Methods to Assess Metrics of Repellency

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Abstract.   Three test methods were developed and validated to assess the repellency performance of repellent cotton fabrics using a number of test liquids with low and high surface tensions, from 22 mN/m to 72 mN/m. These methods were assessed using cotton fabrics coated with a diblock copolymer made of a sol-gel block which grafts the polymer to the cotton and a fluorinated block which imparts the liquid repellent properties.

I. Introduction

Fabrics worn by military personnel may come into contact with anassortment of substances such as petroleum, toxic chemicals, or water based toxic materials. The surface tension of these substances varies greatly from 72 mN/m for water to 34 mN/m for cooking oil for example. Cotton fabrics can be made liquid repellent by coating them with low surface energy chemicals such as fluorinated polymers.[1-2] High surface tension droplets have a tendency to bead up and roll off repellent textiles leaving behind no visible trace. The repellency of the fabric usually decreases as the surface tension of the probe liquid decreases. If any residual liquid is left behind, it can be potentially very dangerous. In this report, we show a method to

fabricate repellent cotton fabrics using a diblock copolymer and we subsequently characterize this coating. We then develop and validate three test methods to assess the repellency performance of this material using a number of test liquids with low and high surface tensions.

II. Development of Cotton Fabrics Coating Method and Analysis

Plain-weave cotton fabrics were purchased for this project from a local fabric store. The fabrics were then washed thrice with soap and water and dried in an oven at 120 $^{\circ}$C for 2h. The fabric morphology was investigated using SEM as can be seen in Figure 1a and 1b. The bundle diameter was measured to be 310 $\pm$ 80 µm, while the spacing between the bundles was 130 $\pm$ 50 µm. At the single fibre scale, the fibre diameter was measure as 20 $\pm$ 6 µm, while the spacing between the fibres was 20 $\pm$ 11 µm. The SEM images also reveal rough fibre morphology.
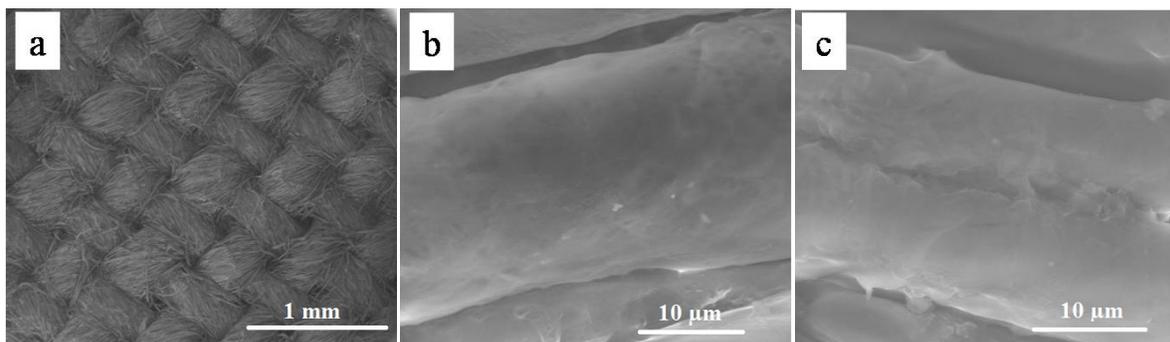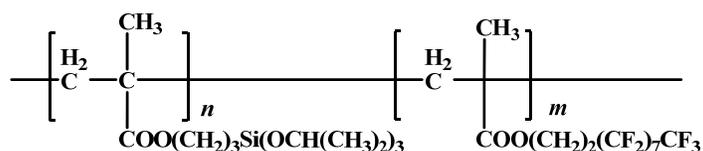

Figure 1. SEM images of cotton fabrics a) and b) uncoated cotton, and c) P1 coated cotton.

Cotton fabrics were coated using poly[3-(triisopropyloxysilyl)propyl methacrylate]-*block*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA, P1). The PIPSMA block of the copolymer undergoes a sol-gel reaction with the cotton and with itself to produce a grafted cross-linked layer, while the PFOEMA block is left on the outside of the fibres to impart water and oil repellency properties. P1 was previously prepared by sequential atom transfer

radical polymerization (ATRP). ATRP is a type of controlled radical polymerization which uses a transition metal complex as the catalyst. The synthesis and characterization protocols can be found in our previous publication.[3] The number-average molecular weight (M_n) was 58 kg/mol and the polydispersity index (M_w/M_n) was 1.13 by size exclusion chromatography. The number of repeat units for the PIPSMA block was 15 and for the PFOEMA block was 31 as determined by[1]H NMR spectroscopy.

$$\left[\begin{array}{c} H_2 \\ C \end{array} - \overset{\overset{CH_3}{|}}{\underset{\underset{COO(CH_2)_3Si(OCH(CH_3)_2)_3}{|}}{C}} \right]_n \left[\begin{array}{c} H_2 \\ C \end{array} - \overset{\overset{CH_3}{|}}{\underset{\underset{COO(CH_2)_2(CF_2)_7CF_3}{}}{C}} \right]_m$$

Scheme 1. Chemical structure of PIPSMA-*b*-PFOEMA (P1).

In a typical optimized coating procedure, cotton fabrics were cut into 2.0×2.0 cm^2 swatches and dried in an oven at 120 °C for 2h. In a vial, 10.0 mg of P1 was dissolved in 2.0 mL of tetrahydrofuran (THF). Subsequently, 40.0 μL of 0.13M hydrogen chloride solution in THF (HCl) was added to the vial. This mixture was stirred for 1 h at room temperature (as determined by the appearance of the Si-OH peak in the FTIR spectrum indicative of reaction hydrolysis), prior to the addition of two 2.0×2.0 cm^2 cotton fabric swatches. The vial was placed in a pre-heated 50 °C oil bath for 30 min. The final cotton samples were dried at 120 °C for 2 h. Figure 1c shows a SEM image of the coated cotton. Since the cotton fibres were rough even before coating, it is difficult to observe any change in morphology after coating.

Other methods for coating the cotton fabrics were also investigated such as using a stronger acid, 12.2 MHCl. Cotton fabrics with high repellency were produced, but the strength of the cotton fabrics decreased. The procedure was then modified to neutralize the acid before the cotton was introduced into the reaction usingsodium hydroxide, 7.2 M triethylamine solution,

or 0.5M ammonia solution in dioxane. However, the salt produced from the neutralization reaction was attached to the cotton fabric.

The amount of polymer grafted onto the cotton fabric was determined using thermogravimetric analysis (TGA). Samples were heated under an air flow from room temperature to 600 $^{\circ}$C at a rate of 10 $^{\circ}$C/min. TGA traces were obtained for uncoated cotton, sol-gel polymer and coated cotton as shown in Figure 2. The sol-gelled polymer trace shows a decomposition peak at 415 °C. Thus, we used the 400-475 °C temperature range to estimate the amount of polymer attached to the cotton.Assuming that the cotton and sol-gelled polymer parts of the coating behaved the same as the uncoated cotton and sol-gelled polymer, we used the weight residues R_C, R_P, and R_{PC} for the uncoated cotton, the sol-gelled polymer, and coated cotton, respectively, to calculate the grafted polymer mass fraction x:

$$R_C(1-x) + R_P x = R_{PC} \qquad (1)$$

The average R_C, R_P, and R_{PC} values of $(1.7 \pm 0.1)\%$, $(13 \pm 1)\%$, and $(1.74 \pm 0.01)\%$, respectively, were obtained by normalizing the residue determined at 475 $^{\circ}$C for a given sample vs. its value at 400 $^{\circ}$C. The ensuing use of equation 1 yielded $x = 0.6$ %.Whilethis value is close to what we estimated from the amount of P1 solution that was sorbed by each piece of cotton, we are presently working on improving the x determination using another method such as by elemental analysis of fluorine.
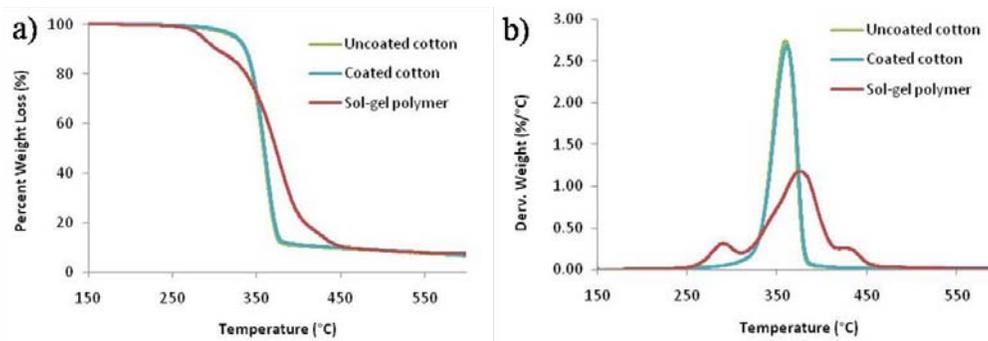
Figure 2.a) TGA, and b) DTGA traces for uncoated cotton, sol-gel polymer and coated cotton.

The coated cotton fabrics showed water repellent properties (Figure 3b). The cotton had a water contact angle of 157 ± 2° using a5.0 µL droplet, a sliding angle of 23 ± 4°, and a shedding angle of 4 ± 1°.On the other hand, when water droplets were placed on uncoated cotton, the droplets spread as can be seen in Figure 3a.The sliding angle was measured as the angle at which a droplet placed on a sample began to roll off its surface. The shedding angle was measured by dispensing droplets from 1.0 cm above the sample and recording the minimum angle of inclination at which the sample was tilted in order for the released droplet to roll off. The coated cotton also stayed afloat when it was placed in a vial with water as shown in Figure 3d. When the cotton was forced into the water, a plastron air layer was trapped between the cotton and the water (Figure 3e). The uncoated cotton sunk in the vial (Figure 3c) and no air layer was observed.
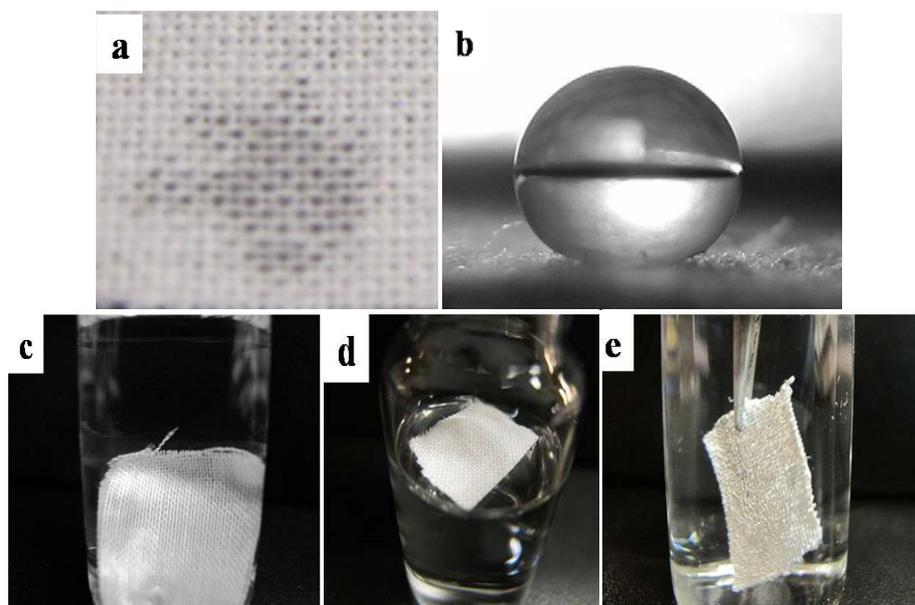
Figure 3. Images of a 5.0 µL water droplet resting on a) Uncoated cotton, and b) coated cotton. Images of c) uncoated cotton, andd) and e) coated cotton in a vial with water.

III. Method 1 – Determination of Dewetting-to-Wetting Transition Caused by Changing Testing Liquid

Test method 1 was developed to assess at what liquid surface tension the dewetting-to-wetting transition occurs for a coated fabric. For a repellent fabric in the dewetting regime, high surface tension liquids usually bead up and roll off the fabric surface without leaving a visible trace. However, in the wetting regime, low surface tension liquids may penetrate into the fabric.

In this method, 2.0×2.0 cm^2 coated cotton fabric swatches were attached to glass slides. The slides were then tilted from the horizontal position to 60˚. In addition, we also used 40˚. Five 10.0 µL liquid droplets were dispensed at the top of each tilted swatch along a horizontal line and their interaction with the swatch was observed. The liquid droplets used had a surface tension range from 72.75 mN/m for water to 21.74 mN/m for 2-propanol. Liquids with surface tension between these two extremes were obtained by mixing 2-propanol with water at different molar fractions.[4]

The behaviour of liquid droplets as they rolled off the coated cotton is summarized in Figure 4. Liquid droplets with surface tensions above 35 mN/m quickly rolled off the coated cotton and no liquid trace was observed. The droplets were in the dewetting regime. Decreasing the surface tension to 31.16 mN/m,20 mass % 2-propanol, lead to droplet pinning, while decreasing the surface tension further to 24.78 mN/m, 50 mass % 2-propanol, resulted in the droplets wetting the cotton. These droplet transitions could be visually discerned when performing the experiment at both 60˚ and 40˚. At the steeper angle, the pinning transition was observed when traces of the droplet were seen on the cotton, while the wetting transition was observed when the droplet traces left a wet residue on the cotton. On the other hand, at the shallower angle, the pinning transition was observed when the droplet did not roll off the cotton, while the wetting transition was observed when the pinned droplet penetrated into the cotton leaving a wet residue. The transitions were more easily discerned when a shallower angle was used for measurements. A fabric worn by a person will adopt many angles which will change with movement. Testing using multiple angles will not only allow for determining the surface tension at which dewetting-to-wetting transitions occurs, but it also show at which angle part of the liquid will come off the garment in the regions where it typically stays on or in the fabric.Thus, Method 1 is a viable test method.
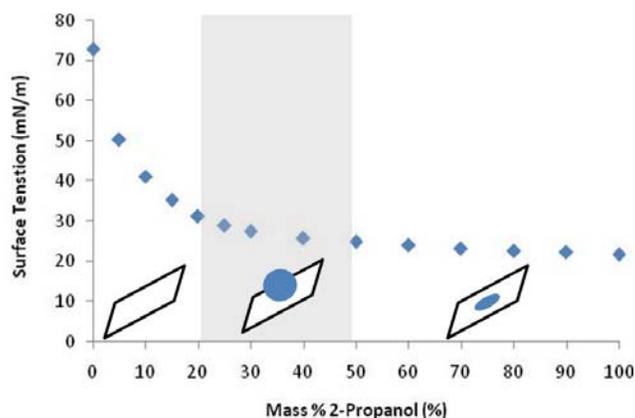
Figure 4. Liquid droplet roll-off behavior on coated cotton titled from the horizon.Dewetting region below 20 mass % 2-propanol (no blue droplet visible on the white coated cotton). Pinning region from 20-50 mass % 2-propanol (blue droplet sits on top of the white coated cotton). Wetting region from 50 mass % 2-propanol (blue droplet spreads and may penetrate into the white coated cotton).

IV. Method 2 – Quantification of the Amount of Liquid Transfer to Fabric

Method 2 was developed to assess the repellency performance of coated cotton fabrics by detectingand quantifying the amount of liquid transferred to the fabric after the liquid droplet rolled off the material.

In this method, the fluorescence intensity of quantum dots were used to detect and quantify the amount of transferred liquid. Hydroxyl functionalized CdSSe/ZnS core/shell quantum dots (QD) with a 540 nm emission peak were purchased for this experiment (Cytodiagnostics). An inverted fluorescent microscope was used to detect the QD and measure their intensity. A filter cube with an excitation wavelength of 460-500 nm and emission wavelength 510-560 nm was used. A mercury lamp with ND4 and ND8 filters set to pass through 3.1 % of the lamp's full power was used as the light source. The fluorescence intensity was determined by acquiring and processing fluorescence images to obtain a mean gray image pixel level which was used as the intensity value.

We first tested the uptake of QD by the coated cotton as a function of time. If the intensity of the QD does not increase with time, then the QD do not significantly adsorb onto the cotton and the detected QD are only due to the QD initially entrenched in the cotton between the fibres and the threads. A 0.60 mg/mL QD solution of 60 mass % 2-propanol in water was used to ensure the coated cotton was in the wetting regime. Four 1.0×1.0 cm^2 coated cotton swatches were submerged in the solution for 10 min, 1 h, 2 h, and 24 h. They were then dried in air in the fumehood before measurements. Six random images of 0.63×0.47 mm^2 of each sample were collected and analyzed. As can be seen in Figure 5, the QD uptake did not increase significantly with equilibration time. We ran the experiment for 24 h to ensure sufficient time for adsorption to occur. However, it would appear that adsorption is not a major process in the system. A similar trend was observed when the experiment was only run to 2 h.
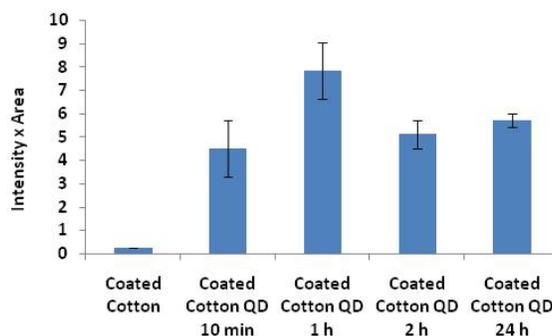

Figure 5.QD uptake as a function of time.

A QD intensity calibration curve was obtained as a function of QD concentration using solutions of 60 mass % 2-propanol with QD concentrations from 0.0 to 1.8 mg/mL. One 1.0×1.0 cm^2 coated cotton swatch was submerged into each QD solution for 20 min. They were then dried in air and in the oven at 120 ˚C before measurements. Six random images of 0.63×0.47 mm^2 of each sample were collected and analyzed. The experiment was repeatedtwice for the

highest two concentrations and four times for the remaining concentrations. The total amount of QD on the coated cotton was obtained from the amount of the solution that was removed from the vial which the cotton uptook. The amount of QD present in the area probed with the microscope was obtained and plotted on the x-axis in Figure 6. The intensity value measured from the probed area was multiplied by the area that was probed and plotted on the y-axis. As can be seen from the plot, the uptake of QD increased as the QD concentration of the solution increased. A straight line fitting the data had the following equation:

$$y = 83836x \text{ with } R^2 = 0.978 \quad (2)$$

The variation between experiments could be due to degradation of the QD with storage time, or fluctuations in the excitation lamp power, or the heterogeneity of the cotton coating (we are assuming the polymer coating is uniform everywhere on the cotton), or bias in the area being imaged (we cannot image the entire cotton, therefore we take a few random images), or experimental errors introduced from the microscope and detector.
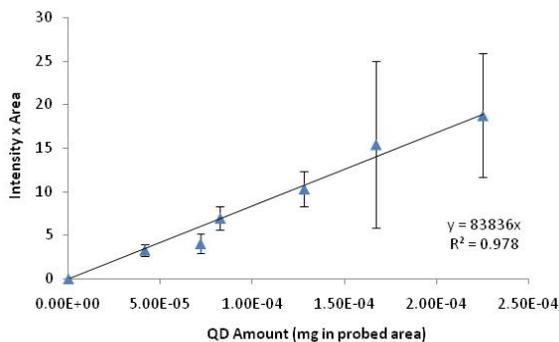

Figure 6. QD Intensity× area as a function of QD amountin the area.

Liquid droplets loaded with QD were used for roll-off experiments on the coated cotton fabrics. QD solutions were prepared with 0, 10, 30, or 60 mass % of 2-propanol to give 10 µL droplets with 1.8×10^{-2} mg QD in each one.1.0×1.0 cm^2 coated cotton swatches were mounted

onto glass slides and tilted from the horizontal direction to 60˚. The experiment was repeated four times. A steep angle was used in order for the droplet to roll off the surface for all liquids tested. If the droplet stays on the surface, the probe liquid will evaporate with time leaving behind all of the QD in both the pinning and wetting regimes. For example, when a 60 mass % 2-propanol QD solution is used with the coated cotton mounted at 60˚ from horizontal, the mean fluorescence intensity is 45 ± 19, but if the same conditions are used at a 40˚ from horizontal, the intensity is 77 ± 8. A steep angle can also ensure no adsorption of the QD onto the cotton.

The mean fluorescence intensity did not significantly change with an increase in 2-propanol content in the probe liquid when uncoated cotton was used for testing. This result was expected since the uncoated cotton was already in the wetting regime for all testing liquids and none of the liquid droplets rolled off. When coated cotton fabrics were used, the mean intensity increased as the surface tension of the probe liquid decreasedand the droplet state changed from the dewetting-to-pinning-to-wetting regime. More of the QD were left behind on the cotton. At 0 mass % 2-propanol (water)the mean intensity is very low as can be seen in the image in Figure 7a. However, some QD were present on the cotton as can be seen more clearly in Figure 8 when the microscope lamp is used at full power. At 10 mass % 2-propanol, the mean intensity is higher as can be seen in the image in Figure 7b. In both of these cases, the droplets were in the dewetting regime and no trace was visible using traditional methods, but the fluorescence test was able to detect some leftover liquid.

We then quantified the amount of liquid left behind during droplet roll off. All the areas that had a fluorescence signal were measured for the 0 and 10 mass % 2-propanol. For the 30 and 60 mass % 2-propanol, 6-8 representative fluorescence images were recorded. These traces were large and it was not possible to image all of them. The dimension of the whole area of the

trace was measured using a ruler and the fluorescence signal as guidance. The amount of quantum dots was calculated using the equation derived from the QD calibration experiment.The data is tabulated in Table 1. More of the QD were left on the cotton as the 2-propanol fraction increased as expected.
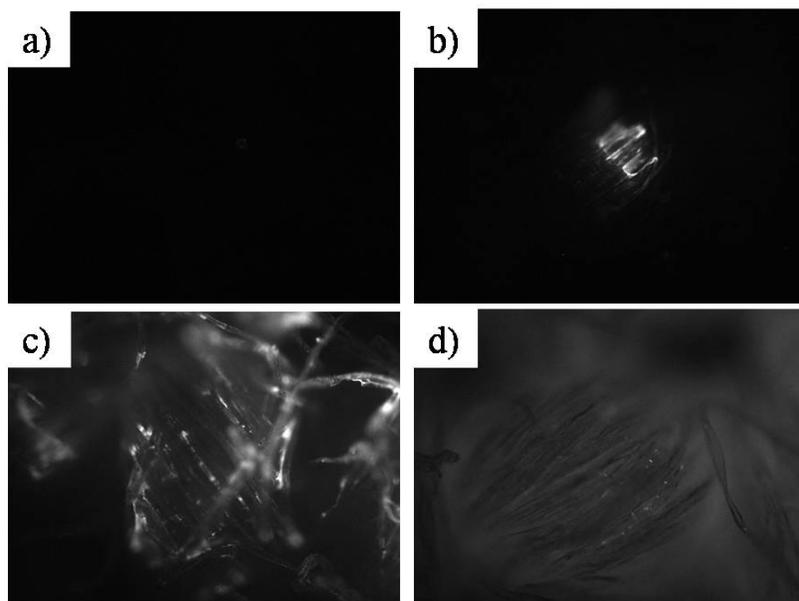

Figure 7. QD fluorescence images of the liquid trace after 10 µL with 1.8×10^{-2} mg QD droplet roll-off test on coated cotton in a) 0 mass % 2-propanol (water), b) 10 mass % 2-propanol, c) 30 mass % 2-propanol, and d) 60 mass % 2-propanol.
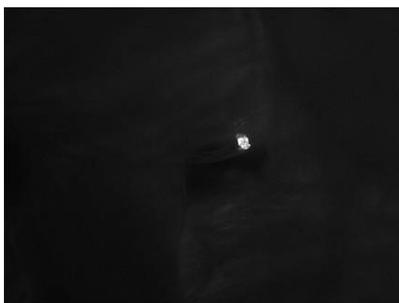

Figure 8. QD fluorescence images of the liquid trace after 10 µL with 4.0×10^{-2} mg QD water droplet roll-off test on coated cotton using no lamp filters (Same imaged area as Figure 7a).

Table 1.QD amount on coated cotton after 1.8× 10^{-2} mg QD in 10 μL droplet roll off.

Mass %2-propanol (%)	QD amount after droplet roll-off (mg)	% QD left on the cotton (%)
0	4.3×10^{-8}	2.4×10^{-4}
10	1.3×10^{-5}	0.07
30	3.3×10^{-3}	20
60	1.0×10^{-2}	60

The liquid droplet roll-off experiment was further investigated with droplets in the dewetting regime. In this area, there is no liquid trace detectable with traditional methods. QD solutions were prepared with 0, 5, or 15 mass % of 2-propanol to give 10 μL droplets with 4.0×10^{-2} mg QD in each one. A sample inclination angle of 60°was used again. The signal is more intense and easier to find at higher QD loading. Figure 9 shows the fluorescence images for the 3 different cases, while Table 2 quantifies the amount of QD left behind after droplet roll-off. In this case too, as the fraction of 2-propanol increased, the amount of residual QD increased.

Method 2 was challenging to develop. The use of QD and fluorescence imaging allowed for both the detection and the quantification of residual liquids on repellent coated cotton fabrics when traditional methods were not adequate. However, for future experiments in the dewetting region, the filters on the lamp should be removed to make detection and measurements easier. A calibration curve for this case should then be prepared using more dilute solutions to not overwhelm the detector.

Figure 9. QD fluorescence images of the liquid trace after 10 µL with 4.0×10^{-2} mg QD droplet roll-off test on coated cotton in a) 0 mass % 2-propanol (water), b) 5 mass % 2-propanol, and c) 15 mass % 2-propanol.

Table 2.QD amount on coated cotton after 4.0×10^{-2} mg QD in 10 µL droplet roll off.

Mass %2-propanol (%)	QD amount after droplet roll-off (mg)	% QD left on the cotton (%)
0	4.3×10^{-7}	0.1×10^{-3}
5	4.3×10^{-5}	0.11
15	3.2×10^{-3}	7.9

V. Method 3 – Measurement of Breakthrough Pressure of a Liquid

Test method 3 was developed to measure the liquid breakthrough pressure for the coated cotton fabrics. A repellent non-permeating fabric becomes permeating to a liquid under an applied stress load. Hydrostatic pressure testing can be used to determine this breakthrough pressure.[5-6]

In this method, 3.5×3.5 cm^2 coated cotton fabrics were tightly attached to a graduated cylindrical plastic column using tape and parafilm as shown in Figure 10a. A 1.5 cm diameter circle of cotton was left exposed. Liquid was slowly added to the column until the liquid flowed through the cotton. The height at which the liquid flowed was measured. Two coated cotton fabrics were tested twice with liquids in the dewetting regime, water and 10 mass % 2-propanol,

in the pinning regime, 30 mass % 2-propanol, and in the wetting regime, 60 mass % 2-propanol. The cotton fabrics after each measurement were dried for 10 min in a 120 ˚C oven.

The breakthrough pressure, P_{bt}, is calculated from the height at which the liquid permeates the coated cotton fabric (h) as follows:

$$P_{bt} = \rho g h \qquad (3)$$

where ρ is the liquid density and g is the gravitational acceleration. This can be seen in Figure 10b. As the surface tension of the probe liquid decreases, the critical height at which the liquid permeates into the cotton decreases resulting in a decrease in P_{bt}. It is easier for a liquid to permeate through the cotton in the pinning regime and very facile in the wetting regime.
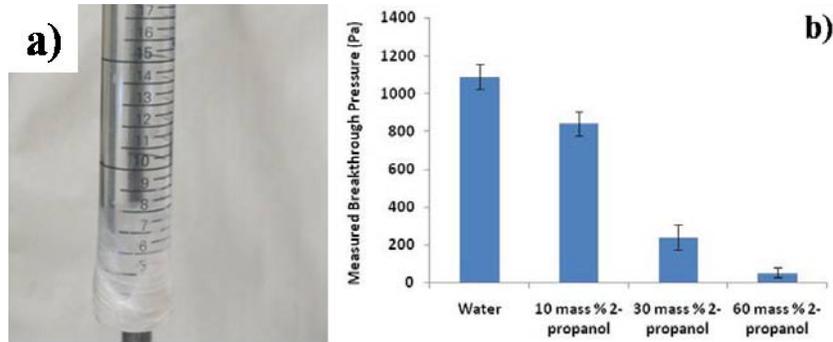

Figure 10.a) Experimental setup to measure breakthrough pressure, and b) Measured breakthrough pressure as the 2-propanol fraction increases resulting in decreasing liquid surface tension.

The P_{bt}can be estimated by assuming the cotton bundles and fibres are periodicuniform cylinders. In this case, P_{bt} is:

$$P_{bt} = \frac{2R\gamma_{1v}(1 - \cos\theta)}{D^2 + 2RD\sin\theta} \qquad (4)$$

where R is the cylinder radius, 2D is the spacing between the cylinders, γ_{1v} is the surface tension of the liquid, and θ is the equilibrium contact angle of the liquid on an equivalent smooth surface.For highly fluorinated surfaces, the equilibrium contact angle with water is 120˚. When

the geometry of the fibre bundle is considered the dominant structure of the material, P_{bt} is predicted at 1600 Pa at a height of 16 cm. When P_{bt} is calculated using the individual fibres, the value is predicted to be 7900 Pa at a height of 81 cm. The measured water P_{bt} of the coated cotton was 1100 Pa at a height of 11 cm. The fibre bundle value was a good approximation for the P_{bt}. The discrepancy could be attributed to imperfect system sealing, defects in the coating, or defects in the cotton. In particular, the bundles are not uniform cylinders and also there is some variation in the spacing. This non-uniformity is worse for the individual fibres. The same fibre can have different diameters along its length. The spacing between the fibres also varies greatly, some fibres cross each other, or others are close together, then separate with distance. Nevertheless, the experimental method developed to measure this P_{bt} is a good test to characterize non-permeating fabrics.

VI. Conclusions

Repellent cotton fabrics were fabricated using a diblock copolymer, PIPSMA-*b*-PFOEMA. The PIPSMA block in the presence of HCl underwent a sol-gel reaction with the cotton fabric as well as with itself to yield cotton grafted cross-linked polymer. The fluorinated block, PFOEMA, was left on the outside of the system and imparted liquid repellent properties to the cotton due to its low surface energy. The resulting coated cotton was used to validate three test methods that we developed to assess the repellency performance of this material. A number of test liquids with low and high surface tensions were prepared by mixing water to 2-propanol to obtain liquids with surface tensions from 72 mN/m to 22 mN/m. The first test method assessed the dewetting-to-wetting transition of the material by observing the roll off behavior of these liquid droplets on the cotton which was mounted at a 60° angle to the horizontal. The

transition to droplet pinning occurred when the surface tension was decreased to 31.16 mN/m, while the transition to droplet wetting occurred at 24.78 mN/m. In the second method, the amount of liquid transferred to the fabric after the liquid droplet rolled off the material was detected and quantified using the fluorescence intensity of quantum dots loaded into the test droplet. The amount of residual liquid left behind on the coated cotton increased as the surface tension of the test liquid decreased. In addition, we were also able to observe liquid residual with droplets in the dewetting regime which we could not detect with traditional measuring methods. Finally, the third test method measured the liquid breakthrough pressureat which a material becomes permeating. The breakthrough pressure decreased as the surface tension of the test liquid decreased. All three methods gave new insight into the repellent properties of coated fabrics.

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