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Full Length Article

Novel coating system on poly(ethylene terephthalate) fabrics with mechanically durable liquid-repellence: Application as flexible materials with striking loading capacity

Jiawei Li, Xiaojie Yan, Lingmin Yi*, Ying Cai, Zhendong Tang

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China
Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China

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ABSTRACT

Construction of the superamphiphobic materials and their application is of particular interest both in academia and industrial circles for years. Herein, a novel coating system for fabricating superamphiphobic poly(ethylene terephthalate) (PET) fabrics was reported based on both aminopropyltriethoxysilane (APTES) and environment-friendly perfluorooctyltriethoxysilane (FAS) co-modified SiO_2 nano-particles, 3-Hydroxytyramine hydrochloride (Dopamine), amino-terminated silicone oils and etched PET fabrics via the one-step Schiff-base reaction and Michael addition reaction. The prepared fabrics displayed superamphiphobic properties, with contact angles of various liquids approaching 150°. In addition, the mechanical durability superamphiphobic fabrics were obtained, which were able to withstand 500 cycles of abrasion test, 20 cycles of sand abrasion test or 20 times standard washing. Furthermore, various liquids, including water and high viscous liquids, can easily slide off the surface of the obtained fabrics in a short time at a small angle. The prepared fabric can not only float on water or oil, but also hold up 25.7 times its own body weight things floated on water or 9 times on sesame oil without sinking. This novel and effective coating system can have more potential applications in the development of soft micro-devices working on liquid surfaces, especially on highly viscous liquid surfaces or under the environment with harsh conditions.

1. Introduction

As the special wettability of the lotus leaf [1,2] was thoroughly explored in the past decade, more and more nature-inspired liquid-repellent materials have been fabricated and adopted in versatile applications such as drag reduction [3,4], microfluidic devices [5,6], oil/water separation [7–10], water collection [11], biomedical devices [12], *etc*. Recently, with the development of functional polymers, especially shape-memory polymers [13–15], the soft matter based devices like soft actuators [16,17] aroused extensive attentions. For example, the soft electronic fishes that could move fast on the surface of the liquid fabricated by Li et al. show great interests [18]. The micro-devices floating and working on liquid surfaces exhibit excellent potential values [19]. Nonetheless, superamphiphobic flexible materials floating on the liquids for sensing electronics have not yet been reported.

Liquid-floating materials refer to materials that exhibit good repellence to both water and oil. The fabrication of oil-repellent or liquid-repellent surfaces is still a challenge due to the demands of introduction of lower surface energy and construction of more specific roughness, such as micro/nano or multi-scales structures. It should be pointed out that, in order to achieve excellent oleophobic performance, fluorinated agents with long perfluoroalkyl chains ($-C_nF_{2n+1}$, $n \geq 8$), such as perfluorooctanoic acid and perfluorooctane sulphonate, were used in many research works [20–24], which were proved to resist degradation, accumulate in organisms, and possess the long biological half-lives [25,26]. So far, to address these issues, close attention has been paid to the design and fabrication of oleophobic fabrics by using the environment-friendly FAS of fluorinated alkyl chain C6 ($-C_nF_{2n+1}$, $n = 6$), which had substantially shorter half-lives bio-accumulation in the human body and were less toxic compared with long perfluoroalkyl chains [27–31]. For instance, Freire [29] and Xu [30] reported the durable superamphiphobic cotton fabrics were fabricated through depositing the organic-inorganic nanoparticles with the FAS of fluorinated alkyl chain C6 modification. Lin and co-workers prepared a superamphiphobic polyester fabric that has a remarkable multi-self-healing

* Corresponding author at: Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China.
E-mail address: lmyi@zstu.edu.cn (L. Yi).

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ability against both physical and chemical damages using the FAS of fluorinated alkyl chain C6-silane and -decyl polyhedral oligomeric silsesquioxane. [31] In the previous work, we also reported amphiphobic coating surfaces of silica nanoparticles modified by methyltrimethoxysilane and FAS of fluorinated alkyl chain C6 via a sol-gel process, in which the chemical incompatibility between methyl groups and 1H, 1H, 2H, 2H-perfluorooctyl groups played a role in the packing of fluorinated groups on the coating surface [27]. Nevertheless, the development of a facile approach using the environment-friendly short fluorinated chemicals, to fabricate superamphiphobic flexible materials, remains a challenge, due to the high molecular mobility of fluorine-containing segments on the solid surfaces, thus it caused poor dynamic water repellency [27,28].

In this regard, poly(ethylene terephthalate) (PET) fabrics become a desirable candidate since they are consumers' preferred fabrics in our daily life due to their low cost and excellent mechanical as well as dimensional stability. More importantly, the chemical etching process of PET fabrics is a desirable method to achieve specific roughness [32]. For example, Xue et al. adopted several protocols including click-chemistry and ATRP [33,34] in the fabrication of lasting superhydrophobic fabrics combining with the chemical etching of PET fibers. Unfortunately, most reports concerning about the superoleophobic PET fabrics used the fluorinated chemicals with long perfluoroalkyl chains to achieve liquid-repellent [35–38].

According to reports [33,34,37,39], building covalent bonds among organic and inorganic moieties is one of effective methods to develop the mechanically durable coatings due to the great bond energy of covalent bond to endure the robustness of the prepared materials. Typically, Ramakrishna et al. fabricated a durable superhydrophobic surface by introduction of oligomeric siloxane as impact energy absorbing unit to the system [39]. Recently, biomass polydopamine (PDA) coating was drawn much attention as a chemically and physically versatile platform for further functional modification because of its nontoxic, strong adhesive capacity and simple deposition condition [40]. The mechanically durable of liquid-repellent PET fabrics could be further improved by using PDA as a modifier.

In this work, we constructed a novel coating system, in which mechanically durable liquid-repellent PET fabrics that shield against water and oils by surface modification on chemically etched PET fabrics of Schiff-base reactions and Michael addition reaction between dopamine, amino-terminated silicone oils and both aminopropyltriethoxysilane (APTES) and environment-friendly perfluorooctyltriethoxysilane (FAS) co-modified SiO_2 nano-particles (as outlined in Scheme 1 and Supporting Information). In this design, benefiting from the rough surface structures derived from the etching, the subsequent low energy chemical modification by environment-friendly fluorinated chemicals, and the connection of covalent bonds due to the Schiff-base reaction and Michael addition reaction, the fabrics exhibited not only great liquid-repellent property, but also excellent mechanical durability as being examined with various tests. Various liquids, including water and highly viscous liquids, can easily slide off the surface of the obtained fabrics in a short time at a small angle. Moreover, the prepared fabric can not only float on the water or oil, but also hold up things on its surface without sinking. The lifting forces in different situations were also discussed in depth in this paper.

2. Materials and methods

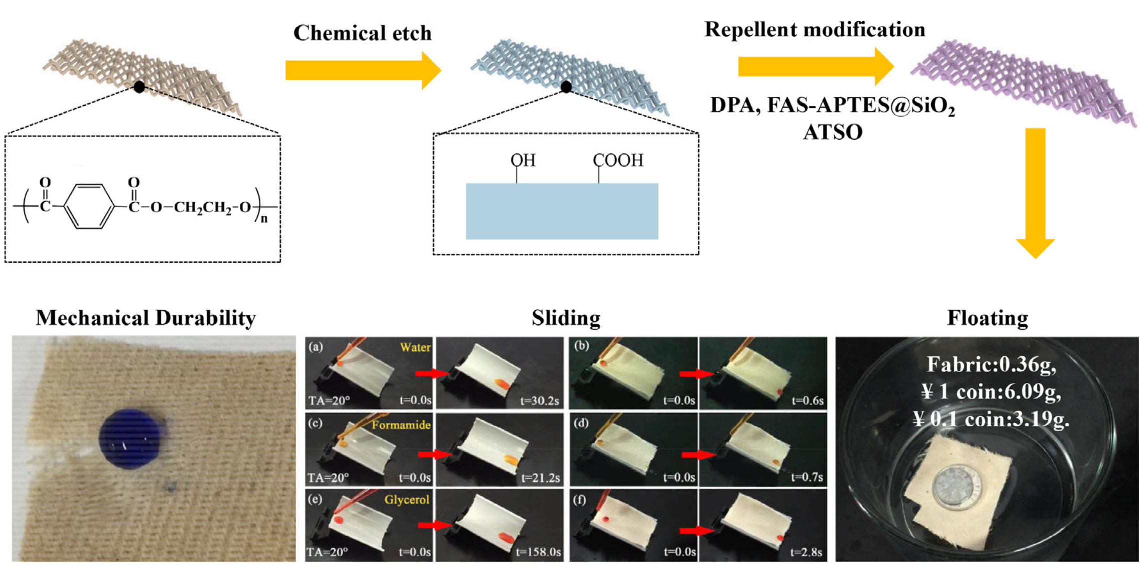
2.1. Materials

PET fabrics (160 g/m^2) used in this experiment were purchased from the local factory. 3-Hydroxytyramine hydrochloride (Dopamine) was purchased from Shanghai Yuanye Co., Ltd. Basic nano-silica sol (R130, pH = 10.5, solid content 50 wt%, water dispersion solution) with diameter of about 130 nm was supplied by Hangzhou Guigu Co., Ltd. Tris(hydroxymethyl)aminomethane, abbreviated as Tris, was purchased from Aladdin. Aminopropyltriethoxysilane (APTES) and perfluorooctyltriethoxysilane (FAS) were purchased from Hangzhou Feidian Co., Ltd. and Shanghai Shangfluoro Co., Ltd., respectively. Amino-terminated silicone oils (ATSO, M_n = 6000 g/mol) were purchased from DOW CORNING. All other chemical reagents were used as received without further purification.

2.2. Preparation of liquid-repellent PET fabrics

2.2.1. Preparation of chemically etched PET (E-PET) fabrics

Chemical etching of PET fabrics was conducted through a modified procedure as reported in the literature [34]. Briefly, the pristine PET fabrics (5 cm × 5 cm) were sequentially cleaned with ethanol and deionized water for 30 min to remove the impurities. The clean PET fabrics were dipped into a concentrated alkaline solutions (380 g/L NaOH aqueous solution) for 5 min. The soaked fabrics were covered with polyethylene (PE) film and heated in an oven at 110 °C for 3 min. The obtained fabrics were washed with abundant water and dried at 80 °C. Finally, the chemical etched PET fabrics (E-PET) were obtained.



Scheme 1. Schematic illustration of the preparation process of mechanically durable liquid-repellent PET fabrics.