Ultrahydrophobic textile surface *via* decorating fibers with monolayer of reactive nanoparticles and non-fluorinated polymer†

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Received (in Cambridge, UK) 21st June 2007, Accepted 20th August 2007
First published as an Advance Article on the web 28th August 2007
DOI: 10.1039/b709429a

By mimicking the hydrophobicity and miniature protrusions of the lotus leaves using a monolayer of non-fluorinated hydrophobic polymer and functionalized nanoparticles, respectively, we have developed a permanent nanocoating to create ultrahydrophobic fibers/textiles with excellent water repellency and self-cleaning ability.

Water and soil repellency has been one of the major targets for fiber and textile chemists and manufacturers for centuries. Combinations of new materials for fiber production with a variety of surface treatments have been developed to reach the condition of limited wettability. On the other hand, nature has already developed an elegant approach that combines chemistry and physics to create super-repellant surfaces. Lotus leaves are unusually water-repellent and keep themselves spotless, since countless miniature protrusions, coated with water-repellant hydrophobic substance, cover the leaves' surface.[1] The "lotus effect" is based on the surface roughness caused by varying microstructures combined with hydrophobic properties of the wax covering the leaves' surface.

A textile surface with both receding and advanced water contact angles above 150° may be considered to be a practically non-wettable ultrahydrophobic boundary.[2] The wettability strongly depends upon two properties, the surface energy and the surface roughness. Surface energy is an intrinsic property of the fibrous material that can be controlled by chemical modification. The common method for enhancing the hydrophobicity is to lower the surface energy. However, even materials with the lowest surface energy (a surface with regularly aligned closest-hexagonal-packed $-CF_3$ groups) give a water contact angle of only around 120°.[3d] In fact, surfaces with water contact angles of more than 120° may be developed only *via* air entrapment, by introducing appropriate roughness on the material's boundary that has low surface energy. Several decades ago Wenzel, Cassie and Baxter, scientists involved in textile research, revealed the interdependence between surface roughness and the wetting characteristic measured in terms of the contact angle.[4] The surface roughness of a fibrous material can be controlled either by changing the textile structure and/or some physical techniques such as imprinting/abrasion or by deposition of (nano)fibers or (nano)particles on the material boundary.

The preparation of ultrahydrophobic fibers/fabrics using different approaches that resemble the "lotus effect" was demonstrated recently.[5,6] The methods show promising results to duplicate the "lotus effect". In this communication, we report a novel and efficient method of replicating the "lotus effect" on a textile surface, which uses a very small amount (per surface area) of non-fluorinated, commercially available polymers and silica nanoparticles. This method is aimed to lead to ultrahydrophobic coatings for fibrous materials that can be applied to most fabrics to convert them into extremely water-repellent surfaces. The permanency of the coating is due to the chemical attachment of the nanoparticles and polymers to the fiber surface. Only a monolayer of the particles and polymers is deposited in a very controlled manner. The total thickness of the robust polymer coating is less than 20 nm.

Specifically to fabricate an ultrahydrophobic textile material, a method of permanent grafting of polymers to polymeric (organic) and inorganic surfaces, recently developed in our laboratory, was employed.[7] In brief, poly(glycidyl methacrylate) (PGMA), an epoxy containing polymer, is used for the initial surface modification and generation of the primary reactive layer on a substrate surface. Next, polymers possessing different functional groups (carboxy, anhydride, amino and hydroxyl) can be grafted to the surface modified with the PGMA anchoring layer. Since epoxy groups are highly active in various chemical reactions, the approach becomes virtually universal towards both surface and (end)-functionalized (macro)molecules being used for the grafted nanolayer formation.

The universality of the grafting approach was used in the work presented for surface modification of a textile with a rough and hydrophobic layer chemically anchored to the fiber boundary. Basically, the modification process consists of two major steps (Fig. 1). In the first step of the surface modification, silica particles covered with an ultrathin PGMA reactive layer, are deposited on the fiber surface. The silica particles covered with epoxy functional groups are capable of reacting with the fiber surface containing complimentary (*e.g.* carboxy, hydroxy) functionality and with hydrophobic polymers possessing the functional groups, which exhibit an affinity for the epoxy modified surface. During the second step, a hydrophobic polymer is grafted to the surface of the fibers and nanoparticles, and an ultrathin rough hydrophobic layer chemically anchored to the fiber boundary is generated.

We demonstrated the efficiency of the method described above using [poly(ethylene terephthalate) (PET)] polyester fabric (Dacron type heat set 122 g m^{-2} fabric) obtained from Test Fabrics (style #777H) as a fibrous substrate. The fabric was initially rinsed in several solvents (water, acetone, toluene, ethanol and final rinsing with water) to remove any finishes and other contaminants. The cleaned textile material was then subjected to a generally accepted

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† Electronic supplementary information (ESI) available: Detailed experimental procedures. See DOI: 10.1039/b709429a

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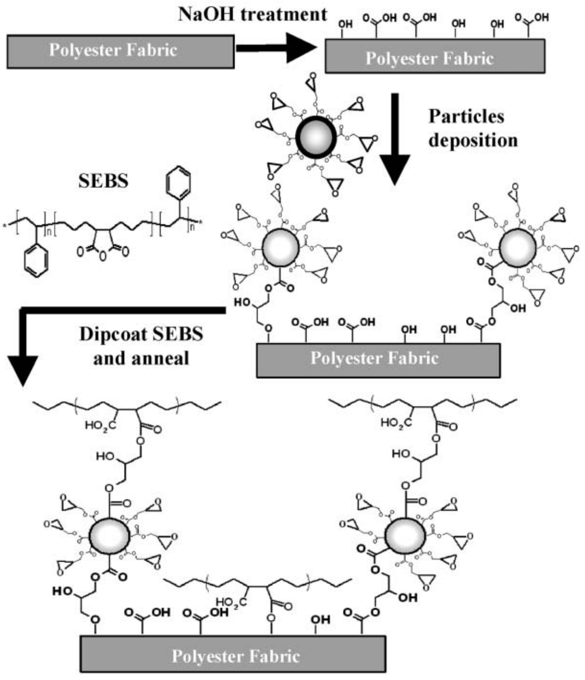

Fig. 1 Attachment of silica nanoparticles and hydrophobic polymer to polyester fabric.

hydrolysis procedure to increase the reactivity of a polyester fabric.[8] Namely, 40% sodium hydroxide (NaOH) treatment for 2 min was carried out to hydrolyze PET on the fiber surface and form additional carboxyl and hydroxyl groups on the fiber boundary. The fabric was then thoroughly rinsed in de-ionized water for *ca.* 1 h to remove all the residuals and dried in an oven at 80 °C until constant weight.

PGMA was synthesized by free radical polymerization of glycidyl methacrylate[7c] and fluorescence labeled with a small amount of Rhodamine B (Alfa Aesar). Unmodified silica nanoparticles (diameter = 150 ± 30 nm, Polysciences Inc.) were purchased as an aqueous suspension. The particles were transferred into tetrahydrofuran (THF, EMD chemicals) to form stable colloidal suspension (*ca.* 1 wt%). The suspension was injected dropwise into 3 wt% PGMA solution in THF under ultrasonication. The mixture was sonicated for 1 h, and then the solvent was rotary-evaporated under a nitrogen stream. The residual was annealed in vacuum at 60 °C for 15 min. The particles modified with PGMA were then re-dispersed in THF.

The thickness of the PGMA grafted layer ($\sim$4 nm) on the silica nanoparticle was determined using atomic force microscopy, thermogravimetric analysis, and elemental analysis. The surface coverage (Γ), the PGMA chain density (Σ) and the surface concentration of the epoxy groups present on the surface of the functionalized silica nanoparticle (epoxy groups nm^{-2} = ΣN, where N is the degree of polymerization) were also estimated as described by Iyer *et al.*[9a]; $\Gamma = 4.3$ mg m^{-2}, $\Sigma = 0.006$ chain nm^{-2}, and the value of surface concentration of epoxy groups of 18 groups nm^{-2} was obtained. Therefore, by deposition of minute amounts of PGMA on the particle surface, a significant number of reactive groups were anchored to the nanoparticles.

The fabric was immersed under constant stirring in a suspension (0.1–0.5 wt% in THF) of the epoxidized silica nanoparticles at 50 °C for 3 h. After the treatment, the PET fabric was thoroughly rinsed in THF under constant ultrasonication, to remove unattached particles from the fibers. A strong fluorescent signal was observed (SpexFluorolog-2 spectrometer) from the fabric, confirming deposition of the reactive nanoparticles. Observation of the textile material under a fluorescent microscope (Olympus MVX) demonstrated that all fibers were evenly covered with the nanoparticles. The permanent attachment of the particles was realized *via* a reaction between epoxy groups on the nanoparticle surface and carboxy/hydroxy groups on the fiber surface (Fig. 1).

A hydrophobic reactive poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS, Kraton FG1901X) triblock copolymer was obtained from Kraton Polymers US LLC. The copolymer was used to generate an ultrathin hydrophobic coating on the fiber's surface. The polymer contained $\sim$29 wt% of styrene and 1.4 wt% of reactive maleic anhydride (MA) groups. The block copolymer was reported to have $M_n = 41\,000$ g mol^{-1}, $M_w/M_n = 1.16$ and $R_g = 6.3$ nm, where R_g is the radius of gyration of SEBS macromolecules.[9b]

The thin SEBS film was deposited on the PET fabric covered with the epoxidized silica nanoparticle *via* dip coating (from 1 wt% SEBS solution in toluene) under constant ultrasonication. The fabric was annealed at 150 °C for 4 h. The reaction between the unreacted epoxy groups of the nanoparticles and the MA groups present in SEBS promoted the attachment of the polymer to the particles.[9b] Additionally, SEBS reacted with multiple hydroxyl groups created on the boundary of PET fibers by NaOH treatment and was grafted to the fiber surface between the particles.[10] The fabric was then thoroughly rinsed in toluene to remove any unreacted SEBS from the fabric.

In a model experiment, we grafted SEBS to flat silica substrates modified with the PGMA layer (thickness 3 nm) and PET film treated with NaOH (thickness 52 nm) using the same annealing and rinsing procedures. The water contact angles, WCA (measured with Kruss, Model DSA10 goniometer) for the substrates covered with the grafted SEBS layer were 99 ± 5°. The values of the angle were significantly higher than the values of 45° (PET) and 60° (PGMA) obtained for the substrates before the hydrophobic polymer was grafted. It is necessary to note that the water contact angle for a thick SEBS film is 100 ± 2°. Therefore, the result indicated that the surface was completely screened from water by the grafted layer. It was determined by ellipsometry (COMPEL, InOmTech, Inc.) that the thickness of the chemically anchored SEBS layer was 10 ± 1.6 nm and 12 ± 4 nm for the PGMA layer and the treated PET film, respectively. The thickness was close to $2R_g$ for the macromolecule. Therefore, the SEBS monolayer was grafted to the surface. We also estimated the parameters of the grafted layers.[9b] The values of Γ and Σ were calculated to be 9–11 mg m^{-2} and 0.13–0.16 chain nm^{-2}. Hence, a very small amount of the hydrophobic polymer was grafted to the surface. However, it was sufficient to create a highly hydrophobic coating.

SEM studies were performed, using a FESEM-Hitachi S4800, to observe the modified PET fabric. Fig. 2 shows the SEM micrographs of the PET fabric after the nanoparticle attachment and SEBS grafting. In general, the functionalized nanoparticles form a monolayer and are also homogeneously distributed with very little aggregation. The aggregation was mostly observed between the fibers because of the fabric's ability to trap the nanoparticles physically at this location. In addition, particles were

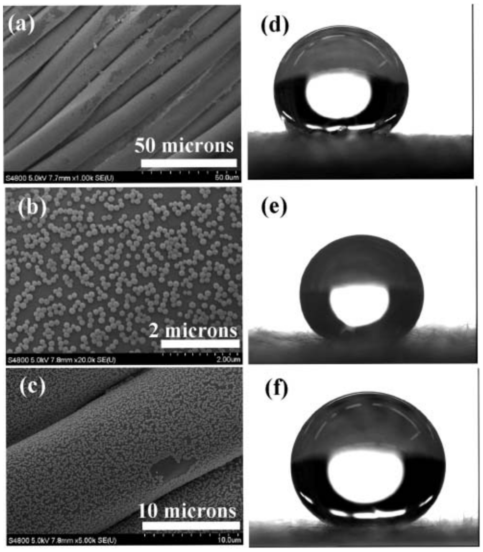

Fig. 2 SEM images of PET fabric: (a), (b) low and high magnification after particle attachment and (c) after grafting the SEBS. WCA: (d) fabric "as is", (e) fabric grafted with SEBS only, (f) nanoparticle modification and SEBS grafting.

removed from some areas during handling before the deposition of the SEBS layer, and this caused some defects in the nanoparticle layer formation.

The water repellency of the PET fabric was evaluated *via* WCA studies. Fig. 2 illustrates the wettability of the original PET fabric (Fig. 2(d)), the fabric grafted with SEBS (Fig. 2(e)), and the fabric modified with nanoparticles with subsequent anchoring of the SEBS monolayer (Fig. 2(f)). Deposition of the SEBS monolayer on the fiber surface increased the WCA from 125 to 140°. WCA increases significantly and crosses the ultrahydrophobic boundary (WCA >150°) for the fabric subjected to nanoparticle deposition and SEBS grafting. Therefore, the significant effect of nanoparticle deposition on wettability was observed. The increase in WCA is attributed to the introduction of the double roughness with the initial roughness coming from the fabric structure itself and the second from the layer of the nanoparticles. As proposed by Patankar, a double roughness profile provides the appropriate geometry to develop ultrahydrophobic, self-cleaning surfaces.[11]

The self-cleaning capability of the nanoparticle/SEBS modified polyester fabric was evaluated. The fabric under investigation was covered with hydrophobic powder produced from graphite present in pencil lead (Fig. 3). The water droplets were then applied to the fabric. The droplets rolled over the textile material, collected the powder, and cleaned the fabric. Fig. 3 also demonstrates that, in fact, the hydrophobic particles stuck to the water drop moving over the surface. The observed self-cleaning effect is similar to the "lotus effect" and originated from the roughness of the hydrophobic PET fabric. Indeed, the contact area between the graphite particles and the fabric was significantly reduced as well as the contact area between the water droplet and the fabric. Also, the interaction between the droplet and the graphite was sufficient to overcome the low adhesion between the fabric and the powder particulates.

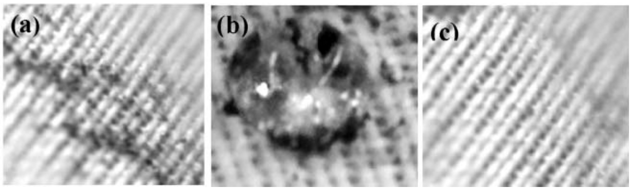

Fig. 3 Self-cleaning ability shown by the removal of graphite from the fabric using a water droplet. (a) fabric with graphite, (b) graphite sticking to the water droplet and (c) cleaned fabric.

In conclusion, this work has demonstrated that the deposition of an ultrathin coating, consisting of non-fluorinated, hydrophobic polymer and reactive silica nanoparticles, led to the generation of an ultrahydrophobic textile surface. The coating was permanently anchored to the fiber boundary due to the chemical attachment of the nanoparticles and polymers to the surface. Only a monolayer of the particles and polymers was necessary to obtain the ultrahydrophobic, self-cleaning textile surface.

The authors acknowledge financial support by the National Textile Center (C04-CL06) and NSF (CTS-0456550) and thank Kraton Polymers US LLC for donating the SEBS sample. Professor K. G. Kornev (Clemson University) is thanked for help with imaging.

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