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Facile fabrication of superhydrophobic films with fractal structures using epoxy resin microspheres

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ABSTRACT

A simple method has been developed to fabricate superhydrophobic surfaces with fractal structures with epoxy resin microspheres (ERMs). The ERMs is produced by phase separation in an epoxy-amine curing system with a silica sol (SS) dispersant. The transparent epoxy solution becomes cloudy and turns into epoxy suspension (ES) in this process. The fractal structure (two tier structure) generated by synthetic epoxy resin microspheres (ERMs) and deposited nanoincrutations on the surfaces of these ERMs, which have been observed by scanning electron microscope (SEM). The curing time of ES is an important condition to obtain films with good comprehensive performances. Superhydrophobic films can be prepared by adding extra SS into ES with a curing time longer than 5 h. The optimal curing time is 10 h to fabricate a film with good mechanical stability and high superhydrophobicity. In addition, a surface with anti-wetting property of impacting microdroplets can be fabricated by prolonging the curing time of ES to 24 h. The gradually decreased hydrophilic groups resulted from a longer curing time enable the surface to have smaller surface adhesions to water droplets, which is the main reason to keep its superhydrophobicity under impacting conditions. The coated surface is highly hydrophobic and the impacting water droplets are bounced off from the surface.

1. Introduction

Superhydrophobic property has gained increasing attention in recent years for its potential applications in various fields, including self-cleaning [1], anti-fouling [2], dropwise condensation heat transfer [3,4], antifogging [5], and delayed frosting [6,7]. Superhydrophobic surface is defined as a surface that has a static water contact angle (CA) larger than 150° and contact angle hysteresis (CAH) smaller than 10°. Surface roughness and surface hydrophobicity are the two prerequisite conditions to form an ultra-hydrophobic surface. Lotus leaf is a well-known superhydrophobic surface, consisting of convex cell papillae and randomly oriented hydrophobic wax tubules [8]. This hierarchical structure is crucial to obtain the robust anti-wetting property for lotus leaf surface.

Various methods have been used to fabricate superhydrophobic surface, such as layer-by-layer assembly [9], photolithography [10], chemical etching [11,12], etc. These approaches are limited in practical applications because of their complexities. They need strict conditions or sophisticated equipment, which is difficult for mass production. Recently colloidal particles and epoxy resin have been widely used to fabricate superhydrophobic surfaces. The former practice can provide roughness and the latter method can provide good bonding effect [13–16]. Colloidal particles have attracted great attention in constructing ultra-hydrophobic surface for their controllable size [17,18] and surface compositions [19]. Ming [20] fabricated a dual-size superhydrophobic surface with silica-based raspberry-like particles. These particles covalently bonded to an epoxy-based polymer matrix. The roughened surface had an advancing contact angle of 165° and a roll-off angle of 3° after being chemically modified with a layer of poly(dimethylsiloxane) (PDMS). Psarski [13] proposed an accessible method to construct superhydrophobic coatings with an epoxy resin composite. Glass microbeads and Al_2O_3 nanoparticles were used to generate surface roughness. The composite exhibited superhydrophobicity after wet chemical modification. Xiu [15] reported the use of epoxy resin and nanoparticles to form a composite surface. He found that the removal of epoxy resin by O_2 plasma etching for 10 min could produce a rough surface with good mechanical stability. Superhydrophobic property was then achieved by fluoroalkyl silane treatment.

Abbreviations: CA, contact angle; CAH, contact angle hysteresis; EDS, energy disperse spectroscopy; ES, epoxy suspension; ERMs, epoxy resin microspheres; FT-IT, Fourier transform infrared spectra; HMDS, hexamethyldisilazane; SEM, scanning electron microscope; SS, silica sol; TEOS, tetraethoxysilane.

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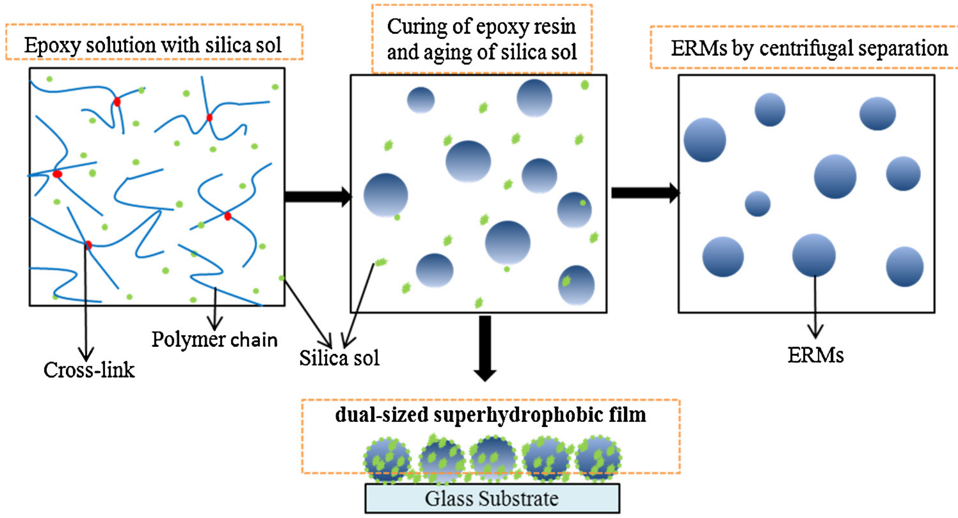

Fig. 1. A schematic diagram for the preparation of ERMs and their superhydrophobic film.

Among these fabricating strategies, epoxy resin usually acts as a bonding media. The surface layers of epoxy resin on composite coatings have to be removed to generate roughness. Chemical modification of these roughened surfaces is necessary to obtain superhydrophobicity. Thus, these anti-wetting surfaces have to be fabricated in multi-steps, which is complicated. In this work, a facile fabrication method is proposed to prepare superhydrophobic films with epoxy resin microspheres (ERMs). Epoxy resin is used not only as a bonding stuff, but also as a source of surface roughness by generating ERMs. The previously necessary step of removing the surface layer of epoxy resin can be avoided, which greatly simplifies the preparation process and creates the maximum use of the epoxy resin.

Polymer microspheres can be prepared by direct polymerization of monomers, such as emulsion polymerization, dispersion polymerization and precipitation polymerization [21–24]. In this work, ERMs are synthesized by phase separation in an epoxy-amine curing system with silica sol (SS) [25] dispersant. The silica sol has two functions in this curing system. First, it acts as a dispersing agent for forming stabilized epoxy resin microspheres. In addition, the alkali curing system promotes the aging of SS which has an increased crosslinking degree [26]. The aging products of sol deposited on these surfaces of microspheres can generate a secondary structure of the superhydrophobic coating. To the authors' best knowledge, it's the first time anti-wetting films with ERMs have been synthesized in this method. The overall procedure is illustrated in Fig. 1. First, silica sol (SS) is prepared [25]. Epoxy resin and polyamide are dissolved in SS to form a homogeneous solution. This solution will become cloudy and turn into an epoxy suspension (ES). In this process, ERMs generate and gradually grow up as the curing process continues. They can be obtained from the ES by centrifugal separation. The curing time of ES has significant influence on the properties of coatings. A superhydrophobic particulate film is formed by spreading ES (with a proper curing time) on a clean glass substrate. This is one-step fabrication of anti-wetting surfaces by prolonging the curing time. To obtain a film with better comprehensive performances, a two-step method is used which will be discussed in this paper.

Compared with other strategies of constructing superhydrophobic surfaces, the method proposed here has many advantages. First, it is a novel and simple method to fabricate superhydrophobic surfaces with two-tier structures. The structure can also be called fractal structure. A surface with anti-wetting property for impacting microdroplets is also fabricated in this method just by adjusting the curing time. At the same time, a new route is formed without complicated procedures to synthetize epoxy microspheres. Second, superhydrophoic property is achieved without using extra low energy substances. Besides the hydrophobic silica sol, the consumption of hydrophilic polar groups and the grafting of methylene long chains from polyamide curing agent will make these microspheres hydrophobic. Third, the prepared epoxy superhydrophobic painting is applicable to a wide range of base materials such as aluminum, copper, glass and plastic. The whole process is easily controlled without relying on precise instruments. Thus, it is a simple and effective method to manufacture superhydrophobic materials which can be down by mass production.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) is purchased from Guangzhou Chemical Reagent Factory. Hexamethyldisilazane (HMDS) and ethanol are purchased from Sinoparm Chemical Reagents Co., Ltd. Bisphenol Epoxy resin (E-44) and low molecule polyamide curing agent of commercial-grade is purchased from Yueyang petrochemical plant, China. Distilled water is prepared by a Purescience water purification system.

2.2. Fabrication of silica sol

Hydrophobic silica sol (SS) is prepared first [25]. TEOS (2.1 ml) is dripped into ethanol (30 ml). After being vigorously stirred for 10 min, HMDS (2.0 ml) is slowly added to the above mixture and stirred for 0.5 h. Then deionized water (3.0 ml) is dropped into the mixture with the same stirring rate at room temperature (16 °C). Then the reaction of the mixture is carried out during a constant stirring rate for 2 h to form a transparent sol. The aging of SS is necessary before it is used.

2.3. Synthesize of epoxy resin microspheres (ERMs)

Epoxy resin (0.63 g) and polyamide (0.33 g) are dissolved in silica sol (9 ml) with magnetic stirring until forming a homogeneous transparent epoxy mixture. The weight ratio of epoxy resin/hardener is 1.9. The curing reaction of epoxy and amine is carried out at room temperature without stirring. The homogeneous solution turns into epoxy suspension (ES) as the reaction continues.

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