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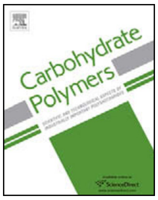

Preparation and characterization of superhydrophobic organic-inorganic hybrid cotton fabrics via γ-radiation-induced graft polymerization

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ABSTRACT

A new kind of non-fluorine-based organic-inorganic hybrid superhydrophobic cotton fabric was successfully prepared by simultaneous radiation-induced graft polymerization of γ-methacryloxypropyl trimethoxy silane (MAPS) and subsequent end-capping modification with hexamethyldisilazane (HMDS). The chemical structure and surface topography of the pristine and modified cotton fabrics were investigated in detail by ATR-FTIR, XPS, ^{29}Si NMR, SEM and TGA to confirm that the graft reaction and end-capping modification had taken place. The above results demonstrated that the grafting polymerization and following end-capping reaction were completed, and a grafting layer was immobilized onto the surface of the cotton fabric. Surface wettability measurement and oil-water separation showed that the modified cotton surface not only exhibited the superhydrophobicity with a water contact angle of 165°, but also afforded a high efficiency of oil-water separation (96%). In particular, this modified cotton fabric retains superhydrophobicity even after 30 laundering cycles or 400 cycles of abrasion.

1. Introduction

Superhydrophobic surfaces with a water contact angle (WCA) larger than 150° have been extensively investigated due to their importance in both academic research and industrial applications (Duan et al., 2011; Gao & McCarthy, 2006; Kulkarni, Ogale, & Vijayamohanan, 2008). Many superhydrophobic phenomena can be observed in some plants and animals (such as the lotus leaf, gecko, rose, water strider, etc.) in nature, and one of the most typical representations is the "lotus effect" (Michielsen & Lee, 2007). Inspired by the lotus leaf structure, numerous superhydrophobic surfaces have been developed based on different materials using various methods and techniques. Amongst superhydrophobic surfaces, water-repellent textiles show great potential for practical applications, and many researchers have attempted to impart superhydrophobicity to the surface of natural and synthetic textiles (Liu, Xin, & Choi, 2012).

Today, cotton fabric is widely used in daily life due to its multiple porosity, softness, comfort and breathability (Shateri-Khalilabad & Yazdanshenas, 2013). However, due to the large number of hydroxyl groups on its surface, the cotton fabric can be easily wetted by water. It is expected that cotton fabric endowed with superhydrophobic properties, called "superhydrophobic cotton fabric" (SCF), could be used in water repellent materials, self-cleaning fabrics, oil-water separation materials and other fascinating functional materials (Teisala, Tuominen, & Kuusipalo, 2014). As is well-known, a superhydrophobic surface results from water-repellent double structures on surface, which are attributable to two physical characteristics: surface roughness owing to the micro-/nano-structures and hydrophobicity due to waxy materials on top of the rough structures (Bae et al., 2009; Feng et al., 2002). Hence, the superhydrophobic coatings on SCF must have an appropriate surface roughness at or below micrometer level along with a low surface energy. Several methods, including dip-coating (Bayer et al., 2011; Li, Xing, & Dai, 2008), spray-coating (Mertaniemi, Laukkanen, Teirfolk, Ikkala, & Ras, 2012; Teisala et al., 2012), poly-

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merization techniques (Nyström et al., 2009; Nystrom, Lindqvist, Ostmark, Hult, & Malmstrom, 2006; Tragoonwichian, Kothary, Siriviriyanun, O'Rear, & Yanumet, 2011), in-situ nanorod/particle growth (Zimmermann, Reifler, Fortunato, Gerhardt, & Seeger, 2008), sol-gel (Gan, Zhu, Guo, & Yang, 2009; Sheen et al., 2009), chemical vapor deposition (CVD) (Jin et al., 2011) and plasma modification (Balu, Breedveld, & Hess, 2008), have been employed to construct a superhydrophobic surface for the cotton fabric. However, many of the aforementioned approaches require complicated equipment, expensive chemicals and exhibit limitations in terms of substrate size and materials, all of which are major drawbacks for practical applications. In addition, a majority of the coating slurry was composed of fluorinated materials, which might carry serious risks to human health and natural environment due to fluorine emissions (Schultz, Barofsky, & Field, 2003). Therefore, it is necessary to minimize the use of fluorinated materials. Compared to other modification methods, radiation-induced graft polymerization is favorable due to its strong penetration into the polymer trunk, uniform formation of active sites for initiating grafting, and great ability to endow new performance characteristics to a material. Therefore, the radiation-induced graft technique is a suitable methodology for activating the cotton fabric surface and building a durable superhydrophobic coating on its surface via covalent bonding. Moreover, the radiation-induced graft polymerization technique is suitable for large-scale industrial production.

In this work, a new kind of superhydrophobic organic-inorganic hybrid cotton fabric was prepared by γ-ray simultaneous radiation-induced graft polymerization and subsequent modification. For improving the surface roughness and hydrophobic of the cotton fabric, γ-methacryloxypropyl trimethoxy silane (MAPS) was grafted onto the cotton fabric (Co-g-PMAPS) via radiation-induced graft polymerization. The MAPS monomer was selected mainly due to its low surface free energy, commercial and non-pollutant nature in comparison with other highly fluorinated monomers often used for fabricating superhydrophobic surfaces. However, during commercial or domestic launderings, an abundance of water-absorbing silanol derivatives will be formed on the grafted cotton fabric surface since the appended methoxysilane moieties have a tendency to hydrolyze, which makes the fabric easily prone to staining by liquids. In order to overcome this drawback, hexamethyldisilazane (HMDS), an end-capping reagent, was utilized to form a hydrophobic surface by replacing –OH groups with (-Si $(CH_3)_3$) groups on the surface of Co-g-PMAPS; the modified cotton fabric was called Co-g-EN/PMAPS. Moreover, it was envisioned that the partially cross-linked —Si—OH groups would induce the formation of a siloxane polymer with water-repellent properties, as an organic-inorganic coating covering the cellulose fiber surface during the process of hydrolysis and end-capping. Superhydrophobicity and durability of the modified cotton fabrics were evaluated by water contact angle measurement, oil-water separation, multiple washing cycles, and abrasion test. Moreover, mechanical properties of the samples were determined through tensile test.

2. Experimental

2.1. Materials

Cotton fabrics (yarn count: 60 × 60, density: 90 × 88, weight: 95 g/m^2, plain weave) were purchased from Kunshan Zhongtian Textile Co., Ltd (China). Hexamethyldisilazane purchased from Aladdin Co., Ltd., was used without further purification. Other reagents, purchased from Sinopharm Chemical Reagent Company, were of analytical grade.

2.2. Preparation of Co-g-EN/PMAPS hybrids

The preparation process of Co-g-EN/PMAPS was illustrated in detail in Scheme 1. Cotton fabric samples (each sample weight was 5 g) were put into irradiation tubes containing methanol solution of MAPS monomer (70 mL), which concentration was 18.75 vol% MAPS in methanol. The tubes were irradiated by a ^{60}Co γ-ray source at room temperature under the protection of nitrogen gas. The total absorbed dose was 20 kGy, and the dose rate was 0.31 kGy/h, 0.50 kGy/h, 0.69 kGy/h, 0.87 kGy/h, 1.18 kGy/h and 3.33 kGy/h, respectively. After irradiation, the grafted cotton fabric was extracted with ethanol in a Soxhlet apparatus for 12 h to remove residual monomer and homopolymer. Subsequently, the grafted sample was dried in a vacuum oven until a constant weight. The Degree of grafting (Dg) was determined according to the following equation:

$$Dg(\%) = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

where W_1 and W_0 represent the weights of the samples after and before grafting, respectively.

After graft polymerization of MAPS, the prepared Co-g-PMAPS and distilled water were suspended into a three-necked flask equipped with a thermometer and condenser. Then, acetic acid was slowly dropped into the flask, which was slightly shaken to keep the solution pH 3–4. After ultrasonic agitation for 15 min at room temperature, the solution was heated to 50 °C and maintained at this temperature with stirring for 10 h. Subsequently, the treated cotton fabric was put into a vacuum oven at 50 °C to remove the water, which was coded as Co-g-HPMAPS. Hereafter, the fabricated Co-g-HMAPS (0.5 g) was added into a solution, which was composed of 10 vol% of hexamethyldisilazane (HMDS) in acetone. After refluxing at 70 °C for 6 h in a nitrogen atmosphere, the cotton fabric was then taken out and washed by ethanol. Finally, the modified cotton fabric was dried in a vacuum oven at 50 °C until the constant weight and the final product was noted as Co-g-EN/PMAPS.

2.3. Characterization of cotton fabrics

The chemical structure of the pristine and modified cotton fabric was determined by a Bruker Tensor 207 Fourier transform infrared spectrometry (FTIR) by the accumulation of 32 scans with a resolution of wave number 4 cm^{-1} in the attenuated total reflection (ATR) mode recorded from 4000 to 600 cm^{-1}.

The chemical composition of cotton fabric was investigated via a Kratos Axis-Ultra DLD X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα radiation under the chamber pressure of 10^{-9} Torr from a 250 W X-ray source. Wide-scans were carried out in the range of 1100–0 eV and narrow-scans were performed for Si2p regions of Co-g-PMAPS and Co-g-EN/PMAPS.

^{29}Si solid-state nuclear magnetic resonance (^{29}Si NMR) spectra of Co-g-PMAPS and Co-g-EN/PMAPS were acquired at 79.49 MHz using 128 scans by a Bruker 400 MHz NMR spectrometer (Germany) under the condition of 20 ± 2 °C. Besides, the outer diameter of glass cells was 5 mm and a 5 s delay time was employed.

In order to observe the surface morphology and microstructure of the cotton fabrics, all the tested samples were coated with a thin gold layer and a FEI Quanta-250 scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) was employed.

Thermogravimetric analysis (TGA) was performed on a TG 209 F3 Tarsus (NETZSCH, Germany) instrument to assess the thermal stability of the modified cotton fabrics. The specimens were heated from 50 to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.