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Fabrication of Ketjen black-polybenzoxazine superhydrophobic conductive composite coatings

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ABSTRACT

Superhydrophobic conductive Ketjen black-polybenzoxazine (KB-PBZ) composite coatings were prepared by a simple drop casting method with high static water contact angle (~160°), low sliding angle (~3°), and low sheet resistance (10^3 Ω/sq). The relationship between Ketjen black amounts and the structure and properties of the composite coatings was investigated. Under appropriate conditions, the composite coatings showed hierarchically structured roughness and possessed superhydrophobicity over the whole range of pH values. These coatings exhibited excellent thermal and environmental stability. Moreover, the superhydrophobic conductive composite coatings also can be obtained on various substrates such as wood, aluminum foil, paper, polyethylene terephthalate film and fabric.

1. Introduction

Water repellency of a solid surface is one of the most important characteristics in both theoretical research and industrial applications [1–3]. Superhydrophobic surfaces are generally prepared by combining surface roughness at both the micro- and nanoscales with low surface free energy materials [4–6]. Fluorine materials are usually used to produce superhydrophobic coatings, because they have extremely low surface energies and a very low polarity [7–9]. However, such materials also present potential risks to humanity health and the environment.

Polybenzoxazine [10], a new class of non-fluorine, non-silicon low surface free energy polymeric material, has attracted great research interest because it is cheaper to prepare and easier to process than fluoropolymers. It is thought a promising material to fabricate superhydrophobic surfaces [11–14]. Ketjen black is a kind of highly conductive carbon with extremely high specific surface area and branched structure. It is widely used as carbon support in fuel cells and electrochemical capacitors [15–17]. In the previous study [18], we have provided the new insights for utilizing Ketjen black in the field of superhydrophobicity. To the best of our knowledge, no work has been reported on combining Ketjen black with polybenzoxazine to prepare superhydrophobic conductive composite coatings.

Herein, we report a simple but effective approach to fabricate superhydrophobic conductive Ketjen black-polybenzoxazine (KB-PBZ) composite coatings by a drop casting method. Under appropriate conditions, the composite coatings showed rough surfaces possessing both hierarchical micro- and nano-scaled structures, the water contact angle (WCA) values of the composite coatings were about 160° and the sliding angle (SA) values were about 3°. These coatings possess superhydrophobicity over the whole range of pH values, and they were also conductive with a sheet resistance of 10^3 Ω/sq. The superhydrophobic conductive surfaces also can be performed on various substrates such as wood, aluminum foil, paper, polyethylene glycol terephthalate (PET) film and fabric.

2. Experimental

2.1. Materials

2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)propane (BA-a benzoxazine) was supplied by Shandong Yineng New Material Co., Ltd. Ketjen black EC-600JD was obtained from Akzo Nobel and used as received. Tetrahydrofuran (THF) was obtained from Sinopharm Chemical Reagent Co., Ltd.

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2.2. Preparation of superhydrophobic conductive KB-PBZ composite coatings

Superhydrophobic conductive KB-PBZ composite coatings on a glass slide were performed through a simple drop casting process. The BA-a benzoxazine (200 mg) was mixed with Ketjen black (10–100 mg) in THF (10 ml). After keeping vigorous stiring for 2 h, the coatings were prepared by drop casting the dispersion onto a glass slide and then cured in an oven at 190 °C for 1 h.

2.3. Characterization

The water contact angle and sliding angle values were measured with a DATA Physics System OCA20 instrument (Germany) at room temperature. The volume of the water droplets for WCA measurements were fixed to 4 μL. The average contact angle was obtained by measuring the contact angle of water droplets at five different places of the sample and averaging the five data points. The SA values were measured by dropping a water droplet (10 μL) onto the tilted surfaces from 4 mm height, and determined as the tilting angles at which the water droplets rolled off the surfaces. The morphologies of KB-PBZ composite coatings were observed by field emission scanning electron microscopy (Hitachi S-4800, Japan) at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained using a JEM-1230 instrument at an acceleration voltage of 120 kV. Sheet resistances were measured by the standard four-probe technique using a RTS-4 four-probe conductive meter (Guangzhou 4 Probes Tech., China).

3. Results and discussion

3.1. Superhydrophobic conductive KB-PBZ composite coatings

Table 1 listed the WCA, SA and sheet resistance values of KB-PBZ composite coatings with various Ketjen black amounts. The WCA value of polybenzoxazine was measured to be only 108 ± 2°. The BA-a benzoxazine monomer concentration was kept constants in solution while increasing the Ketjen black amount, leading to an increasing in the WCA values. At low Ketjen black amounts, the WCA values below 150°, but when the Ketjen black amount is larger than 50 mg, the KB-PBZ composite coatings show a superhydrophobicity with the WCA values over 150° and SA values below 5°. It is believed that the existence of Ketjen black with a certain amount is responsible for the superhydrophobic nature of the composite coatings. However, in our system, Ketjen black amounts that are too high (100 mg) tend to reduce the adhesion of the KB-PBZ composite coating on the glass substrate, and show a cracked structure. In this letter, we choose the optimum Ketjen black amount (50 mg) to carry out a detailed investigation, and the KB-PBZ composite coating have a WCA value of 160 ± 1° and a SA value of 3°.

Besides the superhydrophobicity, the KB-PBZ composite coatings developed in our study had conductivities in the range of 1.7×10^3–12.3×10^3 Ω/sq, varying with the BA-a benzoxazine and Ketjen black compositions. Obviously, the sheet resistances of the composite coatings decrease with the increase of the Ketjen black amounts. It is because more Ketjen black leading to better conductivities. The conductivities make the coatings not only appealing for electrostatic dissipations, but also very promising as anti-wetting sensors and superhydrophobic EMI shielding materials.

3.2. Superhydrophobicity and morphology of KB-PBZ composite coating

Fig. 1a shows optical photographs of water droplets on a KB-PBZ composite coating (50 mg Ketjen black), the behavior of the water droplets clearly reveals the superhydrophobic nature of the composite coating. Fig. 1b is the TEM image of Ketjen black, which shows a hollow nanosphere structure. It is because of its special branched structure [18]. As shown in Fig. 1c, a water droplet (4 μL) is formed at high WCA of 160 ± 1° due to the water repellency of the coating. Besides WCA, SA is another important criterion for superhydrophobic surface, Fig. 1d shows a water droplet (10 μL) rapidly rolling off on the slightly tilted (3°) composite coating.

Fig. 2 presents the typical SEM images of the KB-PBZ composite coatings on the surface of glass slide. It can be observed that the KB-PBZ composite coating exhibits a rough surface (Fig. 2a). There exists a vast number of protruding islands of several or several tens of micrometers. The enlarge SEM images (Fig. 2b and c) show that each microisland on the polybenzoxazine surface is covered with numerous Ketjen black nanospheres. The side-view SEM images in Fig. 2d and e show that the composite coatings are also rough, the Ketjen black exposed on the protruding and lower surfaces, which increasing the surface roughness. Furthermore, Ketjen black has a highly branched and porous structure, leading to a higher porosity and surface roughness. The KB-PBZ composite coatings have abundant hierarchical micro and nano-structures, which is regarded as the critical feature of superhydrophobicity. The composite coatings exhibit both high WCA and low SA values, because with the hierarchically structure roughness, a large amount of air could be trapped at coating surface efficiently. When a water droplet sits on the top of composite coatings, the contact area of water with coatings is only the part of protruding microislands, and the protruding microislands composed of nanospheres can further reduce the real contact area. Therefore, the Ketjen black amounts play a key role on the superhydrophobicity. Fig. 2f is the composite coating surface which has a low Ketjen black amount (20 mg), we can see less Ketjen black on the surface while the surface is rough when comparing with Fig. 2c. That is the reason why the WCA of the coating is lower than 150° and its hydrophobicity are not very well.

3.3. Properties of KB-PBZ composite coatings

Fig. 3a is the relationship between pH and WCA on the KB-PBZ composite coating. It is showed that the surface possesses superhydrophobic properties not only for pure water but also for corrosive water under both acidic and basic conductions. Over the whole pH range, all the WCA values are above 150°, and the water droplet can be moved easily when the surface is slightly tilted. It is suggested that these coatings can be used in a wide pH range of corrosive water.

Table 1
Water contact angle, sliding angle, and sheet resistance (R_s) of composite coatings with various Ketjen black amounts.

THF (ml)	BA-a benzoxazine (mg)	Ketjen black (mg)	WCA (°)	SA (°)	R_s (10^3 Ω/sq)
10	200	0	108 ± 2	–	–
10	200	20	142 ± 3	>10	12.3 ± 0.5
10	200	50	160 ± 1	∼3	3.9 ± 0.4
10	200	80	158 ± 2	∼2.5	2.4 ± 0.6
10	200	100	160 ± 2	∼3	1.7 ± 0.2