Composites Science and Technology 125 (2016) 55–61

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

A facile and fast approach to mechanically stable and rapid self-healing waterproof fabrics

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ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form
21 January 2016
Accepted 25 January 2016
Available online 28 January 2016

Keywords:
Fabrics
Smart materials
Functional composites
Durability

ABSTRACT

The design of multifunctional materials with durability under extreme conditions has raised considerable interest for their highly practical potential. Thus, we developed an efficient and technically simple method to prepare easily repairable and rapid self-healing superhydrophobic fabrics, which only involves one-step coating of polyfluorowax (PFW)/graphite fluoride (GF) complexes. The resulting waterproof fabrics can be easily repaired without any complicated and expensive fabrication procedures. Importantly, the fabrics with a self-healing function can rapidly and repetitively restore the superhydrophobicity when the hydrophobicity is damaged owing to the regenerated fresh surface on the fibers induced by heating. Furthermore, the fabrics can maintain their water repellency even was seriously damaged during the abrasion and mechanical stretch tests. In addition, the self-healing fabric can be further dyed and still exhibits satisfactory durability against strong acidic or alkaline, high temperature and humidity, freezing environment and long-term UV exposure.

1. Introduction

Textiles such as cotton or polyester fabrics are worldwide used, however, they are water absorbing and easily stained, which restrict their practical application. To overcome their disadvantages, functional modification of textiles to render fabrics superhydrophobicity and anticontamination has generated particular academic and commercial interest due to their usage in designing innovative and higher value textiles for applications in harsh conditions, such as self-cleaning textiles, water resistant apparel, antibacterial textiles, and so forth [1–5]. A useful and widely practical approach to design superhydrophobic surfaces involves the fabrication of appropriate roughness and low surface energy. Currently, great efforts have been made to design superhydrophobic fabrics [6–8], while commercially available superhydrophobic fabrics are still rare. Waterproof textiles would lose their non-wettability permanently when applied to a special chemical environment or physical rubbing. The low durability hampers their massive applications [8–10].

Recently, some strategies have been developed to improve the chemical and mechanical stability of the superhydrophobic materials. One strategy is enhancing the attachment between substrates and low surface energy materials [11–13]. We have reported an environmental durability and mechanical resistant superhydrophobic cotton fabric for oil/water separation via in situ vapor phase deposition [5]. Additionally, establishing the chemical bonds between modified materials and fabrics is also considered a serviceable method and has exhibited good improvement [14–16]. Another strategy is preparing easily repairable superhydrophobic materials. A scratched surface can be easily repaired by deposition of new material over the damage via a simple routine [8,17]. By comparison, a more attractive approach to tackle low durability problem is biomimetic self-healing without additional deposition of hydrophobic component [21,22]. Based on the encapsulation of the hydrophobic component in the pores of rough porous materials, self-healing surfaces maintain long-term wetting stability by gradual release of these hydrophobic small molecules to the damaged surface [18–20]. Generally, the release of hydrophobic molecules is usually induced via high humidity, temperature, and pH changes. Sun et al. prepared a self-healing superhydrophobic coating by chemical vapor deposition (CVD) of fluoroalkylsilane in

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http://dx.doi.org/10.1016/j.compscitech.2016.01.021
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porous materials. After damaged, the superhydrophobicity restored spontaneously derived from the migration of fluorinated substance to the surface [18]. Wu et al. reported a self-healable superhydrophobic cotton fabric prepared by means of a radiation-induced graft polymerization technique. The superhydrophobicity could be regenerated by steam ironing after the mechanical damage [16]. While self-healing superhydrophobic materials have been successfully prepared via several methods, unfortunately some disadvantages still hamper their practical application. On the one hand, migration of hydrophobic compounds used to repair damaged surfaces are often expensive and toxic or irritants. Moreover, the long-chain perfluorinated materials have a documented ability to bio-accumulate and the potential adverse effects on environment and human health [23–25]. On the other hand, high cost, time-consuming procedures, and long-time requiring for self-healing process also restricted their commercial applications. Thus, develop a low cost, environmentally benign and time-saving method to fabricate superhydrophobic materials with both easily repairable and rapid self-healing properties is urgent.

Herein, we provide an extremely fast and simple route to fabricate superhydrophobic fabrics with function of easy repairability and rapid self-healing. The waterproof fabrics with high contact angle (CA) of 157.7° are achieved by dip-coating hydrophilic fabrics with PFW/GF composite suspension. Use of PFW and GF with inherent inertness is approved for minimizing bio-accumulation risks associated with long-chain perfluorinated materials. The added superhydrophobicity doesn't influence the fabrics' further dyeing property, which is usually ignored. More importantly, the fabrics display excellent self-healing ability and are able to recover their superhydrophobicity rapidly in just 3 min at 110 °C even after 15 cycles of O_2 plasma-etching damage treatment. Besides, the superhydrophobic fabrics endure mechanical stretch and more than 600 cycles of abrasion using sandpaper (1000 mesh) and show long-term stability at extreme conditions. Thus, this durable and rapid self-healing fabric shows potential application as a multifunctional advanced textile.

2. Materials and methods

2.1. Materials

Polyfluorowax (PFW-150, Mean Particle Size: 4.0–6.0 μm (used in our study); PFW-120, Mean Particle Size: 8.0–10.0 μm) was provided by Micro Power Inc., USA. Graphite Fluoride (GF) with a fluorine content of 63.5% was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Commercially available fabrics were cleaned with acetone and deionized water sequentially before use.

2.2. Fabrication of self-healing superhydrophobic cotton fabrics

PFW and GF with a mass ratio 0.75:1 were added in mixed solvent ($V_{ethanol}:V_{acetone}:V_{ethyl\ acetate} = 1:1:1$) under stirring at ambient temperature and then ultrasonic for 20 min. Cotton fabrics were immersed in ready suspension for 3 min and then were placed to dry in an oven for 20 min at 125 °C.

2.3. Self-healing test

The samples were treated using a plasma machine (Diener Electronic, Germany) at ambient temperature for 2 min to simulate the surface chemistry damage. Such plasma etching treatment could render the sample superhydrophilic (contact angle, 0°). After that, the plasma-treated samples were annealed in an oven for 3 min at 110 °C to restore their superhydrophobicity.

2.4. Characterization

KrüssDSA100 (Krüss Company, Ltd., Germany) apparatus was used to measure CA of water droplets with a volume of 5 μL at ambient temperature. The shedding angle (SA) is used instead of sliding angle according to a previous reported method [26,27]. In essence, a water droplet of defined volume is released onto the substrate from a defined height. The minimum angle of inclination at which the substrate needs to be tilted for the drop to completely roll or bounce off the substrate is determined. Hydrodynamic diameters (D) was measured on a particle size analyzer (Zetasizer Nano ZS, Malvern Instruments, UK) equipped with a 632.8 nm He–Ne laser by dynamic light scattering (DLS) technique. Fourier transform infrared (FTIR) spectra were collected on a Bruker IFS66 V/S spectrometer. Photoelectron spectroscopy (XPS) was obtained on an ESCALAB250xi spectrometer equipped with a focused monochromatic Al X-ray source (1486.6 eV). The morphology of the surface was observed by field-emission scanning electron microscope (JEOL JSM-6701F FESEM). The high temperature and humidity test was carried out in an alternating temperature and humidity test chamber (Wuxi Jinhua Testing Equipment Co., Ltd., China). The axial tensile force was provided by an electronical universal material testing machine DY35 at a speed of 50 mm/min. The optical images were captured by a digital camera (Canon).

3. Result and discussion

Robust and rapid self-healing waterproof fabrics are expected to be of interest for their usage in designing innovative and higher value textiles. In our study, we used PFW and GF, which has non-toxic degradation products compared with long-chain perfluorinated compounds as hydrophobic agents. Their chemical components were verified by FTIR (Fig. S1). The properties and processing of PFW were discussed thoroughly in supplementary materials. To our knowledge, the use of GF has not been reported in preparation of superhydrophobic surfaces until now. The superhydrophobic fabrics could be obtained via an efficient and technically simple solution-dipping method in less than 1 h. Therefore, they can be repaired easily after damaged, which can extend the long-term applications of superhydrophobic fabrics. Moreover, the approach shows good comparability with a variety of substrate materials (see supplementary materials Figs. S5–S9).

3.1. The superhydrophobic mechanism of coated fabrics

The morphological information of pristine and coated fabrics was investigated by FESEM. Fig. 1a and b indicate that the fibers of uncoated fabric are smooth and exhibit micro-scale roughness inherent. Additionally, numerous gaps between the fibers observed. The PFW/GF granules were deposited on the fibers and in the spaces between fibers via physisorption after a dip-coating procedure. After heating, the granules melted resulting in well covered and larger fibers. As shown in Fig. 1d, bumps were obviously observed on the coated fiber leading to rougher surface. The enhanced roughness in conjunct with the micro-scale roughness inherent in the fabric weave is vital to obtain super-repellent fabrics.

For further understand the superhydrophobic mechanism of coated fabrics, their chemical components were verified by FTIR and XPS. As illustrated in Fig. 2a, the vibration peaks at 2918 cm^{-1}, 2850 cm^{-1} and 1710 cm^{-1} appeared, which were attributed to $-C-H$ stretching vibrations of methylene and $-C=O$ stretching vibrations, respectively. A new peak corresponding to C–F stretching vibration was also observed at 1209 cm^{-1} for the coated fabrics. In addition, the intensity of the peaks at $-OH$ (3422 cm^{-1}),