of latex films prepared by batch and semicontinuous emulsion polymerizations were studied in terms of hydrophobicity and sliding behavior of liquid droplets. Compared with homopolymer latex films, higher sliding angles of water droplet were observed in copolymer latex films [17]. The surfaces of films casting from core-shell fluorosilicone acrylate copolymer latexes and linear pentablock fluorosilicone acrylate copolymer solutions

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were intensively investigated. The results demonstrated that the molecular structures and in-solution aggregate structures of these well-defined copolymers had a dramatic influence on the surface structure formation, surface wetting, and adsorption behavior [18].

The adding way of fluorine monomer in the solution radical polymerization also had an important influence on the fluorinated resins and coatings. For this reason, the influences of DFMA adding ways on properties and self-cleaning ability of coatings were investigated in this work. We synthesized the fluorinated acrylate resin by solution radical polymerization and prepared the acrylate polyurethane coating. Two different adding ways of fluorine monomer were adopted in the polymerization: (1) adding DFMA as bottom monomer (AFBM); (2) adding DFMA drop by drop (AFDD). The properties of acrylate resins and coatings were measured by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), attenuated total reflectance FTIR (ATR-FTIR), contact angles, sliding angles, atomic force microscope (AFM), and X-ray photoelectron spectrometer (XPS), respectively. Furthermore, simulating the contamination and rain flushing, a self-cleaning test method was established to analyze the self-cleaning ability of coatings.

2. Experiment

2.1. Materials

Methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), styrene (St), and 2-ethylhexyl acrylate (2-EHA), were obtained commercially and used as received. Dodecafluoroheptyl methacrylate (DFMA, Harbin Xeogia Fluorine-Silicon Material Co., Ltd., China) was used as fluorine acrylate monomer. Di-tert-butyl peroxide (DTBP) used as initiator and lauryl mercaptan (K12) used as chain transfer agent, were obtained commercially. The xylene (XYL) and propylene glycol monomethyl ether acetate (PMA) were chosen as solvents. The hexamethylene diisocyanate tripolymer (N3390, Bayer) was used as curing agent. Silicon carbide (SiC) particles (Beijing Venus Ultrafine Material Co., Ltd., China) and graphite particles (Sinopharm Chemical Reagent Co., Ltd., China) were used as the contaminants.

2.2. Synthesis of fluorine-modified acrylate resins

The acrylate resins were prepared by a solution polymerization. The mixture of solvents XYL and PMA was placed in a 4-neck round type reactor fitted with a thermometer, a mechanical stirrer, a reflux condenser and a dropping funnel. The mixture of MMA, HEMA, 2-EHA, St (at a weight ratio of 1:1:1:1), DTBP, and K12 was added drop wise into the reactor over 5 h period at 150 °C. The reaction continued for 3 h after the acrylate monomers were dripped completely. The fluorinated acrylate resins were prepared by adding 10 wt.% DFMA (meanwhile decrease the equal amount of 2-EHA) into the reactor through two adding ways: (1) adding DFMA as bottom monomer (AFBM), that was adding DFMA into the reactor before heated to 150 °C, (2) adding DFMA drop by drop (AFDD), that was adding DFMA into the reactor by dropping funnel with other acrylate monomers over 5 h.

2.3. Preparation of fluorine-modified coatings

The fluorine-modified coatings (35 μm thickness) were prepared by blending the synthesized acrylate resin with the curing agent N3390. The blended was coated on a tinplate plates with a size of 5 cm × 10 cm using a spin coater and then dried in an oven.

2.4. Methods

2.4.1. Composition and structure characterizations

Fourier transform infrared spectroscopy (FTIR) and attenuated total reflectance FTIR (ATR-FTIR) spectrometric analyzer (Thermo Nicolet AVATAR, USA) were used to analyze the chemical structures of the resins and coatings separately.

Differential scanning calorimetry (DSC) data were obtained from DSC-50 (Mettler Toledo, DSC1, Switzerland). Heating rate of 10 K/min was used for a sample of 10 mg.

Atomic force microscope (AFM, Veeco DI, USA) and X-ray photoelectron spectrometer (XPS, ESCALAB 250, Thermo Fisher Scientific, USA) were employed to measure the surface roughness and do the elemental analysis of coatings, respectively.

2.4.2. Contact angles and sliding angles measurements

The contact angles of water and *n*-hexadecane (each droplet volume was 5 μL) were measured by DSA-10 (KRUSS, Germany), and the surface energy was calculated from the contact angles of the two liquids by Fowkes' equation [19]. The sliding angles were also tested by DSA-10 using 5 different volume water droplets.

2.4.3. Self-cleaning test

Simulating the dust fall and rainy condition, a self-cleaning test method was established to evaluate the self-cleaning ability of coatings by measuring the specular gloss of coatings before contamination and after water droplets flushing.

The self-cleaning test contained the artificial contamination process and the specular gloss measurement. For the deposition of contamination on the specimen surfaces, various specimens were placed in a contamination plastic chamber, measuring 17 × 40 × 30 cm. Hydrophilic SiC particles (10 μm) and hydrophobic graphite particles (50 μm) were chosen as the contaminants separately, because they were similar to natural dirt contaminations. The contaminant particles were filled in a box placed near the right of the chamber and then blew into the chamber by nitrogen. After the particles deposition, the specimen with the particles was subjected to a water reservoir. The water reservoir had six syringes with 2 mm orifices, which released the water droplets. The specimen was fixed to a tilted stage with 45° and the distance between the syringes and the specimen was constant. The flushing process of each specimen by water droplets carried out for 1 min (water volume 100 mL).

The multi-angle glossmeter (XGP 20° 60° 85°, Tianjing Xin Tong Guang Da, Co., Ltd., China) was used to test the specular gloss of coatings before the contamination and after the flushing. For each specimen, nine readings on the different point of specimen were tested and calculated on average. The average specular gloss of the specimen before contamination was marked with A, while the one after flushing was marked with B. Through the following formula (1) the specular gloss loss rate X% could be obtained. The pollution conditions of different coatings were evaluated by comparing the specular gloss loss rate of each coating.

$$X\% = \frac{A - B}{A} \times 100 \quad (1)$$

3. Results and discussion

The fluorine-modified acrylate resins were synthesized by solution radical polymerization. Fig. 1 shows the FTIR spectra of the non-fluorine acrylate resin and the fluorine-modified ones through two DFMA adding ways. 3465 cm⁻¹ is the characteristic stretching peaks of -OH, 2960 cm⁻¹ and 2875 cm⁻¹ are the characteristic stretching peaks of C-H (CH₃), 1730 cm⁻¹ is stretching vibration peak of C=O, 1601 cm⁻¹ is stretching vibration peak of benzene

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