fibers

MDPI

Article

An Experimental Investigation on Optimizing Liquid Repellency of Fluorochemical Urethane Finish and Its Effect on the Physical Properties of Polyester/Cotton Blended Fabric

Sunidhi Mehta

Program of Fashion, Dress and Merchandising, West Virginia University, Morgantown, WV 26505, USA; sunidhi.mehta@mail.wvu.edu

Received: 23 September 2020; Accepted: 17 November 2020; Published: 1 December 2020

Abstract: This paper aims to optimize the liquid repellency performance of fluorochemical urethane (FU)—a patented technology with a shorter fluorocarbon chain (C_4). FU is free from persistent bioaccumulative toxins such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), unlike the long-chain fluorinated chemicals ($>C_6$). Different sets of varied finish concentrations with an extender and a wetting agent were prepared to treat the 65/35% polyester/cotton blended fabric. The finish concentration was optimized based on the liquid repellency (water and oil-repellency) of the treated fabric and its laundering durability. In addition, the effect of the finish concentration on selected physical properties of the treated fabric was studied as well. The liquid repellency, laundering durability, and selected physical properties of the treated and untreated fabrics were analyzed using ASTM and AATCC standard test methods. The results of textile substrates treated with 60 g/L of FU show an optimum balance of desired liquid repellency without affecting the physical properties of the fabric significantly.

Keywords: air permeability; polyester/cotton blend; crease recovery angle; textile finishing; performance textiles; fluorochemical urethane; laundering durability; oleophobicity; tensile strength; hydrophobicity

---

1. Introduction

The phenomenon of water-repellency is timeless. A great example of this effect can be seen on the surface of the lotus leaf and is also known as the "lotus-leaf-effect" [1]. It was first introduced in textiles in the 1930s with the development of durable water repellents (DWRs) [2]. Since then, there have been several advances in the field of DWR technology. These are mainly divided into three categories: fluorocarbon-based, silicon-based, and hydrocarbon-based [3,4]. Fluorocarbon-based DWRs or fluoro-chemicals are the most popular choice due to their lowest surface energy [2,5–8]. They have revolutionized the functional textile market because of their high durability and consistent performance [8].

To achieve the hydrophobic effect, the critical surface energy of the material must be lower than the surface tension of the liquid being repelled [1]. The surface tension of water (73 mN m^{-1}) is two to three times greater than the surface tension range of oils (20–35 mN m^{-1}) [2,5]. Therefore, it is often much harder to achieve a high oleophobic performance than hydrophobic performance. In other words, the oleophobic fabric can repel water due to its lower critical surface energy, but the hydrophobic fabric may not be able to repel oils. Nevertheless, oleophobicity is a necessary function in occupational Personal Protective Equipment (PPE) and is a significant aspect of liquid repellency. Liquid repellency is a property of repelling both water and oil-based liquids and is a highly desirable function in textiles [5,9]. It ranges widely from a "necessary" function in occupational protective clothing to a "desirable" function in outdoor textiles and further to a "luxury" in automobile upholstery. It is an essential property in occupational protective clothing for medical professionals and workers in the petroleum industry [5,7]. Despite providing excellent liquid repellency, the fluoro-chemicals have some environmental implications and have faced criticism by the environmentalists.

1.1. Toxicology of Fluorochemical Finishes

The DWRs using C_8 or longer fluorocarbon polymers have been banned by United States Environmental Protection Agency (USEPA) due to their release of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate PFOS toxins as a byproduct in the environment [10–13]. Consequently, there has been a tremendous amount of research in this area to find an eco-friendly alternative. However, finding an optimum balance of function with lesser/no environmental impact is still a challenge in the field of DWRs [10,12]. C_6 has the closest liquid repellency performance to C_8 without PFOA emissions in the environment. Instead, it releases a byproduct called perfluorohexanoic acid (PFHA) which is 40 times less bioaccumulative than PFOA [10,13]. Nonetheless, it is still present in the environment and is not completely biodegradable. Hence the journey to find the closest substitute remains.

C_4 is the latest advance in the field of fluorocarbon-based DWRs. It is a patented technology and is also known as fluorochemical urethane (FU). It produces perfluorobutanesulfonate (PFBS) as a byproduct [11]. As per US-EPA guidelines, it does not accumulate in the environment to the extent that higher perfluorinated byproducts did [10–14]. Simply put, PFBS does not remain in human and animal bloodstreams for long and is eliminated much quicker than PFOA and PFHA. Therefore, it is considered a safer option with equivalent liquid repellency performance. The EPA recognizes the importance of fluorochemicals (FC) and their broad range of applications. Thus, the EPA has not banned the use of fluoro-chemicals altogether but only the long-chain ($\geq C_8$) FCs that lead to persistent, bio-accumulative, and toxic (PBT) substances found in the food chain, human blood, and the environment [15]. The shorter chain fluorochemicals ($\leq C_6$) are less toxic and less bioaccumulative in wildlife and humans [16]. In general, the shorter the fluorocarbon chain, the lesser the environmental impact in terms of biodegradability. However, the liquid repellency function and finish durability also get reduced with short-chain fluorocarbons.

1.2. Uses of Fluorochemical Urethane and Its Impact on Textile Properties

FU uses a short-chain fluorinated hydrocarbon and is derived from a reaction with a polyfunctional isocyanate compound, fluorinated monofunctional compounds, at least one hydrophilic polyoxyalkylene compound optionally, and isocyanate-reactive silane compounds [11]. Currently, FU-based ready-to-use finishes come in various compositions for several porous as well as non-porous surface applications such as textile, leather, concrete, grout, and paper. Thus, the application of the finish and its uses are well-known. However, the optimum finish concentration and its combination with other chemical compounds to enhance the performance and durability of the finish are yet to be established. Furthermore, the impact of different concentration levels of the finish on fabric properties will provide a better understanding of the optimal finish concentration that must be used to achieve the desired liquid repellency performance without sacrificing the strength and pliability of the treated fabric.

Fluoro-chemical treatment significantly changes the mechanical properties of the treated fabric [2]. Some of the undesirable effects of the finish are static electricity build-up, poor soil removal in aqueous laundering, added fabric stiffness, soil redeposition in laundering, loss in tensile strength, and increased flammability [2,15,16]. On the other hand, some of the mechanical properties that are often improved with the finish application include better durable press property, less drying time, more rapid ironing, and improved resistance to certain chemicals. These negative and positive effects on the fabric properties vary based on several factors (fabric thickness and construction, fiber content and type, yarn properties, finish application method, and curing temperature) and finish concentration is one of the most significant of all.

This study is focused on (1) optimizing the FU finish concentration to achieve the desired water-repellency as well as oil-repellency functions and (2) studying the effect of the finish concentration on the treated fabric by testing selected physical properties of the treated vs. untreated fabric. Since C_4 is a shorter fluorocarbon chain, it also has reduced laundering durability compared to C_6 or C_8. Therefore, a finish extender has been used to improve the laundering durability of the treated fabric. A more detailed composition of the finish solution has been discussed below in Section 2.2. Lastly, the liquid repellency at various laundering cycles has been studied and reported in this paper.

2. Materials and Methods

2.1. Selection of the Fabric and Pre-Finish Preparation

A 1 × 1 plain weave fabric with a blend of 65% polyester and 35% cotton was selected for this study. The weight of the fabric was 210 GSM with 0.38 mm thickness. The fabric was dyed but unfinished, i.e., ready-to-finish (RTF). It was important to use an unfinished fabric for this study because most textile finishes alter the pH and absorption of the fabric, which in turn affects the application of FU finish. Several steps were followed to prepare the fabric for its optimum intake of the FU finish, and these are discussed below:

2.1.1. Pre-Finish Preparation of the Fabric

FU performance can be impaired by the presence of auxiliary residues, especially silicone and cationic softeners. Therefore, it is very important to remove these to assure proper absorption and uniform application of the finishing agent. In order to prepare the fabric for finishing; first, the substrates were soaked in an alkaline wash solution to ensure that the fabric was free of any surface impurities. Each substrate was soaked in a solution of 2 g/L of an anionic detergent (Sigma Aldrich, St. Louis, MI, USA) containing 1 g/L of sodium carbonate (Sigma Aldrich). The pH of the solution was maintained between 8 and 9 and the temperature of the solution was kept at 40 °C. The substrates were soaked in the solution for 20 min and then rinsed well with plain water afterward. Subsequently, the fabric was soaked in an acid wash following the same method as the alkaline wash. The 1 g/L of sodium carbonate was replaced with 3 mL/L of acetic acid (Sigma Aldrich) for the acid wash. This process ensured the removal of any surface impurities or fabric auxiliaries that may obstruct the proper absorption of the FU finish at the later step.

2.1.2. Determination of the Substrate pH

The fluoro-chemicals work best at slightly acidic pH. Fabric treatments such as bleaching and dyeing change the pH of fabric dramatically, so it is important to determine the pH of the fabric before the application of the finish. Hence, the substrates were soaked in 100 mL distilled water, keeping the material to-liquor ratio (MLR) at 1:20. In another beaker, 100 mL of distilled water was taken as a control. Both solutions were brought to boil and then allowed to cool. The pH of the two solutions was measured at room temperature using a digital pH meter.

2.1.3. Determination of Silicone Presence

Silicone forms a hydrophobic film on textile surfaces and is often applied on the fabric surface after dyeing to improve fabric softness and to keep surface impurities/dirt from sticking on the fabric surface. For this study, it was important to test the presence of silicone in the pre-treated fabric, as silicone considerably hinders the absorption of the FU-based finish on to the fabric [11]. The following tests were conducted to determine the presence of silicone.

Method 1: Regular adhesive tape was stuck on the fabric surface. If the tape stuck to the fabric, the absence of silicone in the fabric was presumed.

Method 2: A 1 × 1 cm fabric swatch was dipped in 10 mL of perchloroethylene in a test tube. The test tube was shaken for a few minutes. If no foam formed, it was presumed that no silicone was present in the fabric.

These two tests confirmed that there was no silicone present on the pre-treated fabric, which means that the fabric was ready for the finish application.

2.2. *Preparation of Finish Solution*

A set of finish solutions at various concentration levels of FU i.e., A = 30, B = 40, C = 50, D = 60, and E = 70 g/L were prepared. The fluorochemical urethane was procured from the manufacturer as a standalone compound instead of a ready-to-use commercial product that is used for stain repellent finish on carpets. Each solution set (mentioned above) contained 10 g/L of isopropyl alcohol (Sigma Aldrich) and 10 g/L of oxime-blocked polyisocyanate (Huntsman Chemicals). Isopropyl alcohol acted as a wetting agent and helped with the uniform application of the finishing agent, whereas the oxime-blocked polyisocyanate improved the laundering durability of the finish. Each finish solution was prepared in a glass beaker by mixing all components for 7 min at 500 rpm speed to ensure good homogeneity of the mixture. For example, set A was prepared by mixing 30 g/L of the FU finish along with 10 g/L of isopropyl alcohol and 10 g/L of the oxime-blocked polyisocyanate in a glass beaker at 500 rpm for 7 min. Similarly, finish solutions of sets B, C, D, and E were prepared by changing the FU concentration (as mentioned above) but keeping other chemicals' composition the same. The pH of each finish solution was maintained at 5.5 as the FU application works best at acidic pH.

2.3. *Finish Application on Textile Substrates*

Each finish solution prepared with the above methods was applied on a textile substrate using the lab model padding mangle with a wet pickup of 65%. After the finishing treatment, the textile substrates were dried at 120 ± 5 °C for 8 min using a lab model oven and cured at 130 ± 5 °C for 5 min. The curing treatment ensured the longevity of the finish. The concentration at which the substrates gave the best results in relation to physical properties, liquid repellency performance, and laundering durability test was considered optimum and is reported in the Results and Discussion sections of this paper.

2.4. *Impact of the Finish Concentration on the Selected Physical Properties of the Fabric*

A series of tests were conducted on the treated and untreated textile substrates to study the effect of the finish concentration on the selected physical properties of the fabric, such as durability, fabric hand, and air permeability. It is important to study the effect of the finish on the fabric as the fluoro-chemicals are known to negatively affect the strength, and pliability of the treated fabrics. Nevertheless, the degree to which these finishes impact fabric properties vary based on several factors including, but not limited to, fabric thickness, fiber content, and type, concertation of the finish and finish application conditions such as curing temperature. In order to understand the effect of the finish concentration, only the concentration of the finish was varied, and the rest of the parameters were kept constant.

2.4.1. Tensile Strength

The tensile strength of the samples was determined on a computerized universal tensile strength tester (Instron) [17]. The mean and standard error values for tensile strength and elongation at break were measured in the fabric warp and weft directions using 325 × 40 mm samples. Yarns were raveled from both sides to obtain a substrate of uniform width. Before the test, the specimens were conditioned for moisture equilibrium. For testing, a specimen was held between the two clamps of the tensile strength testing machine such that the same set of yarn was gripped by both clamps. A continually increasing load was applied longitudinally to the specimen by moving one of the clamps until the specimen ruptured. The value of breaking the strength of the test specimen was read from the machine.

In this manner, the tensile strength of the control and all the treated samples was tested five times each, and then the mean and standard deviation values were calculated.

2.4.2. Bending Length and Flexural Rigidity

The bending length of the samples was determined with the help of a stiffness tester (Model 112, Paramount Instruments Pvt. Ltd., Delhi, India) using the ASTM D1388 method [18]. A 6 × 1-inch rectangular strip of fabric was mounted on a horizontal platform. It was supported by two side pieces made of plastic. A mirror was attached to the instrument that enabled the viewer to view both of the index lines from a convenient position. The scale of the instrument was graduated in centimeters of bending length. The specimen was put on a platform in such a way that it overhung like a cantilever and bent downwards. The length of the overhanging portion, when depressed under its own weight, and the angle between the lines joining the tip of the edges of the platform was measured. Using this method, three warp-way and three weft-way specimens were tested. Each specimen was tested four times with the front face and again with the strip turned over for the back face. The mean values and standard deviation for the bending length in the warp and weft directions were calculated for the values of flexural rigidity.

2.4.3. Crease Recovery

Fabric crease recovery, measured quantitatively by the crease recovery angle (CRA), was tested using an AATCC wrinkle recovery tester as per AATCC TM 66-2003 [19]. A 2 × 1 in. wrinkle-free specimen was folded gently end-to-end in half and compressed under a specified load for a specified time. The load was then removed, and the specimen was allowed to recover for the specified time. After the load was removed, the specimen was transferred to the instrument clamp. For this, one end of the specimen was held in the tweezers and the other was placed in the clamp. As the specimen recovered, the dial was rotated to keep the free edge of the specimen in line with the knife edge. Then the CRA in degrees was read on the dial. The procedure was repeated for five specimens each in warp and weft direction and the mean and standard deviation values were calculated.

2.4.4. Air Permeability

The air permeability of the fabrics was determined by ASTM D737-2002 [20]. The test specimen was placed on the air permeability tester (SDL Atlas) between the top and bottom of the column. The fabric should be placed right side down with the air pressure lower at that side. Using a vacuum, the air pressure was different on one side of the fabric. Airflow occurred from the side with higher air pressure, through the fabric, to the side with the lower air pressure. From this rate of airflow, the air permeability of the fabric was determined and displayed on the screen of the tester. The readings were noted, and ten specimens of each fabric were tested. Thereafter, the mean values of each fabric were calculated.

2.5. Performance Testing of the Finished Fabrics

The liquid repellency of the treated fabrics was studied 3 ways; using the hydrophobicity (drop) test, hydrophobicity (spray) test, and oleophobicity test. In addition, the longevity of the finish was studied using laundering durability tests.

2.5.1. Water-Repellency (Drop Test)

Hydrophobicity is the ability of the substrate to resist wetting by water or water-based liquids. The hydrophobicity of the substrates was tested by the water/alcohol drop test [21]. The drops of standard test liquids consisting of specified proportions of deionized water and isopropyl alcohol (reagent grade) by volume were used as test liquids to evaluate the hydrophobicity of the substrates. The substrates were cut into 20 × 20 cm each for the test. Each substrate was put on a flat and horizontal surface. Using a dropper, a drop of ~5 mm in diameter was put gently at three different places on the surface of the test substrate, keeping the dropper at approximately 1 cm from the fabric. Care was taken that the dropper did not touch the fabric. This drop was allowed to stand undisturbed for 10 s. After 10 s, if two of the three drops were still visible as spherical to hemispherical, the substrate passed that particular test liquid. Substrates were rated as pass or fail for the appropriate test liquid that remained visible. The hydrophobicity of the control and the treated substrates were tested in this manner.

2.5.2. Water-Repellency (Spray Test)

The spray test was conducted to measure the resistance of fabrics to wetting by water. The test was conducted as per AATCC Test Method (TM) 22-2001 [22]. The size of the substrate used for the test was 20 × 20 cm. To carry out the test, 230 cm^3 of water at 27 ± 2 °C was poured steadily into the spray funnel. A standard distance of 6 inches from the bottom of the spray funnel to the center of the fabric was maintained. The fabric was placed and stretched in a 6-in. diameter embroidery hoop and fixed on the platform at an angle of 45°. After spraying, the substrate holder was removed and the surplus water was removed by tapping the frame six times against a solid object, with the face of the substrate towards the solid object. The tapping was done in two stages, three taps at one point on the frame and then three times at a point diametrically opposite. The assessment of the fabric hydrophobicity against spray was examined visually by matching against the standard rating chart. Hydrophobicity against the spray of the control and all the substrates treated at various concentrations of fluoro-chemical finishing agents were tested in this manner.

2.5.3. Oil-Repellency Test

Oleophobicity is the ability of textile fiber, yarn, or leather to resist wetting by oily liquids. It was determined using AATCC TM 118-2002 [23]. The drops of standard test liquids, consisting of a selected series of hydrocarbons with varying surface tensions were used to perform the test. A 20 × 20 cm substrate was used to test oleophobicity. The test substrate was placed on a smooth horizontal surface. Using a dropper, a drop ~5 mm in diameter was put gently at three different places, keeping the dropper at a distance of 1 cm from the fabric. Care was taken that the dropper did not touch the fabric. This drop was allowed to stand undisturbed for 30 s. After 30 s, if two of the three drops were still visible as spherical to hemispherical, the substrate passed that particular test liquid. Substrates were rated as pass or fail for the appropriate test liquid which remained visible. The oleophobicity of the control and all the substrates treated at various concentrations of fluoro-chemical finishing agents, different pickups, and different curing temperatures, were tested in this manner.

2.5.4. Laundering Durability

Laundering durability is defined as the ability of a protective finish to continue to perform its function after being subjected to repeated launderings. The laundering durability test was determined on a top-loading automatic washer recommended by AATCC using AATCC TM 43-2003 [24]. The size of the substrate used for the test was 20 × 20 cm. The substrates were put into the washer, which was filled to the high-water level with water at 41 ± 3 °C. Standard detergent (20 g) was put into it and substrates were washed using a 12 min "Normal" wash cycle. After the completion of a specified number of wash cycles, the substrates were taken out and dried in a forced-air circulating oven at 65 ± 6 °C. The performance of these substrates was then tested.

3. Results

3.1. Optimization of the Finish Concentration Based on Liquid Repellency

The first part of this section presents the hydrophobicity and the second part describes the oleophobicity performance of the FU-finished textile substrates as indicators of laundering durability.

The hydrophobicity phenomenon was studied in two ways; water-repellency (drop test) and water-repellency (spray test).

3.1.1. Water-Repellency (Drop Test) Analysis

Table 1 shows the effect of laundering on the hydrophobicity performance of the treated and untreated fabrics. There are two major trends observed in this data set:

Table 1. Effect of laundering on Water-repellency (drop test) of polyester/cotton.

Finish Conc.	**Water-Repellency—Drop Test**							
(g/L)	**Initial**	**5 L**	**10 L**	**15 L**	**20 L**	**25 L**	**30 L**	**% Loss in Repellency**
Control	0	0	0	0	0	0	0	-
30	5.2	5.0	4.5	4.0	3.5	3.0	2.7	48.1%
40	5.3	5.2	4.7	4.2	4.0	3.5	3.0	43.4%
50	6.0	5.7	5.0	4.7	4.2	4.0	3.5	41.7%
60	7.0	6.7	6.2	5.7	5.5	5.0	4.7	32.9%
70	7.5	7.2	7.0	6.5	6.0	5.5	5.2	30.7%

g/L = grams per liter and 5–30 L reports water repellency data gathered after 5 to 30 laundering cycles.

1. *Higher hydrophobicity performance was observed with increased finish concentration*: At the initial stage, the difference between the mean values of the substrates treated at 30 (5.2), 40 (5.3), and 50 (6.0) g/L of FU finish concentrations was statistically non-significant ($p \leq 0.05$). However, a significant increase in the hydrophobicity performance of the textile substrates finished at the 60 g/L concentration was noted.

2. *Conversely, the loss in hydrophobicity was higher at lower finish concentration*: The percent loss of finish displayed fair to very good hydrophobicity even after 30 laundering cycles, depending on the finish concentration used. As the number of laundering cycles increased (Figure 1), a decrease in the hydrophobicity values was observed at all finish concentration levels. The loss of hydrophobicity after 30 laundering cycles ranged between 48.1 and 30.7% at finish concentrations of 30 and 70 g/L, respectively. There was no statistically significant difference in the percent loss of finish performance among fabrics treated at 30, 40, and 50 g/L finish concentration. However, the loss of hydrophobicity was significantly less at 60 g/L of the finish concentration. Interestingly, there was statistically no significant performance loss difference between 60 and 70 g/L.

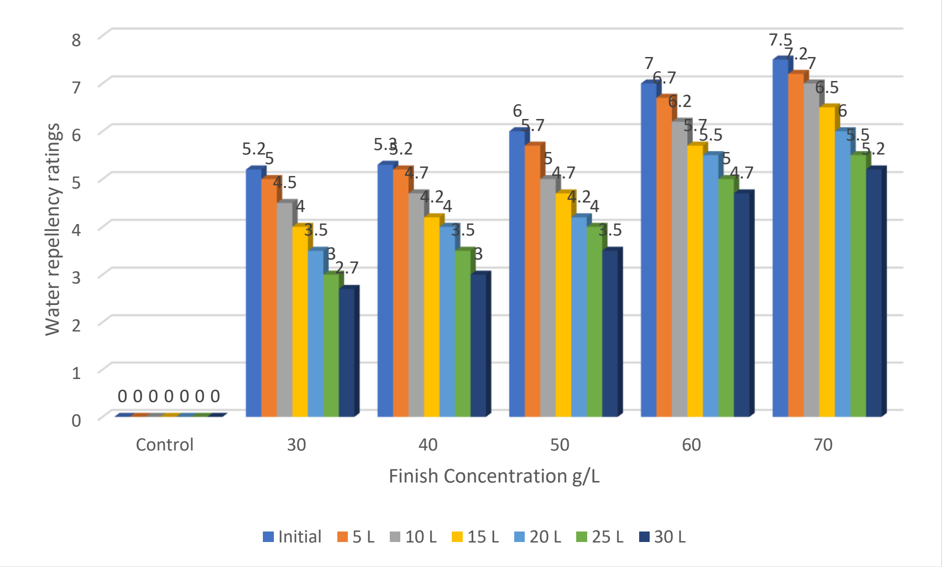

Figure 1. Effect of laundering on Water-repellency (drop test) of polyester/cotton.

3.1.2. Water-Repellency (Spray Test) Analysis

As depicted in Table 2, the laundering durability of the FU finish improved with the higher finish concentrations. An initial rating of 100 was observed at all the finish concentrations. However, a consistent trend of decrease in repellency performance was observed with an increase in laundering cycles (Figure 2). The percent loss of finish performance was higher at the lower finish concentrations and ranged between 33.3 and 10% between 30 and 70 g/L, respectively. Despite the consistent and gradual loss of finish performance at all concentration levels, the fabric treated with 60 g/L finish concentration showed a significantly reduced loss of finish performance. Further increases in finish concentration did not show an improvement in finish performance loss. Therefore, it is not cost-effective to use the higher finish concentration, when the repellency performance is statistically on par with the one at the lower concentration. The use of an optimal concentration can result in cost reduction and is environmentally preferable.

Table 2. Effect of laundering on Water-repellency (spray test) of polyester/cotton.

Finish Conc.	**Water-Repellency—Spray Ratings**							
(g/L)	**Initial**	**5 L**	**10 L**	**15 L**	**20 L**	**25 L**	**30 L**	**% Loss in Repellency**
Control	0	0	0	0	0	0	0	-
30	100	90.0	86.7	83.3	76.7	70.0	56.7	33.3%
40	100	93.0	90.0	86.7	83.3	76.7	70.0	30.0%
50	100	96.7	93.3	90.0	86.7	80.0	76.7	23.3%
60	100	100.0	100.0	96.7	93.3	90.0	86.7	13.3%
70	100	100.0	100.0	100.0	100.0	96.7	90.0	10.0%

g/L = grams per liter and 5–30 L reports water repellency data gathered after 5 to 30 laundering cycles.

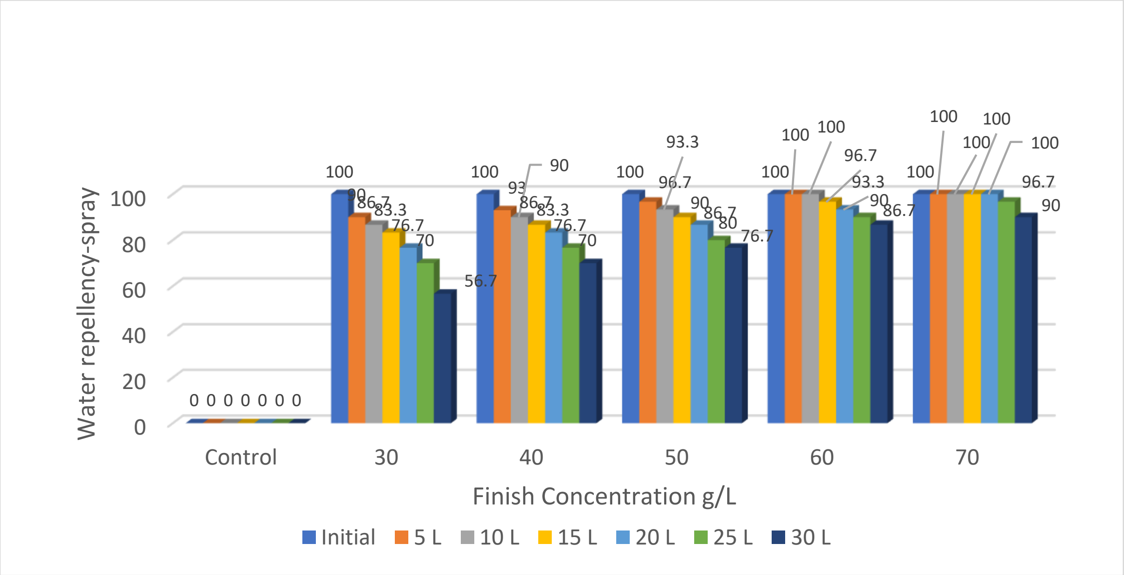

Figure 2. Effect of laundering on water-repellency (spray test) of polyester/cotton.

3.1.3. Oil-Repellency Test

Initially, the difference between oleophobicity values at 30 (5.0), 40 (5.2), and 50 g/L (5.5) FU-finish concentration was statistically not significant. However, the oleophobicity performance rating of 6.3 at the 60 g/L finish concentration was significantly higher compared to oleophobicity ratings at lower concentrations. The mean oleophobicity values after five laundering cycles were 4.5, 5.0, and 5.2 at 30, 40, and 50 g/L finish concentrations respectively (Table 3 and Figure 3). However, the oleophobicity rating of 6.0 at 60 g/L was significantly higher ($p \leq 0.05$) compared to ratings at lower concentration levels. A similar trend was observed in the data after 10, 15, 20, 25, and 30 laundering cycles (Table 3). In terms of oleophobicity loss, a major loss of 60% was observed after 30 launderings cycles of the fabric treated at 30 g/L to a loss of 30.8% at 70 g/L.

Table 3. Effect of laundering on oil-repellency (drop test) of polyester/cotton.

sFinish Conc.	**Oil Repellency-Drop**							
(g/L)	**Initial**	**5 L**	**10 L**	**15 L**	**20 L**	**25 L**	**30 L**	**% Loss in Repellency**
Control	0	0	0	0	0	0	0	-
30	5.0	4.5	4.0	3.5	3.0	2.5	2.0	60.0%
40	5.2	5.0	4.7	4.0	3.5	3.0	2.3	55.8%
50	5.5	5.2	5.0	4.5	4.0	3.2	2.7	50.9%
60	6.3	6.0	5.5	5.2	5.0	4.7	4.0	36.5%
70	6.5	6.5	6.2	6.0	5.7	5.0	4.5	30.8%

g/L = grams per liter and 5–30 L reports water repellency data gathered after 5 to 30 laundering cycles.

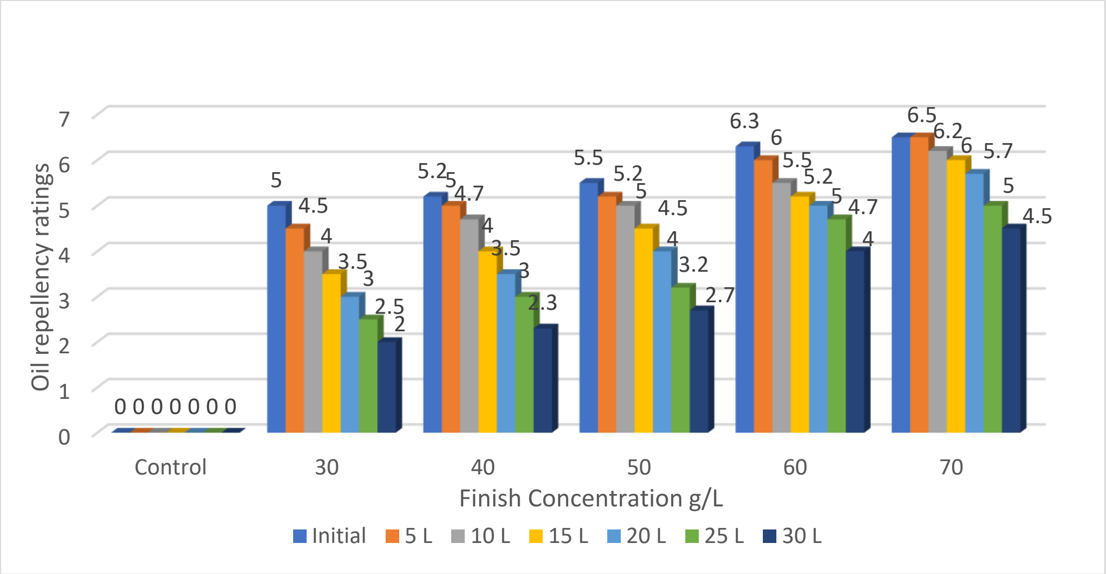

Figure 3. Effect of laundering on oil repellency (drop test) of polyester/cotton.

3.2. Effect of Finish Concentration on Physical Properties of the Polyester/Cotton blend Fabric

3.2.1. Tensile Strength

It is evident from Table 4 that the elongation of textile substrates decreased in both the warp and weft directions with the use of the higher finish concentration.

As per Table 4, warp yarns had a relatively higher loss of elongation compared to weft yarns. Warp yarns face a lot of stress and strain during warp loading on the loom and fabric construction as well, which results in loss of tensile strength to some extent. Even though there was a gradual decrease in elongation (warp direction) of the test substrates with increased finish concentration, the statistical difference in elongation values at 30, 40 and 50 g/L was not significant. However, test substrates finished at 60 g/L showed a statistically higher loss in elongation in both warp and weft directions. The loss in elongation is even higher at 70 g/L. At 60 g/L, the elongation values of treated fabric in warp and weft directions decreased by 18.3% and 13.9%, respectively, compared to the elongation of the control fabric. This was a significant decrease ($p \leq 0.05$), and any further increase in the finish concentration affected the tensile strength of the fabric negatively.

Table 4. Effect of different finish concentrations on the selected physical properties of polyester/cotton woven fabric.

Finish Conc. (g/L)	Elongation		Crease Recovery Angle		Bending Length		Overall Flexural Rigidity	Air Permeability
	Warp	Weft	Warp	Weft	Warp	Weft		
0 (Control)	46.12	48.32	64.0	62.0	2.10	2.00	63.99	22.35
30	43.62 ↓(5.4%)	46.6 ↓(3.6%)	62.6 ↓(2.2%)	61.2 ↓(1.3%)	2.68 ↑(27.6%)	2.49 ↑(24.5%)	65.98 ↑(3.1%)	20.32 ↓(9.1%)
40	42.00 ↓(9.1%)	44.05 ↓(8.8%)	61.8 ↓(3.4%)	59.6 ↓(3.9%)	2.81 ↑(33.8%)	2.66 ↑(33.0%)	66.99 ↑(4.7%)	19.81 ↓(11.4%)
50	40.12 ↓(13.1%)	42.93 ↓(11.2%)	59.6 ↓(6.9%)	57.7 ↓(6.9%)	2.98 ↑(42.0%)	2.72 ↑(36.0%)	67.89 ↑(6.1%)	18.97 ↓(15.1%)
60	37.97 ↓(17.6%)	41.62 ↓(13.9%)	54.4 ↓(15.0%)	52.8 ↓(14.8%)	3.46 ↑(64.8%)	3.13 ↑(56.5%)	70.79 ↑(10.6%)	18.19 ↓(18.6%)
70	35.02 ↓(24.1%)	38.83 ↓(19.6%)	50.8 ↓(20.6%)	48.9 ↓(21.1%)	3.98 ↑(89.5%)	3.77 ↑(88.5%)	74.66 ↑(16.7%)	16.47 ↓(26.3%)

↓ = Percent decrease, ↑ = Percent increase.

3.2.2. Fabric Stiffness

The fabric stiffness was tested three ways in this study using crease recovery angle, bending length, and overall flexural rigidity tests. For the crease recovery data, a statistically significant ($p \leq 0.05$) increase in fabric stiffness was observed, in both warp and weft directions of the textile substrates, when >50 g/L of the FU-finish concentration was used (Table 4). Likewise, the percent increase in bending length did not show statistically significant differences among the 30, 40, and 50 g/L finish concentrations, but there were statistically significant increases (64.8% and 56.5%) in warp and weft directions, respectively, at the 60 g/L finish concentration and higher.

The overall flexural rigidity of textile substrates gradually increased from 3.1% at the 30 g/L finish concentration to 16.7% at the 70 g/L finish concentration (Table 4). The results suggest that as the finish concentration increased, the stiffness of the treated fabric also gradually increased. This increase was statistically significant at the 60 g/L finish concentration. Any further increase in finish concentration led to very high stiffness in the fabric that made it inappropriate for apparel use; this increased stiffness also reduced the fiber elongation, thereby decreasing the tensile strength of the treated textiles as well.

3.2.3. Air Permeability

The air permeability results show a reduction in the air porosity of the fabric as the FU-finish concentration increased (Table 4). After statistical analysis of the data, there were no significant ($p \leq 0.05$) decreases in air permeability values among substrates finished at 30 to 60 g/L finish concentrations. Therefore, the higher finish concentration that resulted in better repellency was more desirable as the air permeability of the fabric finished at lower concentrations was statistically the same as those of finished at higher concentrations up to a 60 g/L finish concentration. Interestingly, the air permeability values were statistically at par below 70 g/L of finish concentration as opposed to tensile strength and fabric stiffness data, which showed that the treated fabric loses a significant amount of tensile strength and pliability at 60 g/L. However, the air permeability was not affected that much at the higher finish concentration levels.

4. Discussion

4.1. Liquid Repellency Performance

The loss of liquid repellency after laundering is common in fabrics treated with fluorocarbon-based DWRs due to their disturbed crystallinity in the aqueous laundering process [4,10,15,25–28]. The washing process influences the orientation of the fluorinated side chains [5]. The fabrics treated with liquid-repellent finish are self-cleaning and may not require frequent washing after all.

Furthermore, crosslinking and uniform coating of the finish on the fibers help with the longevity of the finish as well. Textile fibers have porous surfaces, and the uniform application of the finish is imperative for a long-term liquid-repellent function [12,25]. The experiments in this study provide evidence that an oxime-blocked polyisocyanate, when used in conjunction with the FU finish, extends the laundering durability of the fluorochemical finish. Additionally, the isopropyl alcohol enhanced the wettability of the fabric and ensured the uniform application of the finish [10,11]. Therefore, the durability of the FU finish was significantly better than what has been reported in previous studies [9,12,25]. When used alone the fluorochemical finishes (C_8-C_4) tend to lose their liquid repellency performance after 10 laundering cycles [5]. Fluorochemical treatments are relatively expensive, and when used with less expensive non-fluorinated chemicals such as oxime-blocked polyisocyanate, they not only increase the durability of the finish but also improve the cost-effectiveness of the finishing treatment [9,10,16].

Hybrid fluorochemical type block copolymers such as FU are effective stain repellents against water, as well as oil-based stains, even with successive washing cycles [5,6,11,29–32]. Although the loss in hydrophobicity is reported in this study, the fabric treated with FU finish still has a fair to good hydrophobicity effect even after 30 laundering cycles, which makes it much more durable than its non-eco-friendly counterparts with C_8 and C_6 chemistry [4]. Likewise, the oil repellency data revealed a loss of the oleophobicity after laundering. The loss of oleophobic performance was higher compared to the loss of hydrophobic performance in both drop and spray tests. It is only possible to achieve an oleophobic textile surface with fluorochemical-based DWRs due to their critical surface energy and it is even more difficult to retain the oleophobic performance, especially after laundering [4,5].

To be succinct, the liquid repellency effect decreased gradually with subsequent launderings of the treated textile substrates due to the surface movement of fluorochemical segments resulting from the effects of polarity and surface tension on polymer chains [6,32]. The alkaline pH of the detergent used in the laundering durability test may also be a factor. FU is a cationic finish and works best under slightly acidic pH. It loses the liquid repellency effect under alkaline conditions, which may be another cause of the gradual loss in liquid repellency of treated substrates upon laundering.

4.2. Effect of FU Finish on Physical Properties of the Treated Fabric

Fluorochemical finishes tend to negatively affect the tensile strength of the treated fabric, especially when applied at higher concentration levels. It decreases the tensile strength of the treated fabrics due to increased tensile linearity and resistance to extension [2,5,9–11]. Furthermore, it increases fabric stiffness [2,5,9–11], which in turn lowers the fiber elongation and decreases the tensile strength of the fabric. Additionally, the high curing temperature also contributes to the decreased tensile strength, especially in the case of cellulosic fibers. This trend of decreased tensile strength with increasing finish concentration was evident in the tensile strength data gathered for this study and was in concurrence with the previous studies [5,6,9–11,28] that used fluorochemical treatment on textiles. Likewise, the application of a fluorochemical finish affects the fabric hand negatively, which in turn improves the dimensional stability of the treated fabric. Fluorochemical finishes are known to increase fabric stiffness [2,5,6,9,28–32].

Another fabric property that is negatively affected by the use of fluorochemical finishes is air permeability. Many previous studies [6,28,32–36] reported a reduction in the air permeability of the fluorochemically treated fabrics. However, the data of this study did not reveal a significant change in the air permeability of the treated fabric even at the higher finish concentration levels. Since fluorochemicals change the critical surface tension of the finished material at the nano level, this did not result in a change in fabric air porosity unless a finish concentration greater than 70 g/L was used to treat the fabric, which was not the case in this study.

4.3. Limitations and Future Research

The determination of an optimum finish concentration is very important since the finish concentration has a considerable influence on the physical properties of the fabric, not to mention the cost-effectiveness factor in play. In addition, its liquid repellency performance depends profoundly on the concentration of the finish as noted in the results of this study. This study presents an important relationship of fluorochemical finish concentration with the liquid repellency and physical properties of the treated fabric. Each textile finish has some effect on the mechanical properties of the treated fabric, and therefore it is important to study the optimum concentration of the finish. This study was focused on finding an optimum FU finish concentration for a polyester/cotton (65/35%) fabric only. Fabrics with different fiber contents will be experimented with and compared in future research work. Our future research will also focus on the application of the finished fabric to develop personal protective equipment (PPE) for occupational uses.

5. Conclusions

Despite several options in the field of DWRs, it seems that there are very few, if any, finishes that provide a long-term oleophobic effect to hydrophilic textiles [7,10,28,33,34]. Fluorochemicals are highly dependable and versatile when it comes to the functions of hydrophobicity and oleophobicity. This may not seem a necessary function to a common consumer, but it is a highly desirable function in the field of occupational protective clothing. To achieve the finest performance of fluorochemical finishes, it is imperative to study and compare their performance at different concentration levels, and the effect of each concentration level on the fabric properties. Without a doubt, the liquid repellency performance gets better with the higher finish concentrations, but unfortunately, fabrics treated at the higher finish concentrations negatively affect some of the fabric properties. Moreover, it is not cost-efficient to use the higher finish concentration for large scale applications. Therefore, this study aimed at finding the right finish concentration for optimum liquid repellency performance with the least affected properties of the treated fabric. Based on the liquid repellency data of this study, textile substrates finished at 60 g/L with fluorochemical urethane (FU) finish performed significantly better compared to lower concentrations even after 30 laundering cycles. Some physical properties of the fabric are more affected at lower concentrations of the finish than others. For example, a significant loss in fabric pliability was recorded at 60 g/L—nonetheless, a significant loss in tensile strength and air permeability of the fabric was observed at 70 g/L or higher concentrations. Therefore, it can be concluded that 60 g/L should be considered as an optimum finish concentration for a medium weight P/C blended woven fabric based on optimal liquid repellency, tensile strength, pliability, and air permeability of the FU-finished fabrics. Hence, the cost-effective and excellent liquid repellency of FU finishes can be expected when used in an optimal concentration.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Hoefnagels, H.F.; Wu, D.; De With, G.B.; Ming, W.M. Biomimetic Superhydrophobic and Highly Oleophobic Cotton Textiles. *Langmuir* **2007**, *23*, 13158–13163. [CrossRef] [PubMed]
2. Schindler, W.D.; Hauser, P.J. *Chemical Finishing of Textiles*; CRC Press: Boca Raton, FL, USA, 2010.
3. Wong, W.S.Y. Surface Chemistry Enhancements for the Tunable Super-Liquid Repellency of Low-Surface-Tension Liquids. *Nano Lett.* **2019**, *19*, 1892–1901. [CrossRef] [PubMed]
4. Ferrero, F.; Periolatto, M.; Tempestini, L. Water and Oil Repellent Finishing of Textiles by UV Curing: Evaluation of the Influence of Scaled-Up Process Parameters. *Coatings* **2017**, *7*, 40. [CrossRef]
5. Schellenberger, S.; Gillard, P.; Stare, A.; Hanning, A.; Levenstam, O.; Roos, S.; Cousins, I.T. Facing the rain after the phase out: Performance of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics. *Chemosphere* **2018**, *193*, 675–684. [CrossRef]

6. Holmquist, H.; Schellenberger, S.; Van Der Veen, I.; Peters, G.; Leonards, P.; Cousins, I. Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environ. Int.* **2016**, *91*, 251–264. [CrossRef]
7. Midha, V.K.; Dakuri, A.; Midha, V.A. Studies on the properties of non-woven surgical gowns. *J. Ind. Text.* **2013**, *43*, 174–190. [CrossRef]
8. Wu, L.; Zhang, J.; Li, B.; Fan, L.; Li, L.; Wang, A. Facile preparation of super durable superhydrophobic materials. *J. Colloid Interface Sci.* **2014**, *432*, 31–42. [CrossRef]
9. Sayed, U.; Dabhi, P. *Waterproof and Water Repellent Textiles and Clothing*; Williams, J.T., Ed.; Woodhead Publishing: Cambridge, MA, USA, 2014; pp. 139–152.
10. Mehta, S. Optimization of Fluorochemical Finish Concentration for Liquid Repellency Treatment of 100% Cotton Fabric and Resulting Physical Properties. *AATCC J. Res.* **2018**, *5*, 15–22. [CrossRef]
11. Mitchell, T.J.; Larry, A.L. Method and Apparatus for Treating Perfluoroalkyl Compounds. U.S. Patent 10,352,613, 4 September 2013.
12. Schellenberger, S.; Hill, P.J.; Levenstam, O.; Gillgard, P.; Cousins, I.T.; Taylor, M.; Blackburn, R.S. Highly fluorinated chemicals in functional textiles can be replaced by re-evaluating liquid repellency and end-user requirements. *J. Clean. Prod.* **2019**, *217*, 134–143. [CrossRef]
13. Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA. Available online: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass (accessed on 16 June 2019).
14. Van Der Veen, I.; Hanning, A.-C.; Stare, A.; Leonards, P.E.; De Boer, J.; Weiss, J.M. The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. *Chemosphere* **2020**, *249*, 126100. [CrossRef]
15. Chowdhury, K.P. Impact of Different Water Repellent Finishes on Cotton Double Jersey Fabrics. *J. Text. Sci. Technol.* **2018**, *4*, 85–99. [CrossRef]
16. Yun, C.; Islam, M.I.; LeHew, M.; Kim, J. Assessment of environmental and economic impacts made by the reduced laundering of self-cleaning fabrics. *Fibers Polym.* **2016**, *17*, 1296–1304. [CrossRef]
17. *ASTM D5035*; ASTM International: West Conshohocken, PA, USA, 2002; Available online: www.astm.org (accessed on 23 April 2018).
18. *ASTM D1388-96*; ASTM International: West Conshohocken, PA, USA, 2002; Available online: www.astm.org (accessed on 23 April 2018).
19. *AATCC Technical Manual*; AATCC: Research Triangle Park, NC, USA, 2005; pp. 82–86.
20. *ASTM D737-96*; ASTM International: West Conshohocken, PA, USA, 2002; Available online: www.astm.org (accessed on 23 April 2018).
21. 3M Technical Data. Test Methods. In *Hydrophobicity Test II—Water/Alcohol Drop Test*; St. Paul, MN, USA, 2006.
22. *AATCC Test Method (TM) 22-2001*; AATCC: Research Triangle Park, NC, USA, 2005; pp. 95–98.
23. *AATCC Test Method (TM) 118-2002*; AATCC: Research Triangle Park, NC, USA, 2005; pp. 191–193.
24. *AATCC Test method (TM) 43-2003*; AATCC: Research Triangle Park, NC, USA, 2005; pp. 65–67.
25. Dhiman, G.; Chakraborty, J.N. Soil release performance of cotton finished with oleophobol CPR and CMC-Na salt. *Fash. Text.* **2014**, *1*, 696. [CrossRef]
26. Khoddami, A.; Bazanjani, S.; Gong, R. Investigating the Effects of Different Repellent Agents on the Performance of Novel Polyester/Wool Blended Fabrics. *J. Eng. Fibers Fabr.* **2015**, *10*, 216–227. [CrossRef]
27. Shekar, R.I.; Yadav, A.; Kasturia, N.; Raj, H. Studies on combined flame-retardant and water-repellent treatments on cotton drill fabric. *Indian J. Fiber. Text. Res.* **1999**, *24*, 197–207.
28. Mishra, R.; Militky, J.; Baheti, V.; Huang, J.; Kale, B.; Venkataraman, M.; Bele, V.; Arumugam, V.; Zhu, G.; Wang, Y. The production, characterization, and applications of nanoparticles in the textile industry. *Text. Prog.* **2014**, *46*, 1731–1742. [CrossRef]
29. Norouzi, N.; Gharehaghaji, A.A.; Montazer, M. Reducing drag force on polyester fabric through superhydrophobic surface via nano-pretreatment and water repellent finishing. *J. Text. Inst.* **2018**, *109*, 92–97. [CrossRef]
30. Suri, M.; Chakraborty, M. Development of protective clothing for pesticide industry: Part II—An eco-friendly approach in selection of resin Indian. *J. Fiber. Text. Res.* **2002**, *27*, 259–265.
31. Tarafdar, N.; Sett, S.K.; San, T.N. An experimental study on water repellent breathable plain-woven cotton fabrics. *Man Made Text. India* **2003**, *46*, 223–227.

32. Khoddami, A.; Gong, H.; Ghadimi, G. Effect of wool surface modification on fluorocarbon chain re-orientation. *Fibers Polym.* **2012**, *13*, 28–37. [CrossRef]
33. Chen, L.; Cloud, R.M.; Nelson, C.N. *Protective Clothing Issues and Priorities for 21st Century*; Nelson, C.N., Henry, N.W., Eds.; ASTM: West Conshohocken, PA, USA, 2000.
34. Bougourd, J.; McCann, J. Designing waterproof and water repellent clothing for wearer comfort—A paradigm shift. *Waterproof Water Repel. Text. Cloth.* **2018**, 301–345. [CrossRef]
35. Kothari, V.K. *Textile Fibers: Development and Innovations*; IAFL Publication: New Delhi, India, 2000.
36. Bashari, A.; Koohestani, A.H.S.; Salamatipour, N. Eco-friendly Dual-Functional Textiles: Green Water-Repellent & Anti-Bacterial. *Fibers Polym.* **2020**, *21*, 317–323. [CrossRef]