Development of super-hydrophobic and stain repellent fabric finish

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Abstract. This study intended to develop a health and environmental friendly super-hydrophobic textile fabric using a specific Fluoro Silane (Fs) finish. A novel Fs finish was prepared and applied on an acrylic fabric using a pad-dry-cure method. The finished fabric was evaluated for the degree of hydrophobicity, durability and stain repellency. The finished fabric exhibited static water contact angle greater than 170° and received 90 AATCC (4 ISO) rating that is recognized as super-hydrophobicity and this property was maintained even after a 50,000 cycle abrasion test. FTIR analysis identified the characteristic peaks related Si-O-Si and C-F asymmetric stretching bands of the finish on the fabric indicating a robust attachment of the finish on the fabric. Finish fabric did not show any change in appearance or tactile characteristics of the fabric.

Keywords: Acrylic fabric; Contact Angle; Fluoro silane; Super hydrophobic; Stain repellant

1. Introduction

Super-hydrophobic fabric technology evolved from biomimetic technology. This was derived from the lotus leaf phenomenon as researched by many scientists. In the Greek words, “hydro” means water, “philicity” means affinity, and “phobicity” means lack of affinity. So, the term “Super-hydrophobic” means extremely water repellant. When the static water contact angle θ is >150°, the surface is super-hydrophobic [1]. Under such condition, the water drop forms a spherical shape achieving minimum surface area because of the cohesive forces between water molecules. As the water drops fall on the surface, they effortlessly roll off the surface without wetting it at all. Because of very low surface energy of the super-hydrophobic surface, loosely held dirt and soils get easily attached to the rolling drops and are removed. The lotus leaf is one of the best-known natural super hydrophobic surfaces that effectively removes mud as a water drop flows over the surface. A Nano-level hydrophobic natural wax crystal was found to be present on the top of the micro bumps on a lotus leaf, which makes the lotus leaf a self-cleaning as well as strongly hydrophobic [2]. In order to produce super hydrophobic textiles, researchers have used several techniques. Kawai and H. Nagata [3] have used soft lithography, X-Ray lithography, electron beam lithography, Nano sphere lithography and photolithography to develop super hydrophobic surfaces. Zhang et al [4] and Chen et al [5] used the same technique by creating silicon Nano-pillar arrays. A Phase separation technique was used to prepare Super- hydrophobic surfaces. Polizos et al [6] obtained a hierarchical porous structure through interconnection of different dimensions of pores. They used Polyethylene glycol (PEG) and Polydimethyl siloxane (PDMS) in 1:1 ratio in the phase separation, to create a surface that had a water contact angle of 160°. Bao et al [7] used chemical vapor deposition
method, where a substrate was created in the form of non-volatile film due to reaction of the gaseous reactants. Metal oxide nanoparticles like ZnO, Al$_2$O$_3$ and Fe$_3$O$_4$ etc., were used to fabricate superhydrophobic surfaces. Several researchers have used sol-gel and other chemical to produce superhydrophobic surfaces. Sahoo and Kandasubramanian [8] used organic, inorganic materials and metal alkoxides for sol-gel techniques. Hoeffagels et al. [9] produced super-hydrophobic cotton fabric using silica particles. They reported that WCA was 155°. Ivanova et al. [10] fabricated super-hydrophobic cotton fabric by altering the fabric structure using Fluoro silane (Fs) material. Xue et al [11] used amino and epoxy functionalized silica nanoparticles along with stearic acid and 1H, 1H, 2H, 2H-perfluorodecyl-trichlorosilane on cotton fabric to create super-hydrophobic characteristics and that they claimed was 170° WCA. Meng et al., [12] Das and De, Meng et al. [13] used long chain fluorinated compounds on cotton fabric to create super-hydrophobic characteristics.

The objective of this study was to develop a Super-Hydrophobic, stain repellant fabric finish synthesizing a fluoro-silane compound and apply to acrylic fabrics to create super-hydrophobic properties. However, this finish can be applied to polyester, cotton, wool, nylon, silk and blend fabrics. This silane has been rated as 0 health hazard and 0 physical hazard by US HMIS and NFPA agencies [14] and is extremely durable. The process is straightforward and commercialization friendly.

2. Experimental Methods

2.1 Materials

This finish was applied on plain weave fabric produced from acrylonitrile and 4-5% Methylmethacrylate as copolymer. Fabric weight was 8.24 oz. per sq. yd, having construction 25 x 32 (ends and picks per inch).

2.2. Finish preparation and application

Reagent-grade solvent butanol, Disodium hydrogen phosphate, 72% Sulphuric Acid were obtained from Sigma Aldrich. A specific Fluoro silane (Fs) was obtained from Matrix Scientific. All chemicals were used without further purification. Pre-determined amount of Fluoro silane was added to the reagent-grade solvent butanol and stirred continuously at room temperature at 350 RPM. A small amount of the catalyst, disodium hydrogen phosphate, was added to facilitate the addition of the finish to the prepared acrylic specimens. A few drops of Sulphuric acid were added slowly to the mixture while stirring to maintain the very low pH of 2, to control the condensation reaction. The required amount of additional butanol was added and stirring was continued. The solution was stirred continuously for one hour and was placed in the refrigerator for twenty-four hours prior to application. Care was taken to evade rapid condensation reaction and precipitation by carefully monitoring pH and condensation time. Finish was applied on to the acrylic fabric sample using a pad-dry-cure method. Prior to the padding process, finish was force sprayed on the fabric to ensure even application on the fabric surface. Treated fabric was dried at 60°C for 15 minutes and then cured at 165°-170°C for 15 minutes in an oven. A schematic diagram of the application process is illustrated in Figure.1

![Figure 1](image-url)  
**Figure 1.** The Super-hydrophobic finish application process.
2.3. Water Contact Angle (WAC) measurement
The Static Contact Angle Measurement is one of the measures of hydrophobicity. The Device by First Ten Angstrom (FTA-200) was used for measuring the static contact angle. Images for contact angle measurement were captured using Amscope MU853B 14MP high-speed digital camera, attached to the device set up. Five readings were taken from different areas of the same sample and analyzed by the computer plugin Low Bond Asymmetric Drop-Shape Analysis (LBDSA) [15] available with the open-sourced JAVA application Image R. In the LBADSA method, the theoretical profile of the drop is not fitted to a certain drop contour, instead optimized according to an image energy approach. The measurement is based on perturbation solution of the axisymmetric Laplace equation. During the fitting process, complete pixel information is used. The use of this global model result in highly accurate contact angles and has an edge over the other methods, when a precise accurate contour detection is difficult because of un-sharp or noisy boundaries (as observed in the textile fabrics).

2.4. Water Repellency: Spray test
AATCC Test Method 22 (ISO 4920) was used to determine the degree of hydrophobicity of the fabric after the application of the finish. In this method, water is sprayed against the taut surface of a test specimen, under controlled conditions, that produces a wetted pattern whose size depends on the relative repellency of the fabric. The evaluation is accomplished by comparing the wetted pattern with a given standard chart. Rating ranges from 0 to 100 according to AATCC where a 0 to 5 rating is given according to ISO. A 100 (5) rating means that there was no sticking or wetting of the upper surface, while a 0 rating indicates complete wetting of the whole upper surface.

2.5 Subjective Visual Evaluation
Industries generally follow a popular subjective visual observation method for evaluating superhydrophobic behavior of fabrics. It consists of putting drops of water on the surface of the fabric and observing whether the water drops adhere to and wet the surface of the fabric or not. In this process, water drops poured onto the fabric and it is observed whether the drops take stable spherical shapes, and whether the drops roll over the surface without any residue when the fabric surface is tilted or moved.

2.6 Abrasion resistance
The durability of the finish was measured using 50,000 cycles by ASTM method D4966-12 on a Martindale Abrasion tester. Before and after abrasion, the specimens’ weight was measured and any change in contact angles (WCA) was evaluated.

2.7 Fourier Transform Infrared (FTIR) Spectroscopic Analysis
Attachment of the Fluoro Silane on the acrylonitrile fabric was examined using FTIR spectroscopy. Transmission scans of the fabric before and after the super-hydrophobic finish treatment were produced. Expected bands (peaks) arising from the application of the finish were evaluated. Furthermore, the spectra before and after the abrasion were analyzed to evaluate the durability of the finish on the fabric sample. Secondary derivative transformation of spectra was performed, using a Perkin Elmer software to bring them to a common baseline and to remove some of the noise that may arise from the art effects. This method facilitates the comparison between two or more spectra. The first derivative of a spectrum is simply the measure of the slope of the spectral curve at every point. The slope of the curve; however, is not affected by the baseline offsets in the spectra. Second derivative ignores the offset and it is not affected by any linear “tilt” that may exist in the data. As a result, second derivative spectrum is a very effective method for removing both the base line offset and the slope from the spectrum [16]. It has been observed that second derivative spectra allow us to better understand the overlapping broad bands that often exist in complex material like polymeric fibers spectra. From the second derivative spectra, appropriate bands’ peak is evaluated.

2.8. Stain Repellency Evaluation
Stain repellency test against ketchup, mustard, and jam were performed on the fabric surface separately. The test specimens were left for 15 minutes after the application of the staining substances. Then, the fabric was rinsed with normal tap water and dried. The post-washing samples were rated for stain using AATCC Test - 130 Stain Release Replica where 5 is no stain and 0 is maximum staining of the specimens.

3. Results and Discussion

Acrylic fabric specimens were treated with Fluoro silane finish and cured at an elevated temperature. Acid group present in the copolymer were expected to get attached with the silane through a condensation reaction under acidic condition. The fabric containing COO- groups was immersed in the Fluoro silane solution containing triethoxy silane. As a consequence, plenty of silane groups reacted with COO- groups on the substrate followed by curing which resulted in a robust attachment of finish on the fabric surface.

Fluorinated methyl groups are less reactive and possess lower surface energy compared to the usual hydrophobic -CH₃ groups, owing to the presence of very strong C-F bonds [17, 18]. Consequently, this finish is expected to provide very high hydrophobicity while it does not attach to the soil strongly. It is important to consider that silica based, and other hydrophobic coatings are not stable enough for day-to-day commercial uses [12]. This Fluorosilane finish; however, is very sustainable and durable for practical uses. This fluorine complex was chosen because US health and environmental agencies like OSHA and NFPA rated the compound as 0 for health and physical effects [14].

WCA is considered a good indicator of hydrophobicity of a fabric. The fabric is recognized as super hydrophobic, when WCA exceeds 150°. In this investigation, treated acrylic fabric was tested for static contact angle at 5 different locations. As seen in Figure 2, WAC values of treated fabric varies from 177.5 to 175.4 degrees which is significantly greater than 150° confirming a very high level of super-hydrophobicity of the test specimens. Another practical super-hydrophobicity test on these Fs treated acrylic specimens was carried out using AATCC 22 spray test that is most commonly used by the industry. In this study, Fs treated specimens received >=90 rating where a rating of >=80 is considered as a super hydrophobic substrate. After 15 minutes, the specimen was tilted, and it was observed that the liquid drops rolled off the fabric leaving the specimen fabric completely dry and without any stain.

Figure 2. Contact angle values of the Fs treated test specimens and an illustration of the water drop on the fabric specimen and the liquid drops on the treated specimen after 15 minutes.

FTIR study was performed to understand the chemical bonding of Fs finish on the acrylic fabrics. Second derivative of the transmission spectra of Fs treated, and untreated fabric specimen is shown in Figure 3. The peaks that appeared at 724 cm⁻¹ and at 996 cm⁻¹ are associated with C-F bond [19] found on the Fs treated specimen which was not seen on the untreated acrylic fabric. The peaks at 852 cm⁻¹ and at 1094 cm⁻¹ arising from asymmetric stretching vibration of Si-O-Si [18] were found with high intensity on the treated fabric spectra. These bands on the treated samples support that the Fs finish attachment on the acrylic fabric.
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Figure 3. The 2nd Derivative FTIR spectra of the untreated and treated with Fs finish fabrics.

The durability of the Fs finish on the fabric was determined by abrasion testing using 50,000 cycles of abrasion on the fabric surface on a Martindale Abrasion Tester. Post 50,000 cycles of abrasion fabric did not show any changes in surface appearance and had no loss in super hydrophobic finish applied to the fabric. The weight loss percent was 0.22%, which is attributed to insignificant amount of unattached finish. The abraded fabric did not show any changes in surface appearance and in tactile (hand) properties.

FTIR scan, Figure 4 exhibited the same peaks at 724 cm\(^{-1}\), 852 cm\(^{-1}\), 996 cm\(^{-1}\) and 1094 cm\(^{-1}\) associated with the Fs finish on the fabric before and after abrasion.

Figure 4. FTIR scan of the Fs finish treated fabric before and after abrasion.

The contact angle of the specimen remained the same value (above 170°) before and after abrasion. So the contact angle didn’t change before and after 50,000 cycles of abrasion.

For the stain repellency test, ketchup, mustard, and jam were applied to the fabric surface separately and left for 15 minutes. Then, the fabric was rinsed with normal tap water and dried. No residue and stain was observed on the washed fabric; therefore, a 5 rating was given according to the Stain Release Replica AATCC Test 130.

4. Conclusion
This study developed a Super-hydrophobic acrylic fabric using a specific Fs finish. The treated fabric did not show any changes in the surface appearance and in tactile property. Experimental data showed that super-hydrophobic property of the fabric was maintained even after undergoing 50,000 abrasion cycles. The spherical drops of liquid rolled off the fabric surface without wetting or adhering to the fabric. The treated fabric had a water contact angle $\geq 170^\circ$, even after 50,000 abrasion cycles, implying the finish was durable. Water Repellency: spray test provided 90 (AATCC Rating) which is the commonly accepted value by industry for a super-hydrophobic fabric. No residue and stain was observed on the washed fabric during the stain-repellency test against Ketchup, Mustard and Jam. FTIR data identified the presence of Fs finish on both the treated fabric before and after abrasion. It is concluded from the experimental data that the Fs finish used on the acrylic fabric provided a durable super hydrophobic characteristic. A unique feature of this finish and the method for the super-hydrophobic fabric is its suitability for the commercial process and cost.
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