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Full Length Article

A superhydrophobic EP/PDMS nanocomposite coating with high gamma radiation stability

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ABSTRACT

The superhydrophobic coatings with high gamma radiation stability were prepared by using epoxy/polydimethylsiloxane (EP/PDMS) resins as the matrix and silica nanoparticles as the fillers. The nanocomposite coatings exhibit superhydrophobicity with a high water contact angle (WCA) of 154° and a low sliding angle of 7°. With the amount of SiO_2 increasing from 0 to 30%, the surface shows the hierarchically structure gradually and its roughness raised from 4 nm to 278 nm. And little change in the WCA of the coatings (from 155° to 149°) was observed when the pH of the droplets varied from 2 to 14. In addition, the coatings also show good adhesion grade (5B), high hardness (6H) and outstanding stability for high dose gamma radiation.

1. Introduction

The strong penetration of ionizing radiation like X-rays, gamma-rays and neutron generated by radioisotope in nuclear environment does great harm to nearby instruments and human being. Especially, the massive long-lived and highly radioactive materials released in severe nuclear accidents like the Chernobyl and Fukushima Daiichi disaster caused great trouble for the environment [1]. The soluble and insoluble radioactive substances behave differently. The insoluble particles will be adsorbed on the surface of the materials and retained longer time [2], which brings about the second contamination through the mobile instruments and equipments such as rescue robot.

In recent years, superhydrophobic surfaces have aroused increasing interest due to their wide practical applications, such as self-cleaning [3–5], anti-icing [6], anti-fogging [7], oil-water separation [8] and anti-corrosion [9]. And many methods like electrochemical deposition [10], self-assembly [11], plasma treatment [12], chemical vapor deposition [13], sol-gel method [14–16], phase separation [17] have been tried to fabricate superhydrophobic coating. However, the mechanical stability of most of the superhydrophobic surfaces is low, and many of them even cannot withstand finger touch [18]. The low stability and complicated preparation process have hindered many of their applications. Moreover, the materials with low surface energy for fabricating superhydrophobic surfaces often contains fluorine-, alkane-, or silicone-based compounds with soft, weak or uncrosslinked bonds, which are instable towards corrosive liquids, organic solvents and even low energy UV radiation [19], let alone high energy gamma radiation [20].

Owing to excellent mechanical properties, superior solvent and chemical resistance, good dimensional stability and adhesive strength, epoxy composite is widely used in some severe environment [21–23]. And epoxy matrix composite loaded with high concentrations of high-Z fillers is also an attractive candidate for radiation shielding [24]. However, the rich hydroxyl and epoxy groups of the resins would form strong hydrogen-bonding with the water, so the coatings prepared by using the epoxy resin as the matrix usually exhibit strong hydrophilicity [25]. In order to achieve high radiation stability, adhesive strength and low surface energy, polydimethylsiloxane (PDMS), owing to intrinsic deformability and hydrophobicity is selected to modify epoxy resin in the paper. And chemistry and texture are combined to achieve superhydrophobic surfaces with silica oxide nanoparticles as the fillers. In addition, the properties of contact angle, self-cleaning, radiation and environment stability as well as the adhesion of the coatings are evaluated.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A epoxy resin (E51) was supplied by Shanghai Resin Company. Hydroxyl-terminated poly-

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dimethylsiloxane was purchased from DOW Corning with a viscosity of 25 mpa s. And 3-aminepropyltriethoxysilane (KH550), dibutyltindilaurate (DBTDL), isophoronediamine (IPDA) and silica oxide nanoparticles with a mean of 15 nm were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. 1H,1H,2H,2H-perfluorodecyltrichlorosilane(FAS-17) was got from Energy Chemical. All chemicals were used as received without any further purification.

2.2. *Preparation of superhydrophobic coating*

Hydroxyl-terminated polydimethylsiloxane, 3-aminopropyltriethoxysilane as well as dibutyltindilaurate catalyst were put into a three-necked round bottom flask together and reacted at 80 °C for 20 min. The molar ratio between the epoxy resin and PDMS is 7:3. Then SiO_2 nanoparticles treated by KH550 were dispersed in 25 ml of xylene, and mixed with the matrix to get a homogeneous solution. Then curing agent (IPDA) was added. After removing of the trapped air bubbles by vacuum, the composites were evenly distributed onto a tinplate substrate by a wire rod, and then cured at 80 °C for 4 h. The obtained composites were named as EP/PDMS-x, where x represents the mass proportion of SiO_2 in the composites. Further surface modification of EP/PDMS-25 coating was performed by soaking the sample in a ethanolic solution of FAS-17 (1 wt%) for 60 min, then dried at 60 °C for 120 min.

2.3. *Characterization and measurement*

The surface morphologies of as-prepared samples were observed by a field-emission scanning electron microscope (SEM, Hitachi S-4800) after the samples were coated with a thin film of gold. Atomic Force Microscope (AFM) observation was performed on a DI Multimode V scaning probe microscope (Veeco, USA). Fourier transform infrared spectra (FITR) were conducted on a Nicolet 5700 spectrometer from 4000 to 400 cm^{-1}. The water contact angle (WCA) and sliding angle (SA) were evaluated by using contact angle meters (JC2000D2 and JC2000D3, Shanghai Zhongchen Digital Technology Apparatus Co. Ltd.), respectively. Cross-cut adhesion was evaluated according to ASTM D3359, where grade 5B indicates the highest adhesion and 0B represents the lowest. In addition, the hardness of the coating was tested according to ASTM D3363. From 6H to 6B, the hardness of the coating decreases gradually.

2.4. *Self-cleaning test*

To evaluate self-cleaning property of the coating, dirt-removal test was carried out as the reported method [26]. An artificial dust (graphite powder) was put on a slant (7°) coating surface evenly and water droplets were then dropped on the sample to simulate cleaning model.

2.5. *γ radiation resistance*

Cobalt-60 irradiation facility with the activity of 1.5×10^4Ci was used as the irradiation resources. The as-prepared coating was irradiated in dry air at ambient temperature with a dose rate of 1.30 KGy/h, 1.55 KGy/h, 2.57 KGy/h, 5.12 KGy/h and 15.22 KGy/h for 8 h. The total doses are 1.04×10^4Gy, 1.24×10^4Gy, 2.06×10^4Gy, 4.14×10^4Gy and 12.1×10^4Gy, respectively. The WCAs, adhesion grade and pencil hardness of the coating were tested after gamma irradiation. The arrangement of irradiation chamber and specimens is shown in Fig. 1.

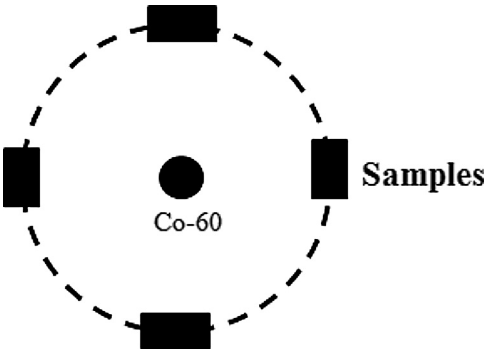

Fig. 1. Irradiation chamber and specimens geometry.

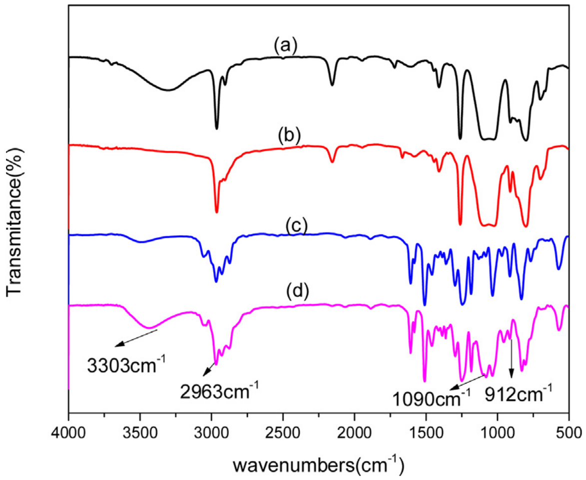

Fig. 2. FTIR spectra of PDMS (a), PDMS treated by 3-aminopropyltriethoxysilane (b), epoxy resin (c), and EP/PDMS (d).

3. Results and discussion

3.1. *Synthesis low surface energy matrix*

Polydimethylsiloxane (PDMS) was treated with 3-aminopropyltriethoxysilane first to graft amine groups, then reacted with epoxy resins to obtained low energy surface matrix. The reaction equations are sketched in Scheme 1.

FITR spectra of PDMS, PDMS treated by 3-aminopropyltriethoxysilane, epoxy and EP/PDMS resin are all shown in Fig. 2. The absorbances at 801 cm^{-1} and 1090 cm^{-1} correspond to stretching of Si—C and Si—O—Si, respectively. And the peaks at 2905 cm^{-1} and 2963 cm^{-1} are formed due to the asymmetric methyl group stretching of $Si{-}(CH_2)_3$ and $Si{-}O{-}CH_3$. The absorptions appearing at 1261 cm^{-1} are associated with the $Si{-}CH_3$ deformation vibration. After treated by 3-aminopropyltriethoxysilane, the absorbance at 3303 cm^{-1} of PDMS assigned to the —OH bond disappears, indicating the reaction between hydroxyl group and the $-OC_2H_5$. In addition, the peak of EP/PDMS at 912 cm^{-1} corresponding to the epoxy bond gets weak, attributing to the partial reaction with PDMS.

The contact angle of coating by using EP/PDMS resins as the matrix increases from 68° to 105° compared with that of pure epoxy resin, indicating the significant improvement of hydrophobicity. It should be ascribed to low surface energy PDMS migrating to the surface automatically, which serves as the wax layer as that of lotus leaf [27]. At the same time, part of epoxy and hydroxyl groups of epoxy resins, which would form strong hydrogen bonding with water, are consumed by reacting with PDMS.