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Breakthrough pressure is an important parameter associated with the performance of water-resistant fabrics. Hydrostatic testing has been utilized to experimentally determine the breakthrough pressure of commercial cotton fabrics treated with various combinations of octakis(1H,1H,2H,2H-perfluorodecyl) Polyhedral Oligomeric SilSesquioxane (F-POSS), a compound with the lowest reported solid surface energy, and the commercial fluoroelastomer, Tecnoflon®. The breakthrough pressure values (amounting to a few inches of water) were found to be similar to predicted values based on the geometry of the samples and the surface energy of the components. The theoretical predictions, however, do not explain all differences observed among samples, such as the fact that a single dip coating with both F-POSS and Tecnoflon® produced a higher breakthrough pressure than a single dip coating in either F-POSS or Tecnoflon®, or sequential dip coating (in either order) of the two components. SEM analysis of the coated fabrics indicated that coatings were conformal at the microscale, but did result in sub-micron scale roughness. Although this roughness may help to increase the contact angles with water, the breakthrough pressure appeared to be primarily determined by the geometry of the individual filaments.

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“Water Breakthrough Pressure of Cotton Fabrics Treated with Fluorinated Silsesquioxane / Fluoroelastomer Coatings”

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Abstract

Breakthrough pressure is an important parameter associated with the performance of water-resistant fabrics. Hydrostatic testing has been utilized to experimentally determine the breakthrough pressure of commercial cotton fabrics treated with various combinations of *octakis*(1H,1H,2H,2H-perfluorodecyl) Polyhedral Oligomeric SilSesquioxane (F-POSS), a compound with the lowest reported solid surface energy, and the commercial fluoroelastomer, Tecnoflon®. The breakthrough pressure values (amounting to a few inches of water) were found to be similar to predicted values based on the geometry of the samples and the surface energy of the components. The theoretical predictions, however, do not explain all differences observed among samples, such as the fact that a single dip coating with both F-POSS and Tecnoflon® produced a higher breakthrough pressure than a single dip coating in either F-POSS or Tecnoflon®, or sequential dip coating (in either order) of the two components. SEM analysis of the coated fabrics indicated that coatings were conformal at the microscale, but did result in sub-micron scale roughness. Although this roughness may help to increase the contact angles with water, the breakthrough pressure appeared to be primarily determined by the geometry of the individual filaments.

Keywords: Breakthrough pressure, F-POSS, Superhydrophobic, Dip-coating

The treatment of cotton fabrics to obtain superhydrophobicity and even superoleophobicity[1-4] has received increasing attention in recent years. Various surface treatments involving siloxanes[5-7], silsesquioxanes[8-10], highly fluorinated surfaces [2-4, 7, 11-18], and/or nanoparticles[6, 15, 16, 19-30] have all been recently reported. Although most of these reports focus on contact angles as a means of describing liquid repellence properties, additional measures of performance, such as the breakthrough pressure, are also important. For re-entrant surface profiles (such as those formed by layers of fibers in a fabric), the partially wetted Cassie-Baxter state for contacting liquids is metastable. Therefore, with sufficient input of external energy (in the form of hydrostatic pressure due to immersion, or collision of moving droplets), the energy barrier to the fully wetted state may be overcome. Hydrostatic pressure is a convenient means of quantitatively measuring the energy required to achieve breakthrough of a fabric sample, with the resultant values being highly significant for practical applications. Unfortunately, there has to date been scant experimental work[24] focused on this aspect of superhydrophobicity in cotton fabrics. Herein, we report experimental breakthrough pressures for commercial cotton fabric samples treated with a combination of fluorinated nanoparticles and a fluoropolymer binder, and compare these values to theoretical expectations.

Fabrics, due to the weave of the individual fibers and bundles, possess a fairly regular reentrant cylindrical structure. For a re-entrant structure made from cylinders, the breakthrough pressure (P_{bt}) can be given by the following: [31]

$$P_{bt} = \frac{2R\gamma_{\mathrm{lv}}(1-\cos\theta)}{D^2 + 2RD\sin\theta} \tag{1}$$

where $2D$ is the spacing between cylinders, R is the cylinder radius, θ is the equilibrium contact angle of the fluid on a smooth surface, and γ_{lv} is the surface tension of the fluid. For hierarchical structures, such as cotton fabric, the model can be used to calculate a breakthrough pressure associated with the gaps between the approximately cylindrical bundles of twisted filaments, as well as with the gaps between filaments within each bundle.

In order to test this model, fabric samples from a single 100% cotton T-shirt, purchased at a commercial retailer, were dip coated in solutions containing *octakis*(1H,1H,2H,2H-perfluorodecyl) Polyhedral Oligomeric SilSesquioxane (herein referred to as “F-POSS”), the commercial fluoroelastomer Tecnoflon® BR9151, obtained from Solvay-Solexis with no curatives added, and the commercial solvent Asahiklin AK225G (1,1,2,2,3-pentafluoro-1,3-dichloropropane), which was purchased from AGC Chemicals America. F-POSS exhibits the lowest known surface energy of any crystalline solid,[32] and was synthesized at the Air Force Research Laboratory. The elastomer and solvent were chosen on the basis of their known compatibility with F-POSS.

The dip coating procedure involved six different treatment options based on four separate coating solutions. The solutions used were: 1) pure AK225G (to determine if the solvent was washing away a coating from the as-received fabric), 2) 1 wt% Tecnoflon in AK225G, 3) 1 wt% F-POSS in AK225G, and 4) 0.5 wt% Tecnoflon and 0.5 wt% F-POSS (total solids 1 wt%) in AK225G. The latter mixture of solids has been used previously for treating fabrics by dip coating in AK225G.[31] Four test conditions involved a single dip coating in each of the four solutions described above. Two additional treatments involving sequential dip coating were investigated. In one case, fabrics were dip coated in the Tecnoflon solution followed immediately by dip coating in the F-POSS solution. In the second case, fabrics were dip coated in the F-POSS solution followed by the Tecnoflon solution (reversal of the sequence). Approximately 2 inch diameter circular sections of the cotton fabric were dipped into each of the solutions and agitated gently. Samples remained submerged in the coating solution for 5 minutes, followed by oven drying in air at 60 °C for 30 minutes. For each test condition, two samples of cotton fabric were prepared and tested.

The morphology of one sample of fabric (sputtered with gold) from each test condition was investigated using SEM. The SEM was operated in low-vacuum mode with a working distance of approximately 10mm. These investigations were also used to determine the geometrical parameters R and D, at both the individual filament level and the bundle level, for use in Eq. (1), with the aid of image analysis software supplied with the SEM, based on several representative measurements of each sample.

For hydrostatic breakthrough pressure testing, the samples were placed between two silicone rubber rings leaving a 1 inch diameter circle of fabric exposed. The rings were sealed together using waterproof tape. The rings were then fitted snugly into a cylindrical glass tube, creating a sealed column above the exposed sample surface to which water could be added. Addition of water proceeded slowly until water began to flow through the fabric surface. The height of the water was measured at this point, and used to calculate the breakthrough pressure. Each sample was tested, dried, and then tested again. Because two samples were tested per condition, there were a total of four measurements per experimental condition.

Figure 1 presents a typical low-magnification SEM image used to determine the geometrical parameters for Eq. (1), while Figure 2 displays representative high-magnification images used to examine surface morphology. All samples treated with either Tecnoflon and/or F-POSS showed additional surface roughness at the micron scale. The overlaying of textures at multiple length scales is known to enhance the liquid repellence of many surfaces.[33]

************FIGURE 1 GOES HERE************

************FIGURE 2 GOES HERE************

Using measurements from single filaments within intact bundles (from images separate from Figure 2), 2D was determined to be 30 μm and 2R 2μm, while, for bundles, 2D was 10 μm and 2R 350 μm, as seen in Figure 1. An equilibrium contact angle of 120° was used in all cases, representing the typical value for highly fluorinated surfaces. For the case of the individual fibers, the predicted pressure at failure is ≈900 Pa, or 4 inches of water, while for bundles, the breakthrough pressure according to Eq. (1) amounts to ≈ 1900 Pa or 8 inches of water.

Figure 3 illustrates that the breakthrough pressures actually obtained were best predicted by the individual fiber level values from Eq. (1). AK225 treated fabric was less effective than the as received cotton, an indication that indeed the solvent dissolved an existing coating. The difference between samples tested initially and those re-tested after breakthrough and subsequent drying was not significant, thus the values in Figure 3 are based on all four measurements from each test condition.

************FIGURE 3 GOES HERE************

According to Eq. (1), all treatments tested, except for AK225G only, were expected to exhibit a similar breakthrough pressure, yet the samples coated with Tecnoflon only showed significantly lower breakthrough pressure values, while those coated with the mixture of Tecnoflon and F-POSS in a single step were somewhat higher than those coated with the same ingredients in a two-step process. The surface energy of F-POSS is lower than that of Tecnoflon, though in terms of contact angles the difference is only about 10° and lowers the breakthrough pressure by just 15% according to Eq. (1). Although F-POSS is likely to impart a different morphology than Tecnoflon at the nanoscale, it is unclear how such differences would affect fluid breakthrough, which, for nanoscale textures, occurs at far higher pressures than observed.

As for the mixed component system, we could detect no difference in fine-scale morphology compared to the other treatments (except AK225G only, as seen in Figure 2) that would explain the higher breakthrough pressure. One possibility is that the Tecnoflon prevented interstitial migration or perhaps crystallization of F-POSS, thereby providing more uniform coverage of the lower surface energy F-POSS through gradual surface migration. Furthermore, in a two-step process in which F-POSS is deposited first, the presence of the lower energy F-POSS may have curtailed subsequent deposition of Tecnoflon, with the result that both “two-step” coating processes result in the same type of surface formed by deposition of F-POSS only.

In general, these results indicate that, while the breakthrough pressure for treated fabrics can be roughly estimated with existing models, there are still numerous details of the deposition process that models such as Eq. (1) do not take into account, but that do have a significant influence on the performance of the system and require future investigation.

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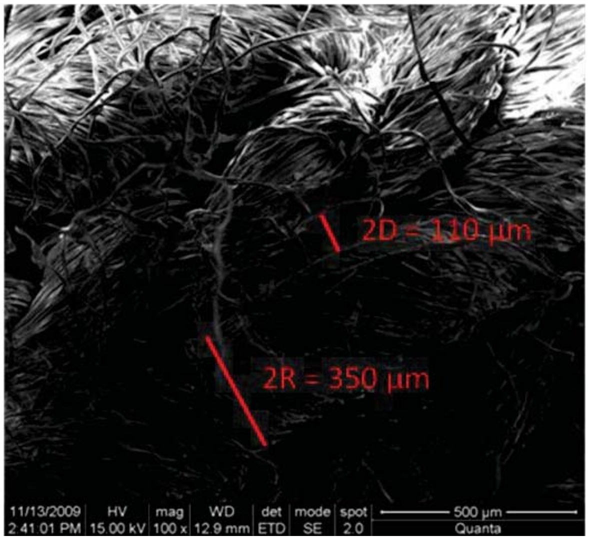

Figure 1. Representative low-magnification SEM image of cotton fabric dip coated in 0.5 wt% Tecnoflon and 0.5 wt% F-POSS (1 wt% total solids).

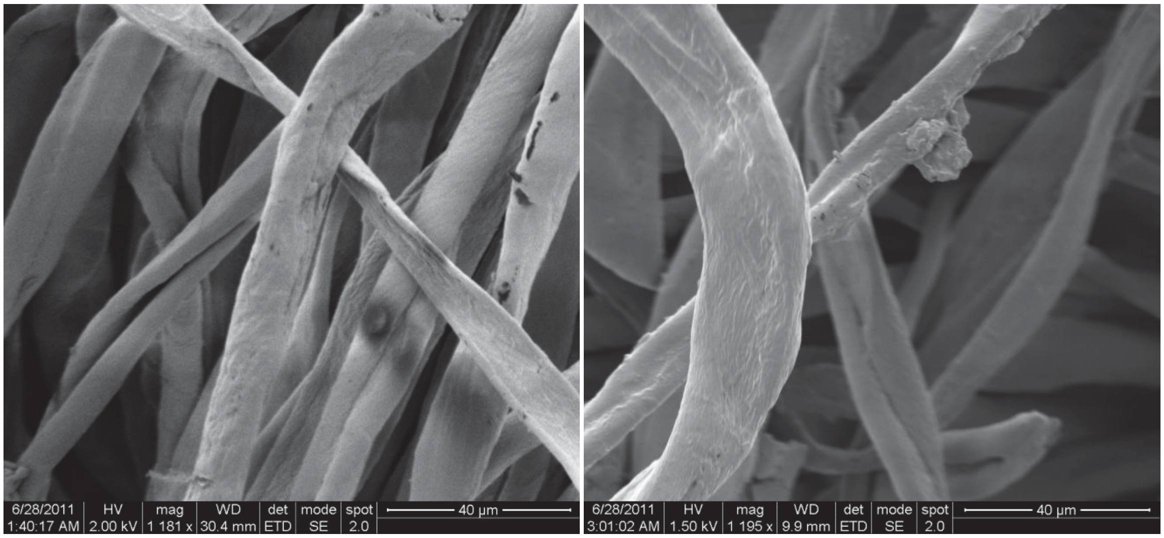

Figure 2. SEM images of cotton fabric treated with AK225G only (left), and 1% (w/w) total solids, comprised of 50 wt% F-POSS and 50 wt% Tecnoflon, in AK225G (right), showing individual filaments (selected from areas with frayed bundles for clarity).

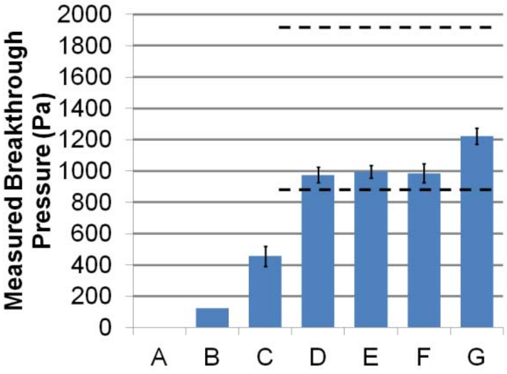

Figure 3. Breakthrough pressure results for the following dip coating solutions: A) AK225G only, B) no treatment, C) 1 wt% Tecnoflon in AK225G, D) 1 wt% F-POSS in AK225G, E) 1 wt% Tecnoflon in AK225G, then 1 wt% F-POSS in AK225G, F) 1 wt% F-POSS in AK225G, then 1 wt% Tecnoflon in AK225G, G) 1 wt% of mixed solids (50 wt% F-POSS and 50 wt% Tecnoflon) in AK225G.