Applied Surface Science 450 (2018) 492–501

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Positive effect of polymeric silane-based water repellent agents on the durability of superhydrophobic fabrics

Miao Yu [a], Peijia Li [a], Yufei Feng [a], Qianqian Li [a], Wei Sun [a], Miao Quan [b], Zhengtang Liu [b], Jiajia Sun [b], Suqing Shi [a,*], Yongkuan Gong [a]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Material Science, Northwest University, Xuefu Ave, Guodu, Chang'an District, Xi'an 710102, PR China
[b] Shaanxi Baotashan Paint Stock Co., Ltd, Xingping 713000, PR China

ARTICLE INFO

Article history:
Received 4 January 2018
Revised 17 April 2018
Accepted 23 April 2018
Available online 24 April 2018

Keywords:
Silane-based water repellent agents
Durability
Superhydrophobicity
Polyester fabrics

ABSTRACT

A series of superhydrophobic polyester fabrics are fabricated via *in situ* deposition of a sol–gel derived silica primer layer on alkali-treated polyester fabric surfaces and subsequent hydrophobization with silane-based water repellent agents. The contribution of the polymeric silanes on the durability of corresponding superhydrophobic fabrics under mechanical damages (i.e. ultrasonication in THF and Martindale abrasion) has been confirmed, using a small-molecule fluorinated silane (5-(perfluoro hexyl)isohexyltrimethoxysilane, FAS) as control. Their water contact angles could still reach at least 137° even after 120 min of ultrasonication in THF and 340 cycles of Martindale abrasion, exhibiting durable water repellency and anti-stain performance. It is acribed to their formation of dense and highly crosslinked hydrophobic layers on the silica modified fabric (SiO_2@fabric) surface. Moreover, higher amount of fluorinated monomer unit in the polymeric silanes leads to more efficient hydrophobization of SiO_2@fabric and much more durable water repellency for the corresponding superhydrophobic fabrics. The possible mechanism is also proposed.

1. Introduction

Superhydrophobic surfaces exhibiting water contact angle (WCA) greater than 150° along with a low rolling angle for water have aroused great attention in fabrication of waterproof textiles due to their extraordinary surface properties, such as water-repellency, soil/stain repellent performance, etc [1–5]. Two essential features are generally required for superhydrophobicity: a dual-sized surface texture and a nonpolar surface chemistry [1,6,7]. Based on this principle, numerous superhydrophobic fabric surfaces have been developed by various methods and techniques with different hydrophobic materials (water repellent agents) [1–5,8–15]. However, such surface textures are usually susceptible to mechanical forces, i.e. abrasion and ultra-sonication, etc., which may alter their surface topography and chemical composition, resulting in the loss of water repellency. Therefore, water-repellent durability of superhydrophobic fabrics becomes a great concern for practical applications.

Creating strong interaction between fabric surface and water repellent agent has been considered as an effective strategy to improve the durability of superhydrophobic fabrics [3–5,14,16–24]. Grafting fluorinated polymer brush or covalent attachment of the designed fluorinated polymers onto fabrics have been endeavoured [3,5,16–18]. Nevertheless, the resultant superhydrophobicity is greatly relied on the aggregation behavior of fluorinated polymers on the fabric surfaces, as the fabric only inherently has primary micro-sized roughness by itself. By contrast, simultaneous introduction of stable nano-scale roughness and durable hydrophobic outer layer seems to provide a feasible solution [4,13,14,19–28]. A variety of approaches have already been devoted to deposition of nanoparticle layers onto fabric surfaces with enhanced interfacial adhesion, including electrostatic layer-by-layer assembly [13,14,19,20], "adhesive + painting" technology [4,21], sol-gel process [22–24], etc, offering durable secondary surface geometry. Most of them are then followed by silanization with silane-based water repellent agents (fluorinated and non-fluorinated silanes) [4,12–14,19,20,22–24]. The latter step is often responsible for construction of a nonpolar surface, which also plays a crucial role in governing the superhydrophobicity.

* Corresponding author.
E-mail address: shisq@nwu.edu.cn (S. Shi).

https://doi.org/10.1016/j.apsusc.2018.04.204
0169-4332/

However, the effect of silane-based water repellent agents on the durability of superhydrophobicy or water-repellent performance is not so clear up till now.

To better understand the roles of silane-based water repellent agents in the fabrication of durable superhydrophobic fabrics, four polymeric silane-based water repellent agents are designed and synthesized by conventional free radical polymerization using 3-trimethoxysilylpropyl methacrylate (TSMA), 2,3,4,5,5,5-hexa fluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate (FMA) and/or isobutyl methacrylate (IBMA) as monomers. A series of superhydrophobic polyester fabrics are then fabricated via *in situ* deposition of a sol–gel derived silica primer layer on the alkali-treated polyester fabric surfaces, followed by hydrophobization with the obtained silane-based water repellent agents. A small molecule fluorinated silane, 5-(perfluorohexyl)isohexyltrimethoxy silane (FAS) is used as control. The effect of chemical structures of silanes on the water repellency durability of polyester fabrics is investigated. The possible mechanism is also proposed.

The chemical structures of FAS and polymeric silane-based water repellent agents are demonstrated in Scheme 1.

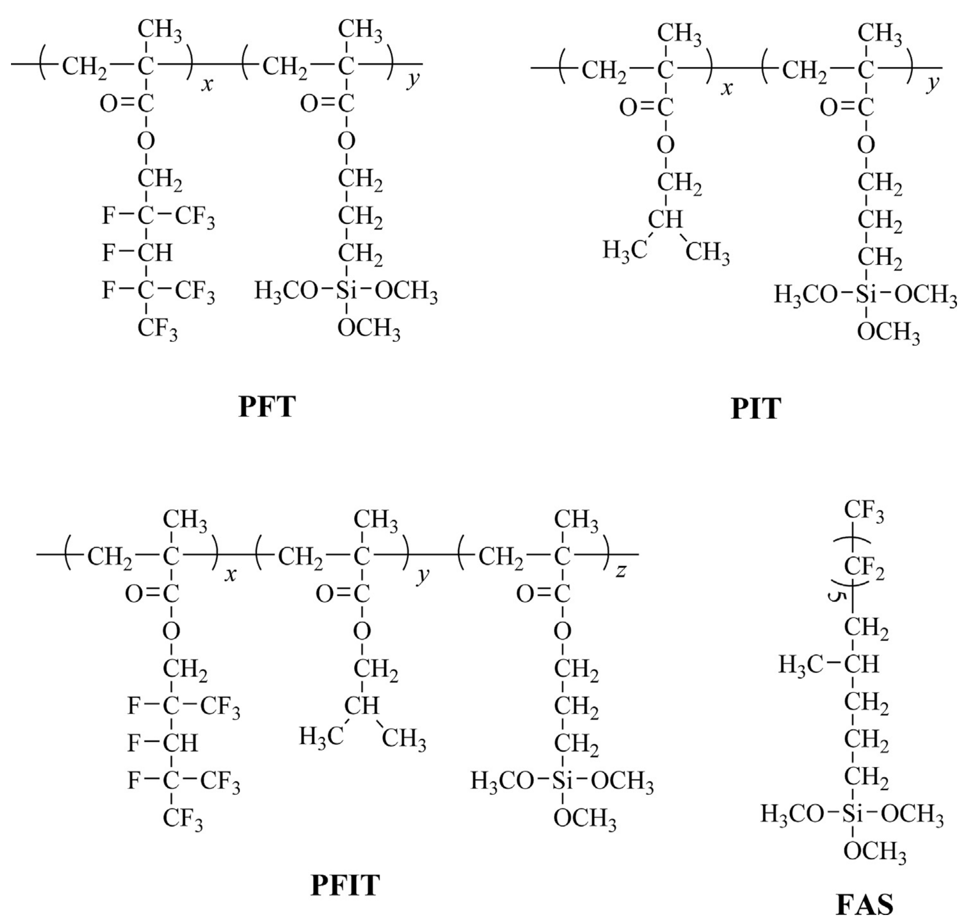
2. Experiment

2.1. Materials

Polymeric silane-based water repellent agents, including poly (2,3,4,5,5,5-hexafluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate-*co*-3- methacryloxy-propyltrimethoxysilane) (PFT), poly (2,3,4,5,5,5-hexafluoro-2,4-bis(trifluorinated methyl) pentyl methacrylate-*co*-isobutyl methacrylate-*co*-3-methacryloxypropyl trimethoxysilane) (PFIT), poly(isobutyl methacrylate-*co*-3-metha cryloxypropyltrimethoxysilane) (PIT) were synthesized via free radical polymerization procedure previously reported [29,30], by using 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluorinated methyl)pentyl methacrylate (FMA, Xeogia Fluorine-Silicon Chemical Co. Ltd., China), isobutyl methacrylate (IBMA, J&K Co. Ltd., China) and/or 3-methacryloxypropyl-trimethoxysilane (TSMA, Luosenbo Tech. Co. Ltd., China) as monomers, 2,2-azobisisobutyronitrile (AIBN, Adamas, China) as initiator. The synthesis procedure and ^{1}H NMR data of the obtained polymeric silane-based water repellent agents could be seen in Electronic Supporting Information section (ESI, S2.1). The composition, molecular weight and molecular weight distribution, and surface free energy (SFE, mN/m) of polymeric silane-based water repellent agents were shown in Table 1. 5-(Per fluorohexyl)isohexyltrimethoxysilane (FAS) was purchased from Xeogia Fluorine-Silicon Chemical Co. Ltd. (Harbin, China). Tetrahydrofuran (THF), trichloromethane and *n*-hexane were dried and distilled over calcium hydride (CaH_2). Tetraethoxysilane (TEOS) and aqueous ammonia (25%) were commercially available and used without further purification. The commercial poly (ethylene terephthalate) (PET) fabric (twill weave, 176 g/m^2, thickness = 320 μm) was used as polyester textile substrate.

2.2. In situ deposition of silica layer onto alkali-treated polyester fabric surfaces

Polyester fabrics were cut into slices about 40 × 40 mm^2 and cleaned by ultrasonication in detergent for 1 h and shaking in 95% ethanol for 12 h, successively. The clean polyester fabrics were then boiled in 2 wt.% NaOH aqueous solution for 15 min to gener-



Scheme 1. The chemical structures of polymeric silane-based water repellent agents (PFT, PIT and PFIT) and FAS.