Effect of Weft Knitted Polyester Fabric Structure on its Hydrophobicity after Fluorocarbon Finishing

Sanaz Ghapanvari¹, Akbar Khoddami², Hossein Hasani³
Department of Textile Engineering, Isfahan university of Technology, Isfahan, 84156-83111, Iran
¹sanazghapanvari@gmail.com; ²khoddami@cc.iut.ac.ir; ³h_hasani@cc.iut.ac.ir

Abstract

A superhydrophobic surface with self-cleaning properties can be fabricated with a combination of both low surface energy and the proper surface roughness. In this paper, the possible effects of structural parameters of weft knitted fabrics were applied to produce surface roughness while a fluorocarbon compound was coated on the surface in order to generate low surface energy. In addition, to create dual surface roughness on the polyester fibers, chemical etching with alkaline hydrolysis and application of nanoparticles were investigated. The water repellency of the treated samples was evaluated by 3M, tilting angle and contact angle hysteresis.

Comparison of a smooth polyester film and the knitted fabrics showed that various knitted structures and stitch density had a great effect on superhydrophobicity. Polyester alkaline hydrolysis efficiently roughened the surface and after the fluorocarbon coating, remarkable improvement in repellent properties was observed. Thus, there was no necessity to use nanoparticles.

Keywords

Single Jersey Weft Knitted Fabrics; Fluorocarbon Finishing; Hydrophobicity; Fabric Structure

Introduction

Non-wettable surfaces with high water contact angles (greater than 150°) and low tilting angle of drops, which are called superhydrophobic or ultrahydrophobic, have received remarkable attention in the recent years [1-7]. To achieve superhydrophobicity both appropriate surface roughness and low surface energy are required.

To obtain excellent tilting behaviors, proper design of a rough surface and formation of air pockets between liquid droplet and solid surfaces are more important than increasing roughness. On the superhydrophobic surface, the distinct contact manner of droplet is qualified to the Wenzel state or the Cassie state and the triple-phase liquid/air/solid contact line (TCL) [8-10].

Structure of woven, or non-woven fabrics can play an important role in producing superhydrophobicity without altering their surface roughness [11]. However, as the roughness of the cloth is usually on a relatively large scale, some efforts have been made to generate smaller scale structures on the fiber surface to increase the superhydrophobicity and pressure resistance of the structures [12, 13]. It has been reported [14,15] that these fractal structures could effectively enhance the repellency of a solid surface, but so far there has been only limited research on how surface shapes and dimensions enhance surface hydrophobic behaviors.

Since facile and inexpensive method are crucial to manufacture a superhydrophobic surface, in the present study, the effects of created surface roughness due to the weft knitted structures were investigated in an attempt to enhance the level of hydrophobicity or fabricate superhydrophobic fabric with self-cleaning properties. Besides, with the concept of usefulness of chemical etching and nanoparticles in nano roughening of the fiber surface, these methods are also studied. All the samples with different surface topologies were coated via a fluorocarbon compound to generate low surface energy with stain repellent characteristics.

Experimental Section

Materials

The yarns (20-Ne and twist coefficient of 3.8) were spun from 100% polyester fibers on a ring frame machine.
Fabrics with a variety of single jersey weft knitted structures: a plain single jersey, double cross tuck and double cross miss were fabricated from the polyester yarns using a circular knitting machine (Falmac, 22 E, 18” diameter) equipped with positive feeding mechanism. The technical face and technical back of produced structures are shown in Figure 1.

The utilized fluorocarbon (Rucostar EEE) and nano-silica particles (MP-4540) were purchased from Rudolf, Germany, and Nissan Chemical-America Corporation, respectively. The selected fluorocarbon derivative, Rucostar EEE, is a fluorocarbon resin with polymeric, hyperbranched dendrimers in a hydrocarbon matrix with cationic nature and acrylate base. It is noteworthy that this finishing agent is not of the modified type which is free of perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) and alkylphenolethoxylate (APEO). Non-ionic detergent (Sera Wet C-NR) was purchased from DyStar. Other chemicals were of analytical grade from Merck, Germany.

Sample Preparation

The fabrics produced from the circular knitting machine were air dried for 48 hours in the standard conditions (20°C, 65 % RH), and then treated to three cycles of mechanical relaxation using repeated washing and tumble dryings. The fabric was washed for 75 minutes at 40°C in a revolving drum washing machine (Mile Co.) with the 1% detergent (Persil). After the final spin cycle, the samples were tumbling dried for 57 minutes. Samples were then stored for 48 hours under standard conditions, after which their physical properties were measured. Wale and course count per cm of the knitted fabrics were measured.

To remove any natural or synthetic impurities, all fabric samples were washed using a solution containing 1 mL/L non-ionic detergent and 0.2 g/L sodium carbonate with L: R of 30:1 for 40 min at 50–55°C. Then samples were rinsed with water for 60 min and air dried without any tension.

Hydrophobization Using Fluorochemical

The scoured polyester fabrics were impregnated in a treatment bath containing 45 g/L Rucostar EEE, acetic acid (1
mL/L) and propane 2-ol (5 mL/L). Acetic acid and propane 2-ol were used as a pH adjuster and wetting agent, respectively. Next, the sample was immersed in the bath, padded with laboratory padder (Mathis, Switzerland) to reach a wet pickup of 75–80%, dried and then cured for 2 min at 100°C and 160°C, respectively, in a lab dryer (Warner Mathis AG, Niederhasli, Zürich).

**Hydrophobization Using Fluorochemical and Nano-Silica Particles**

The silica nanoparticles (with a particle size of 300-400 nm and 0.4% dry add on) and fluorochemical, Rucostar EEE (concentration of 45 g/L) were co-applied into the polyester fabrics according to the method of Mazrouei-Sebdani et al [16].

**Alkaline Treatment**

The polyester fabric was treated with a sodium hydroxide solution (60 g/L), for 15 min at 80±5°C and liquor ratio of 20:1. Neutralization was performed with much diluted acetic acid for 20 min. The samples were air dried with no strain and then treated according to section above.

**Characterization Techniques**

In order to study the samples hydrophobicity, tilting angle [16, 17], contact angle hysteresis and the 3M water repellency tests [18] were examined. Tilting angle of droplet on the fabric was measured [16] on the technical face and back (wale and course directions) by a home-built instrument as shown in Figure 2. The fabrics were attached to a horizontal surface which will begin to slip against another surface of a similar material. During an experiment, an inclined plane is increased at a rate of 1.5 ± 0.5° per second by an electric motor until the test block begins to slip. The first movement of the sled is the tilt Angle or Factor of Static Friction of the material. The inclined plane stops when the test block just begins to slide and the operator can read the tilting angle result. All the amounts were repeated fifteen times and their average values were taken for all calculations.

Water repellency of samples was tested using the water/alcohol drop test, 3M. The samples were placed on a smooth, horizontal surface. Beginning with the lowest numbered standard test liquid, 3 small droplets (approximately 5mm in diameter) are placed on the sample using a pipette. The droplets are observed for 10 s. If after 10 s, 2 of the 3 droplets are still visible as spherical to hemispherical, the fabric passes the test. Samples are rated as pass or fail of the appropriate test liquid, W–10. The rating given to a sample is for the highest test liquid remaining visible after 15 s. In general, water repellency rating of 2 or greater is desirable [18].

**Results and Discussion**

**Hydrophobicity of Fluorochemical Treated Fabrics with Different Structures**

1) **Effect of Fabric Structure on the Tilting Behaviors**

According to Table 1, fluorocarbon finishing leads to maximum water repellency of 10 for all fabrics. The
samples surface analysis has already been reported in our previous papers [19, 20, 21]. In order to investigate the effect of fabric structure on hydrophobicity, the analysis was carried out in the wale and course directions and also on the technical face and technical back. Figure 3 illustrates the wale and course directions of a weft knitted structure.

![FIGURE 3. SCHEMATIC DIAGRAM OF WALE AND COURSE DIRECTIONS OF A PLAIN WEFT KNITTED FABRIC](image)

Results of Table 1 suggested that the air trapped in the surface structure played an important role in producing low tilting angle. Tilting angle of the water droplets on the smooth polyester film decreased from 71.7±1.2° (for the untreated) to 33.5±0.8° (for the fluorocarbon treated); while the maximum tilting angle of water droplets on the weft knitted polyester fabrics after fluorocarbon finishing was 12.4±0.5°. Therefore, it was revealed that the fabric structures could remarkably control the surface roughness with great effect on engineering superhydrophobic fabric, compared with smooth polyester surface.

This effect on hydrophobic polyester textiles could be attributed to the porosity of weft knitted fabric structures which is dependent to the length of loops, courses spacing, wales spacing and thickness of fabric. This structure can trap air isolated from the atmosphere and can create composite contact mode, causing the droplet easily rolls off the surface.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Technical Face</th>
<th>Technical Back</th>
<th>Water Repellency 3M Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wale Direction</td>
<td>Course Direction</td>
<td>Wale Direction</td>
</tr>
<tr>
<td>Plain</td>
<td>10.3±0.4</td>
<td>11.4±0.5</td>
<td>11.7±0.4</td>
</tr>
<tr>
<td>Double cross miss</td>
<td>11.8±0.2</td>
<td>12.4±0.5</td>
<td>11.4±0.5</td>
</tr>
<tr>
<td>Double cross tuck</td>
<td>9.5±0.6</td>
<td>11.1±0.6</td>
<td>9 ±0.4</td>
</tr>
</tbody>
</table>

2) Tilting Behaviors on the Technical Face

The difference between values of tilting angle in the technical face of the mentioned structures can be attributed to the surface profile and loop dimensions.

As can be seen at Table 1, tilting angles in the wale direction were less than those of the course direction for each structure pattern. This phenomenon could be possibly created by the fundamental difference in the three-phase contact line topology with probable continuous line for the wale and discontinuous for the course direction. It was reported that the length and continuity of the three-phase (solid-water-air) contact line affected the tilting behavior of water droplets on the surface [8] with a more desirable continuous short three-phase contact line for a surface with an excellent water-shedding property. It was shown that for the grooved structure in the wale direction, the three-phase contact line toward the tilting direction was less continuous and longer than toward the orthogonal direction (course direction) [8]. In the other words, the tilting of a water droplet on a solid surface was known to be governed by the movement of the three-phase line toward the tilting direction [22, 23].
For single jersey knitted structures, double cross tuck (Figure. 1 (c),(c′)) presented the smallest tilting angle. This effect could be related to the presence of tuck stitches in this structure. In structures containing tuck stitches, the pressure of tuck-loop legs applied into the adjacent loops leads to increase of the space between fabric wales. Created spaces between the adjacent wales decrease the contact surface of solid-liquid as well as the trapped air. Thus, the droplet tilts in smaller angle.

Also, the presence of miss stitches in double cross miss structure (Figure. 1 (b),(b′)) , which is held on the needles during two consecutive courses, causes a decrease in the loop dimensions through yarn robbing back. Therefore, in comparison with plain single jersey knits (Figure. 1 (a),(a′)), the fabric wales get closer together. Thus, in this structure the contact surface of solid-liquid as well as tilting angle will increase. The float yarns produced by miss stitches did not have any effect on surface geometry of technical face; because these float yarns have not situated on the fabric technical face.

3) Comparison the Tilting Behaviors of the Technical Back and Face

As for plain structure in the wale direction; the tilting angle in the technical face is lower than that of technical back, Table 1. It is noteworthy that the technical back (Figure. 1a) of this structure formed within the half-circle created of loop attached together. Thus, when the droplet moves in the wale direction, due to the needle loops toward the legs loop, it was impacted with an obstacle. In the case of double cross miss pattern, miss loop in technical back (Figure. 2b′) appears in the form of float yarn and resulted in increasing of tilting angle in comparison with technical face.

These results suggest that the tilting angle corresponds to that of the energy gap for movement of the three-phase line in the tilting direction.

For the double cross tuck there (Figure. 2c′) is a special tilting behavior in the technical back and wale direction with easier and faster motion of water droplets in comparison with that for wale direction of technical face. This phenomenon can be related to the existence of tuck stitch that makes cellular structure in the technical back of this structure. In fact appropriate projection, overhang by suitable height and proper distance with enough trap air reduce solid-liquid interface; so the droplet begins to tilt in 9°.

Alkaline Hydrolysis of Polyester Fabrics and Treatment with Fluorochemical or Fluorochemical-Nanosilica Particles

According to the study of Mazrouei and Khoddami [16], an alkaline hydrolysis process is able to create proper surface roughness with an enhancement in the textiles hydrophobicity after fluorocarbon treatment. By the alkaline treatment, the nucleophilic attack of NaOH on PET chains leads to chain scissions at the ester linkages and in the presence of TiO2, particles makes some pits and cavities on the surface [24]. Accordingly, as can be seen in Table 2, the tilting angle in the technical face decreased after alkaline hydrolysis-fluorochemical treatment in comparison with the samples treated by the fluorocarbon alone with statistically significant difference. Thus, in such a way superhydrophobic textiles were obtained by creation double scale topography containing fabric structure and created cavities, mimicking the lotus leaf effect, which is compatible with the previous reports [16].

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Tilting Angle (°)</th>
<th>Water Repellency Test 3M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wale</td>
<td>Course</td>
</tr>
<tr>
<td>plain</td>
<td>9.1±0.5</td>
<td>10±0.1</td>
</tr>
<tr>
<td>Double cross miss</td>
<td>10.1±0.1</td>
<td>11.0±0.2</td>
</tr>
<tr>
<td>Double cross tuck</td>
<td>8.6±0.2</td>
<td>9.1±0.5</td>
</tr>
</tbody>
</table>

In this section double cross tuck as a best specimen (with lowest tilting angle) was selected. The tilting angle values in the technical face of untreated and treated sample with silica nanoparticle are listed in Table 3. According to the results, the alkaline hydrolyzed sample treated by fluorocarbon-nanoparticles and fluorocarbon alone led to uncertain trend in tilting angle as compared with the only fluorocarbon treated sample. Generally, the liquid-solid adhesion is chiefly governed by the surface geometrical structure and composition. Existence of air pocket in the macro and nanoscales structure to form air layer and to achieve certain solid/liquid contact modes is necessary [8,
It seems that the silica particles were not dispersed uniformly on the polyester fabric due to the roughness of the textile itself that led to no significant increase in hydrophobicity.

### Table 3. Water Repellency on the Technical Face of Alkaline Hydrolyzed-Fluorochemical Treated and Alkaline Hydrolyzed-Fluorochemical & Nanoparticles Treated Fabrics with Double Cross Tuck Pattern

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Tilting angle (°)</th>
<th>3M water repellency test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorochemical &amp; nanoparticle</td>
<td>10.1±0.4</td>
<td>9.9±0.3</td>
</tr>
<tr>
<td>Alkaline hydrolysis and Fluorochemical</td>
<td>8.5±0.4</td>
<td>9.3±0.3</td>
</tr>
<tr>
<td>Alkaline hydrolysis and Fluorochemical &amp; nanoparticle</td>
<td>10.8±0.3</td>
<td>9.1±0.3</td>
</tr>
</tbody>
</table>

**Effect of Stitch Density on Knitting Structure**

In order to examine effect of fabric stitch density, sample with lowest tilting angle, double cross tuck, was chosen. Stitch densities of the resulting samples and their water repellency were indicated in Table 4.

### Table 4. Water Repellency on the Technical Face of Fluorochemical Treated Fabrics with Double Cross Tuck Pattern and Different Stitch Density

<table>
<thead>
<tr>
<th>Stitch Density</th>
<th>Feed</th>
<th>wpc</th>
<th>cpc</th>
<th>Tilting angle (°)</th>
<th>wale</th>
<th>Course</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>160</td>
<td>7</td>
<td>8</td>
<td>13.6±0.2</td>
<td>14.4±0.6</td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>130</td>
<td>8</td>
<td>7</td>
<td>9.7±0.3</td>
<td>10.5±0.5</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>90</td>
<td>11</td>
<td>9</td>
<td>13.1±0.1</td>
<td>11.6±0.6</td>
<td></td>
</tr>
</tbody>
</table>

It was found that the tilting angle of the pattern with the medium stitch density was significantly lower than those of low and high stitch densities because of the proper contact area between solid and water, which showed a better water-shedding property. In fact when the distance between the loops together and the legs of loops is close enough together, the droplet cannot penetrate intervals. Such surfaces are known as composite surfaces with contact between solid-liquid and air. On the other hand, it could be recognized that droplet on the surface with higher stitch density cannot easily move or revolve due to contact of water with a larger number of fibers.

**Relationship between Tilting Angle and Contact Angle Hysteresis**

The contact angle hysteresis of samples, which is the difference between the Advancing and the receding contact angles were showed in table 5.

The experimental results illustrate that both the contact angle hysteresis and the tilting angle are strongly affected by the surface structure and the tilting angle depends on the contact angle hysteresis. For double cross tuck lowest hysteresis contact angle (9.5°) with a small tilting angle was obtained. It seems that the air pocket formation and the reduction of pinning in the patterned surface play an important role in a surface with both low hysteresis and tilt angle.

### Table 5. Contact Angle Hysteresis in the Wale Direction of Alkaline Hydrolyzed & Fluorochemical Treated Fabrics

<table>
<thead>
<tr>
<th>pattern</th>
<th>Advancing contact angle</th>
<th>Receding contact angle</th>
<th>Tilting angle (°)</th>
<th>Contact angle hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>plain</td>
<td>156.6</td>
<td>146.2</td>
<td>9.1</td>
<td>10.4</td>
</tr>
<tr>
<td>Double cross miss</td>
<td>154.5</td>
<td>142.5</td>
<td>10.1</td>
<td>12</td>
</tr>
<tr>
<td>Double cross tuck</td>
<td>158</td>
<td>148.5</td>
<td>8.6</td>
<td>9.5</td>
</tr>
</tbody>
</table>

**Conclusion**

In the present study, superhydrophobic fabrics were prepared with a variety of weft knitted structures and the tilting angles were evaluated. It was demonstrated that fabric structures had a great effect on the surface roughness and engineering superhydrophobic fabric with maximum tilting angle of 12.5°, as compared with smooth polyester surface after fluorocarbon finishing with tilting angle of 33.5°. Also, the results indicate the capability of certain fabric macro structure for trapping air as crucial characteristics of the surface with both low contact angle hysteresis and tilting angle.
Comparison of tilting behavior of water droplets in the wale and course directions as well as technical face and back indicate the lower values in the wale directions than those of the course directions. Also, tilting properties of drops were different on the anisotropic substrates with different stitches shapes and sizes so that cellular structure achieved the best result on the technical back of double cross tuck with the tilting angle of 9°. The results showed that the tilting angle was strongly affected by the space intermediate to the loops together and the legs of loops as proper contact area by the arrangement and continuity of the three-phase contact line. Therefore, the tilting angle and contact angle hysteresis could be decreased on the double cross tuck by appropriate design of the three-phase contact line. The hydrophobicity of anisotropic substrates was improved by creation double scale topography, containing fabric structure and manufactured cavities caused by alkaline hydrolysis.

Furthermore, it was indicated that by the optimization of the fabric surface structure with appropriate pattern stitch density a superhydrophobic surface was successfully organized.

REFERENCES


