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Regular Article

Sustainable and long-time 'rejuvenation' of biomimetic water-repellent silica coating on polyester fabrics induced by rough mechanical abrasion

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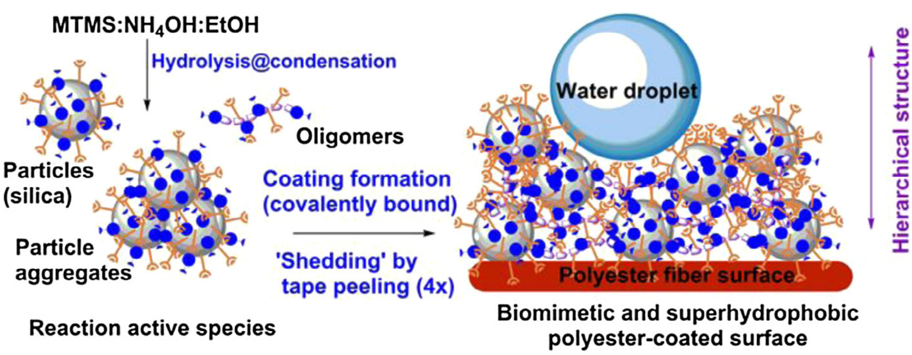
GRAPHICAL ABSTRACT



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ABSTRACT

The economical use of water-repellent coatings on polymeric materials in commercial and industrial applications is limited by their mechanical wear robustness and long-term durability. In this study, we demonstrate that polyethylene terephthalate (PET) fabric modified with inorganic, methyltrimethoxysilane (MTMS)-based coatings shows excellent resistance against various types of wear damage, thereby mimicking superhydrophobic biological materials. These features were facilitated by the rational design of coating processing that also enabled tunable hierarchical surface structure. A series of custom and standard testing protocols revealed that coating-to-substrate adhesion was remarkably high, as was the resistance to various mechanical abradents. The most intriguing characteristic observed during aging and abrasion cycles was the enhancement in non-wettability or 'rejuvenation' reflected by water droplet roll-off behavior, a characteristic of self-cleaning materials. Water-repellent properties of coated polyester were also enhanced by prolonged thermal annealing and were maintained after custom laundry. The developed technology offers opportunities to design low cost, durable and functional textiles for both indoor and outdoor applications.

1. Introduction

Polymeric fabrics are an important component in manufacturing of many modern commercial products for both indoor and outdoor activities [1–4]. Therefore, textile processing focuses on

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developing materials with specific properties, including fire retardancy [5,6], UV resistance [4], (super)hydrophobicity [7], (super) oleophobicity [8], (super)amphiophobicity [9], antimicrobial [10] and self-cleaning [11]. The most challenging tasks in the textile industry are double-edged: engineering multifunctional fabrics and, most importantly, designing appropriate protocols that will validate their performance and functionality. A key to achieve and control these features is the rational modification of surface chemistry and morphology through protective coatings [12].

Nature offers limitless examples of living organisms able to develop specific structured materials that display diverse functionality [13–16]. Well-known are the unique non-wettability properties of the lotus leaf, rose petal and gecko feet that have inspired an impressive volume of research on the design of biomimetic synthetic superhydrophobic and self-cleaning surfaces [12,17]. Recently, surfaces displaying the wetting behavior of natural homologs have been used to prevent icing [18], and to capture and release tumor cells [19]. Snake skin is an example of biological material programmed with outstanding resistance to mechanical abrasion [20,21]. Made of layered proteins and covered with lipids, the micro-ornamentation of the snake skin must adjust to different environmental conditions, often involving aggressive friction, until it is renewed by shedding [20]. Despite these factors, the skin preserves extraordinary water-repellent and self-cleaning properties due to continuous self-lubrication. Inspired by these natural materials, a few mechanically resistant and superhydrophobic wood [22,23], metal [24], paper [25,26] substrates have been developed. However, the possibility to design long-time robust textile substrates with similar performance has received little attention.

Inorganic, in particular silica-based coatings, have received increased interest in the fabric industry because of their economic potential and versatility [27,28] when compared to popular organic coating processes largely using fluorine-based polymers [29,30]. The latter technology raised health and environmental concerns in the past [31] leading to new and complex synthetic routes to more ecofriendly alternatives [32,33]. Synthetic silica is a low-cost, nontoxic material prepared through the hydrolysis and condensation of predominantly tetraethylorthosilicate (TEOS) under either acidic or basic conditions, the so-called sol-gel method [34,35]. Silica has remarkable fire retardancy [36], UV resistance [37] and antibacterial properties [38]. While TEOS has been used to modify polyurethane [3], cotton [1], knitted cellulose [39], and polyester [40] fabrics, methyltrimethoxysilane, (MTMS) alone has not been explored for the design of coatings to enhance textile moisture resistance, wearability and durability. Rather, MTMS has mostly been used in tandem with other siloxane derivatives. For example, Xu et al. used MTMS in alkaline conditions to build multi-scale roughness on the surface of cotton fibers; subsequent addition of hexadecyltrimethylsilane, (HTMS) led to superhydrophobic behavior [41]. Daoud et al. reported the fabrication of complex superhydrophobic coatings on cotton via co-hydrolysis and condensation of HTMS, TEOS and 3-glycidyloxypro pyltrimethoxysilane [42]. Solely MTMS, as a coating precursor, has been used to alter wettability of paper [43] and wood [44]. Yet, prior wet processing, plasma treatment was necessary to achieve optimum surface chemistry and morphology of paper substrates. Owing to its chemical structure, MTMS is more appealing in coating industry than its homologue, TEOS, because MTMS imparts hydrophobic character and has low surface energy. MTMS-derived silica exhibits similar properties as those of TEOS-based homologues, but in addition, it is expected to readily form highly water-repellent and mechanically durable textile coatings.

Exposure of coated fabrics to a variety of environmental conditions often causes degradation; thus, knowledge of the specific physical parameters and testing protocols necessary to evaluate textile performance is of paramount importance [45,46]. The hydrophobic character of coated materials is, in general, reflected by a static contact angle (SCA) which is >90°. This value defines the equilibrium condition of a water droplet placed on a solid substrate. SCA is measured as the angle between the tangents to the liquid-fluid interface and to the solid interface at the three-phase contact line, as measured through the liquid phase. SCA for extremely water-repellent surfaces (superhydrophobic) exceeds 150° [47]. A few parameters quantify the extent of liquid adhesion to surface: roll-off angle (RA), the surface tilt maximum at which the water droplet starts to roll or slide [47], contact angle hysteresis (CAH), the difference between advancing and receding angle of the expanding-retracting three-phase contact line [48], and shedding angle (SHA), similar to RA, except the water droplet is launched from a certain height [45]. Low RA and SHA angle values signify surfaces with low tendency to pin the water droplet. For superhydrophobic surfaces these values are less than 5–10° [47].

Adhesion and abrasion testing are critical tests to define coating durability. Tape peeling, cross-cut test, linear and circular abrasion, blade/knife test, oscillating steel ball/ring, pencil hardness test and bare finger contact are several examples of more or less standardized protocols used to assess the performance of the coated substrates; an extensive review detailing these procedures has recently appeared [45]. Because the coated substrates will suffer liquid and particle collision events, procedures to test dynamic impact durability are important, such as solid particle impact, liquid spray/jet/droplet impact and aerodynamic impact [45]. While some of these tests are used routinely, others are rarely reported (e.g. tape peeling), rendering it difficult to establish an overall perspective on long-time durability and mechanical wear of the surface-modified material. Multifunctional fabrics therefore demand rational protocols that employ a series of tests necessary to efficiently evaluate their complex nature and performance.

In this study, methyltrimethoxysilane (MTMS) – the silane reagent, ammonium hydroxide (NH_4OH) – the catalyst and anhydrous ethyl alcohol (EtOH) – the dispersion medium were reacted in various ratios to yield silica-coated polyester fabrics. The initial morphology of the coated textile surface was further modified by sequential peeling and aging. The behavior of the resulting silica-coated polyester mimicked that of natural surfaces that undergo shedding. A series of testing protocols was employed to evaluate the long-time durability, mechanical resistance, and liquid adhesion of these biomimetic silica-coated polyester fabrics. The modified fabric showed good non-wettability behavior under static and impact conditions, essentially independent of the reaction time used to synthesize the silica coating. The textile surface was able to withstand a series of custom and standard abrasion-peeling-aging-impact tests. Notably, the wetting resistance improved over time, pointing to effects of multiscale morphology, which is a primary feature of natural (super) hydrophobic materials. The coating and testing protocols described in this work offer a platform for durable, biomimetic and multifunctional textile engineering.

2. Experimental section

2.1. Materials

Methyltrimethoxysilane (MTMS, 98%) and ammonium hydroxide (NH_4OH, 28–30%) were purchased from Sigma-Aldrich. Ethanol 200 proof (EtOH, 100%, USP, KOPTEC) polystyrene and glass Petri dishes (60×10 mm) were purchased from VWR. All chemicals were used as received. Polyester (polyethylene terephthalate (PET), Anticon 100® Heavyweight Series Cleanroom Wipes, 9×9 in, Contec® brand) was obtained from VWR. Wipes contain 100% continuous filament polyester double-knit interlock fabric. Glass