Supporting Information

Effect of the Geometrical Structure on the Superhydrophobicity and Self-cleaning Properties of Plasma-treated PVDF Fabrics

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**Figure S1.** Representative examples of surface void fractions of all fabrics composed of polyvinylidene fluoride (PVDF) filament yarns. (a) Example of the threshold value derived for PVDF/polyester (PET)-H, and (c, e, g) resulting binary images of the fabrics converted from (b, d, f) digital images based on the threshold value: (b, c) PVDF-L, (d, e) PVDF/PET-L, and (f, g) PVDF/PET-H, where the suffixes “H” and “L” indicate a high- and low-density fabrics, respectively.
To determine the area percentage occupied by the direct open pores present in the fabric, the specimen surfaces were photographed using a digital single-lens reflex DSLR camera at a vertical distance of 33.5 cm under direct illumination in a dark room with all external light sources blocked. The fabric specimen was photographed on white A4 paper, and the histograms were extracted from the images using ImageJ software. The threshold was determined as the value at which the cumulative distribution of the pixel brightness intensity reached 99.5%. Subsequently, the same fabric specimen was photographed again on black paper, and the fabric and background were separated using the threshold value to determine the ratio of the non-fabric area to the total area. Measurements were taken at three different positions over a 40 mm × 27 mm area on each fabric specimen, and an average value was obtained.
Effect of the plasma treatment condition on superhydrophobicity of fabrics

The surface morphologies and chemical compositions after treatment with O₂ plasma for 12 min were investigated using PVDF/PET-H, and the obtained results are shown in Figure S2–S3 and Table S1. A similar nanoscale roughness was introduced on the surfaces of both PVDF and PET fibers as those after treatment with O₂ plasma for 12 min and CF₄ plasma for 4 min (Figure S2). However, the role of CF₄ plasma treatment in surface fluorination could be confirmed from the XPS results of PVDF/PET-H fabric and the PVDF film used as reference material. Unlike the pristine surface and surface after treatment with O₂ plasma for 12 min, new peaks such as those for –CHF, CF₂–CHF, and CF₃–CHx emerged. The fluorine peak broadened and shifted by +0.5 eV after treatment with O₂ plasma for 12 min and CF₄ plasma for 4 min (Figure S3). Atomic concentrations (%) of fluorine present on each surface analyzed using the XPS profiles also increased after the subsequent CF₄ plasma treatment (Table S1).

To investigate the effect of plasma treatment conditions on the superhydrophobicity of fabrics, the contact angles of all fabrics after only O₂ plasma treatment were analyzed. As shown in Figure S4, after O₂ plasma treatment, the contact angle decreased for PVDF-L, and could not be measured for PVDF/PET fabric because those surfaces absorbed the water drop in less than three seconds. These results represent that the surface energy must be lowered to achieve superhydrophobicity on the roughened surface after O₂ plasma treatment. Thus, fluorine was introduced on the surface by additional CF₄ plasma treatment in this study.
Figure S2. Surface nanoscale roughness on (a) the PVDF fiber and (b) PET fiber of PVDF/PET-H introduced after treatment with O$_2$ plasma for 12 min. The scale bar in each image represents 1 μm at a magnification of 100 000×.
Figure S3. X-ray photoelectron spectroscopy (XPS) profiles of (a, c, d) PVDF film and (b) PVDF/PET-H fabric before (Pristine) and after treatment with O\textsubscript{2} plasma for 12 min (O\textsubscript{2} 12 min), and after O\textsubscript{2} plasma for 12 min and CF\textsubscript{4} plasma for 4 min (O\textsubscript{2} 12 min & CF\textsubscript{4} 4 min). (a, b) Wide survey scan and high-resolution spectra of (c) C 1s, and (d) F 1s.
Table S1. Surface concentrations (at.%) of carbon, fluorine, and oxygen according to XPS results of the surfaces of PVDF film and PVDF/PET-H fabric before and after treatment with O₂ plasma for 12 min, and after O₂ plasma for 12 min and CF₄ plasma for 4 min.

| Plasma treatment condition | PVDF film | PVDF/PET-H |
|---------------------------|-----------|------------|
|                           | C 1s      | F 1s       | O 1s      | C 1s      | F 1s       | O 1s       |
| Pristine                  | 58.6±0.3  | 37.5±0.2   | 3.9±0.1   | 58.8±0.4  | 31.8±0.4   | 9.4±0.2    |
| O₂ plasma for 12 min      | 50.4±0.4  | 43.5±0.3   | 6.1±0.2   | 46.6±0.4  | 44.0±0.4   | 9.4±0.2    |
| O₂ plasma for 12 min and CF₄ plasma for 4 min | 50.5±0.3  | 46.8±0.3   | 2.7±0.1   | 44.5±0.4  | 50.6±0.4   | 4.9±0.2    |
**Figure S4.** Surface wettability of PVDF-L, PVDF/PET-L, and PVDF/PET-H according to the plasma treatment. Unlike (a) pristine state, (b) after treatment with O$_2$ plasma for 12 min, water droplets were absorbed by the surface of PVDF/PET-L and PVDF/PET-H, and the contact angle (CA, °) on the surface of PVDF-L decreased. (c) After treatment with O$_2$ plasma for 12 min and CF$_4$ plasma for 4 min, the CA increased to > 150° in all fabrics.
Figure S5. Surface structure, chemical composition, and wettability of PVDF film. Field emission-scanning electron microscopy (FE-SEM) images of the (a) surface and (b) cross-section, and energy dispersive X-ray spectroscopy (EDS) mapping of (c) carbon, (d) oxygen, (e) fluorine of the pristine PVDF film. (f, g) AFM results with different root mean square roughness (Rq) values (scan size: 5 µm × 5 µm), and (h, i) the contact angle values of the PVDF film (f, h) before and (g, i) after plasma treatment with O₂ plasma for 12 min and CF₄ plasma for 4 min.
Significant differences were observed in the dynamic behavior of water droplets according to the microstructure in this study. Even after the nanoroughness induced by plasma treatment and contact angle increased over 150°, the water droplet did not roll off of the PVDF film without microroughness (Figure S5). However, the water droplet could roll off of the surface of fabric made with PVDF and PET fibers at a tilt angle of ~41.3° before and ~10.5° after plasma treatment (Table 2). Furthermore, the different microscale weave structures of those fabrics resulted in the variation in the degree of superhydrophobicity, and the shedding angle followed the same order, i.e., PVDF-L < PVDF/PET-H < PVDF/PET-L before and after nanoroughness induced by the plasma treatment. The PVDF-L is made of thinner and denser PVDF yarns (524–598 μm composed of ~1 μm fibers) than PET yarns (807 μm composed of ~22 μm fibers) of PVDF/PET-L, resulting in a smaller solid area fraction in the Cassie–Baxter model at the macroscale and shorter distances between fibers at the microscale. Thus, PVDF-L is the most advantageous for achieving superhydrophobicity, which might contribute to a relatively small contact area with the water droplet and enough anti-wetting pressure to overcome wetting pressure. These results indicated that along with nanoroughness, microscale roughness of the surface is also conducive to achieving superhydrophobicity, thereby confirming the importance of the inherent microstructure of the fabric.
Evaluation of the suitability of the fabric as clothing material

The suitability of the developed superhydrophobic fabric as clothing materials was evaluated for PVDF/PET-H, which had the lowest air permeability (Table S2). The effect of plasma treatment on the mechanical properties, color, and comfort of the PVDF/PET-H were investigated.

The mechanical properties were evaluated by measuring tensile strength, elongation at break, and stiffness. By referring to ASTM D 5035 a strip method, both ends of a sample with a width of 1 cm and a length of 7 cm were fastened by clamps, which were set 4 cm apart; 1 kN load was applied with the loading speed of 10 cm/min. The stiffness was assessed based on the ISO 4606: 2013 measurement method using a fixed angle bending tester. Five measurements were carried out for each sample and the results were averaged.

The color changes according to the plasma treatment were measured by a color difference meter (CM-2600d Spectrophotometer, Minolta, Japan). The L* (lightness, 0–100), a* (red-green), b* (yellow-blue), and the K/S value (the surface reflectivity) at 520 nm wavelength were analyzed using the Commission internationale de l’éclairage (L*, a*, b*) color space (CIELAB).

To assess the comfort of clothes, the air permeability and water vapor permeability were measured in accordance with ASTM D 737-04 (the Frazier method) and KS K 0594:2015 (the calcium chloride method), respectively. For this purpose, an air permeability tester (FX 3300, Textest AG Co., Switzerland) at a pressure of 125 Pa and a water-permeable cup containing 33 g of calcium chloride were used.

Table S3 shows the tensile strength, elongation at break, flexural stiffness, CIELAB coordinates and K/S values, air permeability, and water vapor transmission rate of the PVDF/PET-H before and after plasma treatment. The tensile strength and elongation at break decreased after the plasma treatment. This might be attributed to the breakage of fine PVDF fibers and etched sites of PET fibers on the surface due to the O2 plasma etching. Meanwhile, the flexural stiffness was not significantly affected by the plasma treatment, because the plasma etching affected only the surface, not the bulk properties. The color difference, \( \Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \), was a low level of 0.81. Further, air and water vapor permeabilities of PVDF/PET-H after plasma treatment were similar to those of the pristine fabric. Based on these results, the developed superhydrophobic fabric can provide wearing comfort with excellent flexibility and breathability, and thus, are promising materials for smart textiles.
Table S2. Air permeability of pristine PVDF-L, PVDF/PET-L, and PVDF/PET-H

|                      | PVDF-L       | PVDF/PET-L   | PVDF/PET-H   |
|----------------------|--------------|--------------|--------------|
| **Air permeability** | 693.0±50.7 cfm | 143.0±4.0 cfm | 112.0±8.7 cfm |

a) cfm is the units of the volume of the permeated air, which indicates cubic feet per minute (1 cfm = 471.9 cm³/s).

Table S3. Tensile strength, elongation at break, flexural stiffness, CIELAB coordinates and K/S values, air permeability, and water vapor transmission rate of the PVDF/PET-H before and after plasma treatment

|                      | Pristine          | After plasma       |
|----------------------|-------------------|--------------------|
| **Tensile strength** |                  |                    |
| Weft a)              | 33.6±3.4 kg/cm²   | 17.9±1.8 kg/cm²   |
| Warp b)              | 135.9±3.4 kg/cm²  | 73.8±7.7 kg/cm²   |
| **Elongation at break** |                |                    |
| Weft a)              | 160.0±68.9%       | 121.1±42.7%       |
| Warp b)              | 55.6±1.1%         | 25.7±4.8%         |
| **Flexural stiffness** |                   |                    |
| Weft a)              | 0.027±0.011 mN·m  | 0.022±0.002 mN·m  |
| Warp b)              | 0.004±0.002 mN·m  | 0.005±0.005 mN·m  |
| **CIELAB coordinates and K/S values** c) | | |
| L*                   | 89.69±0.86        | 89.43±0.76        |
| a*                   | 0.19±0.22         | 0.07±0.03         |
| b*                   | 4.03±0.42         | 4.79±0.51         |
| K/S value            | 0.04±0.01         | 0.05±0.01         |
| **Air permeability** |                  |                    |
|                      | 112.0±8.7 cfm     | 111.6±17.7 cfm    |
| **Water Vapor**      |                  |                    |
| Transmission Rate    | 8849.0±736.0 g/(m²·24 h) | 8676.3±640.9 g/(m²·24 h) |

a) The length of fabric corresponds to the weft direction parallel to the PVDF filament yarns.
b) The length of fabric corresponds to the warp direction parallel to the PET filament yarns.
c) K/S value measured at 520 nm wavelength.
d) cfm is the unit of the volume of the permeated air, which indicates cubic feet per minute (1 cfm = 471.9 cm³/s).
Evaluation of the mechanical stability of superhydrophobicity

To evaluate the mechanical stability of the developed superhydrophobic properties by the plasma treatment, the contact angle and the shedding angle of the plasma-treated PVDF/PET-H fabric after standard laundering and abrasion tests were measured. The laundering durability was tested using a household drum washing machine (Tromm, LG, South Korea) without detergent. The PVDF/PET-H (size 8 cm × 8 cm) was stitched to a pillowcase, and washed with a total of 15 pillowcases as a dummy according to a standard condition consisting of washing, rinsing (twice), and spin-drying for 59 min. The washed fabric was then dried at room temperature, and the contact angle and the shedding angle were measured at five spots and averaged. The abrasion durability of the PVDF/PET-H was investigated after conducting a tape test according to ASTM D3359 using a commercial clothing tape cleaner (Scotch-Brite, 3M) and abrasion with commercial nylon knit (Testfabrics, Inc., USA). After repeating abrasion 5, 10, 15, 20, 25, and 30 times, respectively, the contact angle and shedding angle of the fabric were measured.

After laundering the plasma-treated PVDF/PET-H, the shedding angle increased from 4.6°±0.7° to 19.0°±1.2° (Figure S6), which might be attributed to the deformation of the surface nanostructure after washing. On the other hand, the contact angle was almost the same within the margin of error, 161.0°±2.1°. Moreover, the plasma-treated PVDF/PET-H shows good abrasion resistance. As shown in Figure S7, although the shedding angle gradually increased with increasing the number of tape tests, it remained low at 11.4°±2.1° after repeating abrasions 30 times, and the contact angle remained more than 160°. Besides the tape test, mechanical durability against the abrasion with nylon knit was also evaluated. Figure S8 shows that the contact angle gradually decreases and the shedding angle gradually increases according to the number of abrasions. However, even after repeating abrasions 30 times, PVDF/PET-H still demonstrated superhydrophobicity, exhibiting a contact angle of 160.1°±2.2° and a shedding angle of 6.2°±0.8°. These results indicate that the developed superhydrophobicity of fabric, which is endowed by the plasma treatment, is mechanically stable against abrasion with a commercial clothing tape cleaner and nylon knit. Thus, the developed superhydrophobic fabric can maintain water repellency and self-cleaning properties when applied to smart textiles, i.e., harvesting triboelectric energy by rubbing with another surface.
Figure S6. Laundering durability of the developed superhydrophobic properties according to the standard laundering. The contact angle and the shedding angle of PVDF/PET-H before and after washing, rinsing (twice), and spin-drying without detergent.
Figure S7. Abrasion durability of the developed superhydrophobic properties according to the number of tape tests. Changes in the contact angle and the shedding angle of PVDF/PET-H after repeating the tape test 5, 10, 15, 20, 25, and 30 times.
Figure S8. Abrasion durability of the developed superhydrophobic properties according to the number of abrasion cycles. Changes in the contact angle and the shedding angle of PVDF/PET-H after abrasions with nylon knit 5, 10, 15, 20, 25, and 30 times.
**Figure S9.** Example of analyzing the area fraction of dust to the total area to evaluate the self-cleaning properties of the fabric: (a) threshold value derived from the cumulative pixel distribution of the brightness intensity of the initial surface, and (b) image processing based on the threshold to calculate the area fraction of hydrophilic dust (Fe₂O₃) on the plasma-treated PVDF/PET-H.
References

(1) Hopkins, J.; Badyal, J. CF$_4$ plasma treatment of asymmetric polysulfone membranes. *Langmuir* **1996**, *12* (15), 3666–3670.

(2) Sigurdsson, S.; Shishoo, R. Surface properties of polymers treated with tetrafluoromethane plasma. *J. Appl. Poly. Sci.* **1997**, *66* (8), 1591–1601.

(3) Tressaud, A.; Durand, E.; Labrugère, C. Surface modification of several carbon-based materials: comparison between CF$_4$ RF plasma and direct F$_2$-gas fluorination routes. *J. Fluor. Chem.* **2004**, *125* (11), 1639–1648.

(4) Hong, H. R.; Kim, J.; Park, C. H. Facile fabrication of multifunctional fabrics: Use of copper and silver nanoparticles for antibacterial, superhydrophobic, conductive fabrics. *RSC Adv.* **2018**, *8* (73), 41782–41794.

(5) Youn, S.; Park, C. H. Development of breathable Janus superhydrophobic polyester fabrics using alkaline hydrolysis and blade coating. *Text. Res. J.* **2019**, *89* (6), 959–974.

(6) Cao, C.; Ge, M.; Huang, J.; Li, S.; Deng, S.; Zhang, S.; Chen, Z.; Zhang, K.; Al-Deyab, S. S.; Lai, Y. Robust fluorine-free superhydrophobic PDMS–ormosil@fabrics for highly effective self-cleaning and efficient oil–water separation. *J. Mater. Chem. A* **2016**, *4* (31), 12179–12187.