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Facile design and fabrication of highly transparent and hydrophobic coatings on glass with anti-scratch property via surface dewetting

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ABSTRACT

Highly transparent hydrophobic coatings with scratch-resistant property attract tremendous interest from both scientific research and practical applications. The present study demonstrates that hydrophobic coatings with high transmittance and anti-scratch performance on glass substrates can be easily created by dewetted epoxy structures in large scale, followed by the attachment of a low surface energy material. The influence of epoxy solution concentrations on the surface dewetted structures, as well as the hydrophobicity and transmissivity of glass substrates were investigated. It was found that the epoxy solution concentration of 5% combined with a low surface energy material coating on glass exhibited the highest contact angle of ~113°. UV–vis spectrum studies indicated that the coatings fabricated by our method had almost the same transmittance as that of the glass substrate. In addition, nano-scratch test illustrated that the prepared coating was capable of delaying crack generation, further strengthening the glass surfaces. Furthermore, our approach also facilitates the large-scale fabrication of hydrophobic anti-scratch coatings on glass as demonstrated by the preparation of mobile phone screen coatings. The detailed mechanism of large-scale hydrophobic coatings on glass with high transmission and anti-scratch performance was carefully elaborated.

1. Introduction

Hydrophobic coatings have been widely used in industrial applications, such as anti-corrosion [1,2], self-cleaning [3–5], anti-icing [6,7], oil-water separation [8,9] etc. due to their unique low surface energy performance. Inspired by the lotus leaf which has a waxy surface with micro-nano levels roughness, research efforts have been increasingly focused on the combination of low surface energy materials with multi-level micro-nano structures to achieve the surface hydrophobicity [10–15]. Essentially, there are two indispensable requirements for fabricating hydrophobic coatings: one is the low surface energy material and the other one is the micro-nano hierarchical structure. For example, Takahara et al. [16] successfully prepared "non-sticky" superhydrophobic surface via self-assembly of low surface energy fluoroalkyl phosphonic acid on the alumina gel film with hierarchically micro-nano structures. Kim et al. [17] fabricated a superhydrophobic, robust, hierarchical alumina nanowire structure with large areas by combining an anodization process with self-assembly of low surface energy fluorosilane monolayers, as well. Therefore, from the above discussion, it may be concluded that it is necessary to combine low surface energy materials with micro/nanostructure surfaces together to prepare hydrophobic coatings.

There are two main approaches to make transparent hydrophobic coatings. One is the Bottom-up method, such as electrostatic spinning [18], sol-gel [19] process, chemical vapor deposition [20], self-assembly [21], etc. The other one is the Top-down method, like plasma treatment [22], template method [23], etching method [24], lithography patterning [25] etc. As an easy and simple approach, the sol-gel process has attracted lots of attention to fabricate hydrophobic coatings through preparing coarse surfaces with silica and subsequently modifying with low surface energy materials [7,14,15]. However, most of these methods require complicated process control, special equipment, long period or expensive raw materials, limiting the large-scale productions.

Among the commonly used sol-gel methods, fabricating surfaces with different levels of micro and nano-structures will definitely decrease the transparency of coatings due to the extra light scatterings caused by the microstructures on the surfaces. Wang et al. [26] fabricated the superhydrophilic coating on glass via nylon/silicon dioxide and polyurethane/titanium dioxide composites. However, the coatings

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exhibited a quite poor light transmittance performance in spite of the excellent wear resistance. Even in some cases the transparency can be managed, it is still a challenge to prepare large-scale transparent hydrophobic coatings [27,28]. Therefore, it prevents the hydrophobic coatings to be used for the glass protection which requires ultrahigh transmittance to be applied in mobile phones, automobiles, spacecrafts, etc. As a result, fabricating highly transparent hydrophobic coatings, especially using an economical and simple method, is an urgent need.

Besides the need for high hydrophobicity and transmissivity, the anti-scratch property for coatings is of equal importance for practical applications due to the inevitable scratch damages in service. It has been well documented that polymer coating is a good choice for the scratch-resistant protections on diverse substrates [29–32]. In practice, epoxy coatings have been extensively used in glass protections [33–35] and adhesive layers [26,36] due to the strong cohesive strength of epoxy coatings and intense adhesion to the glass. Moreover, many inorganic filler can be used to further strengthen epoxy resin, such as carbon fiber [37,38], graphene [39], graphene oxide [40], silica nanoparticles [41], carbon nanotubes [42,43], etc. Hand et al. [33] used dip coating technique to create epoxy coatings on the glass substrate. They found out that the concentration of the epoxy solution played a significant role in the degree of strengthening that could be realized via their coating. Nevertheless, to our knowledge, there are only few researches about using different concentration of epoxy solutions to construct diverse micro-nano hierarchical morphologies for the study of hydrophobic coatings on glass substrates. And this type of epoxy coatings with different surface roughness will be destined to influence the hydrophobicity of the applied surfaces [44–46].

In this study, a two-step technique was developed to prepare highly transparent, hydrophobic, and scratch resistant coatings on glass. The micro/nanostructures of the epoxy coatings on the glass substrates were firstly created via surface dewetting [47–49] to obtain rough hierarchical surfaces. Subsequently, a low surface energy material was painted on the coarse epoxy surfaces. The influence of different epoxy concentrations on the hydrophobicity and transmissivity of the glass substrates was investigated. The detailed mechanism of hydrophobic coatings on glass with high transmissivity and anti-scratch performance was carefully discussed. It can be deductive that such low cost and simple hydrophobic coatings with high transmittance and anti-scratch performance based on epoxy will have great potential to be used in large-scale glass protections and many optical applications.

2. Experimental

2.1. Materials

E-44 epoxy resin was bought from Shenzhen Jitian Chemical corporation. Polyetheramine D230 curing agent was purchased from Aladdin Chemical corporation. Low surface energy material, heptadecafluorodecyl triethoxysilane solution (FS), was provided by Shenzhen EUBO New Material Technology Co., Ltd. Acetone was bought from Shanghai Lingfeng Chemical Reagent Corporation. The microscope glass slides were used as the glass substrate and the mobile phone screen were also treated for the demonstration of practical use. Before conducting experiments, the glass substrates were washed by an ultrasonic cleaner with acetone for 30 min and deionized water to remove possible impurities. All reagents were used as received.

2.2. Sample preparation

The amounts of E-44 epoxy resin and D230 amine curing agent were 100 and 26 parts by weight, respectively. The resultant mixture was dissolved in acetone to obtain epoxy solutions with different concentrations, namely 0.01%, 0.1%, 0.5%, 1%, 3%, 5%. For example, 0.01% represents that the total weight concentration of epoxy monomer and curing agent is 0.01%, and the weight concentration of acetone is 0.99%. The mixtures were stirred for 20 min and ultrasonicated to obtain uniform and transparent dispersion systems. The glass slides ($25 \times 25 \times 1$ mm) were vertically dipped into the solutions for 10 s and then vertically hung in vacuum oven to be cured. The curing procedure was 70 °C for 2 h and 120 °C for 2 h. FS with 5 μl calculated by pipette (Eppendorf Research plus, Germany) was dropped onto the glass substrates previously coated with different epoxy solutions, and finally dried in the vacuum oven at 70 °C for 2 h. All the experiments are carried out at 25 °C and the relative humidity is about 80%.

2.3. Characterization

The morphology of the original epoxy coating on the glass substrate was observed by optical microscopy (OM, Leica, Germany). The surface topological structures and surface roughness were conducted at room temperature via atom force microscopy (AFM, Bruker, USA). The scanning speed is 0.1 Hz/s with tapping mode. AFM images were obtained under a resolution of 512×512 data points. The contact angle was investigated by a contact angle meter (VCA optima, USA) with deionized water droplets of about 2 μl at ambient temperature. The contact angle values were obtained at five different positions for each sample to obtain the mean value. The transparency of different coatings on glass substrates was performed using a Lambda 950 UV–vis-NIR spectrophotometer (PerkinElmer, USA). The nano-scratch test was performed on the Nano Indenter G200 with a diamond Berkovich tip. The scratch load increased linearly from 0 mN to 10 mN at a constant scratch velocity of 30 um/s over a distance of 500 um. The real-time scratch depth during the scratch and the residual depth after scratch were documented and plotted vs. the increasing load and the scratch distance. At least five tests were conducted on each sample to obtain more consistent results.

3. Results and discussion

3.1. The morphology of original epoxy coating on the glass substrate

The surface morphology of the epoxy coating on glass substrates prepared from the epoxy solutions of different concentrations is shown in Fig. 1. As shown, when the epoxy concentration is 0.01% and 0.1%, only some disconnected small island droplets on glass substrates can been seen, which indicates that the epoxy coverage on the glass substrate is very low due to the limited amount of epoxy used. It can also be attributed to the low viscosity and fast absorption of epoxy monomer and curing agent molecules, which makes them rapidly spread out on the glass substrate. With increasing the concentration of the epoxy solutions, the island droplets size and density are obviously enhanced. This indicates that large amounts of epoxy are able to be coated on the glass substrate, which can be ascribed to the fact that more epoxy monomer and curing agent molecules are adsorbed to the glass substrate and thus form more nucleating points for the growth of epoxy island droplets. From the above phenomenon, it is suggested that the epoxy concentration is critical for the formation of the surface distinguished structures on glass, which is the typical surface dewetting behavior [50]. Surface dewetting is the procedure by which the unstable thin (≈ 100 nm) liquid films spontaneously separate on the substrate, driven by unfavorable intermolecular forces at the interface between the two materials [51–53]. The unstable film is able to break apart into holes that develop with time, eventually converting the film into a number of isolated droplets [48]. It is commonly used in creating patterned and biomimetic surfaces. In this case, the surface pattern is determined by the solid (epoxy and curing agent) concentration in acetone and increased liquid viscosity caused by acetone evaporation [54]. As observed, different concentration of the epoxy solutions is able to create various surface morphologies with island droplets of different sizes and size distributions that are exhibited in Fig. 2. The higher the concentration of the epoxy solutions in acetone is, the larger the size of