

Development of a Superhydrophobic Digital-Printed Cotton Fabric

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Abstract: Superhydrophobic digital-printed cotton fabric has been developed by the dip coating method to find applications in the apparel and textile industries due to the exposure of apparel and textiles products to the environment regarding water-repellency and self-cleaning abilities. The microstructure and surface morphology of the prepared digital-printed fabrics was examined using scanning electron microscopy. Fabrics proved breathable based on the air permeability of the prepared samples. Evaluation of coating durability of the modified digital-printed fabric was done by a washing method. This revealed the durability and self-healing properties of the treated digital printed cotton fabric after heat treatment with a water contact angle of 156° lower than the water contact angle recorded before the evaluation of coating durability at 162° . The water-shedding angle for the developed digital-printed fabric could not be recorded due to the stickiness of the surface of the treated digital-printed cotton fabric which produced an angle above the accepted angle at 10° . Therefore, this technique produced a digital-printed fabric with double functionalities of water-repellency and self-healing properties and could be used in the apparel and textiles industries, especially for fashion accessories.

Keywords: Superhydrophobic, digital-printed fabric, water contact angle, self-healing, repellent.

1 Introduction

Cotton fabrics and apparel with special wetness and self-cleanable characteristics have evoked a large amount of quality curiosity in experimentation and practical fields. This is due to new research on superhydrophobic fabrics in the apparel and textile industries. These applications are self-cleaning [1], ‘oil and water separation [2].’ and ‘water repellence [3]. Superhydrophobic surfaces in recent studies have mainly been concentrated on pristine fabrics and few studies on dyed or printed fabrics. However, in order to be used in the apparel and textile industries, dyeing or printing is essential for the fabrics. It is, therefore, necessary to develop a method to impart super hydrophobicity to the dyed or printed fabrics hence this research to develop a digital-printed cotton fabric having superhydrophobic and self-healing properties by the application of non-fluorinated zirconium nanoparticles using the dip coating method. Besides, the treated digital-printed cotton fabric samples were compared with only the treated cotton fabrics to examine the bonding mechanism between the reactive pigment and the non-fluorinated hydrophobic reagents in figure 1.

The developed fabric had self-cleaning functionalities since self-cleaning mechanisms have been reproduced after the lotus leaves with less surface energy substance and surface features which are dependent on the surface roughness to acquire a water-repellent uppermost layer [4], colour

fastness with other practical usages in the apparel and textile environment.

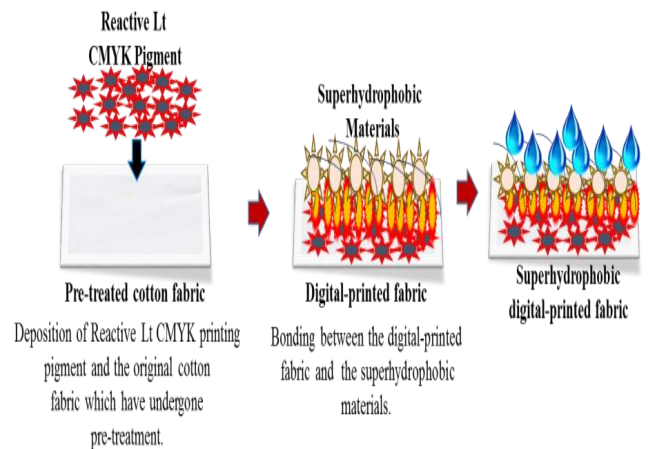


Fig. 1. Mechanism of surface treatment of the digital-printed

The interest in ink-jet printing on textile surfaces has increased in academic and industrial fields. Some benefits of ink-jet printing include customization, high speed, cleanliness, flexibility, substrate independence and integration with existing production lines [5]. Superhydrophobic fabrics have been available and are the recent concentration of studies in textile research because of their numerous applications in the textile industry. An

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example is the 'lotus effect' which shows an excellent super anti-wetting with the self-cleanable property of the surfaces of the leaves by which rainwater rolls off more smoothly than attaching to the surfaces. These unique features have been accredited to the combination of the waxed covering that results in the lowering of the surface energy and the dual-scale structure of the surface. The dermal tissue of the leaves develops projections which attribute to the lowering of the surface energy with a single covering of the cells which have been closely packed. This covering which acts as skin: covers and protects the plants [6].

Superhydrophobic surfaces have also been described as surfaces that repel water. In addition, the observed water contact angles have water droplets beyond 150° while the droplets that produce the roll-off angle are recorded as less than 10° to confirm that the fabric is truly superhydrophobic [7]. In addition to the above studies on superhydrophobicity, other researchers have come out with the development of superhydrophobic coloured cotton fabric by the 'sol-gel technique'. This development was done by combining 'silica nanoparticles', 'silane hydrophobes (alkyltrialkoxysilanes)', and 'silane cross-linkers (tetraethoxysilane (TEOS) and 'tetraethoxysilane TMOS)' after dyeing fabrics with 'drimarene reactive red 5B' and 'drimarene reactive blue BR' dyes by the 'dip-dry-cure process' [8].

The research concluded that observations confirmed a long-lasting hydrophobic property achieved on the treated dyed fabric with the 'non-fluorine sol-gel process' [9]. The silica nanoparticles used exhibited good fastness to colour and some effect on the shade. In addition to the above observations, the SEM images of the dyed-coated fabric showed irregular surface behaviour when compared to the uncoated dyed samples. Other steps used in superhydrophobic cotton fabric development are the production of cotton fabric with properties that resemble superhydrophobic inspired objects in nature either by a 'one-step' or 'two-step' reaction [10]. The varied methods used are outlined in table 1 for development on cellulosic-based surfaces.

With the use of zirconium nanoparticles for producing a superhydrophobic surface, 'fluorinated silyl-functionalized' zirconia with a high permanent sol-gel derived experimented with an immersion method [11]. Results from the researcher indicated that the fabrication did not deteriorate the original flexibility of the fabric but rather possessed an excellent long-lasting superhydrophobic and superoleophilicity property with a good water contact angle at 163° and a contact angle hysteresis at 3.5° . In addition, the studies indicated that the 'fluorinated silyl-functionalized' zirconia coated fabric rather produced a very good sustainable and durable superhydrophobic fabric than particles with silica and other hydrophobization coatings which are not suitable for everyday technical usages [11].

2 Materials and Methods

A piece of digital-printed cotton fabric was printed with UJET MC3 Premium by Yuhan Kimberly on a piece of pre-treated cotton fabric. The digital-printed samples were cut $15\text{cm} \times 15\text{cm}$ and cleaned with Ethyl alcohol anhydrous 99.9% - ($\text{C}_2\text{H}_5\text{OH}$) purchased from Daejung KOSDAG listed Company Korea, and deionised water before subjecting to treatment. Methyl alcohol - (CH_3OH) also obtained from Daejung KOSDAG listed Company, Korea; used as a dissolving agent for dodecyltriethoxysilane ($\text{C}_{15}\text{H}_{34}\text{O}_3\text{Si}$) as silane hydrophobes obtained from Sigma-Aldrich, was used for synthesizing the sol to lower the surface energy.

For hierarchical nano roughness, zirconium (IV) propoxide solution 70 wt. % in 1-propanol ($\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$) from Sigma-Aldrich, the product of U.S.A. was dissolved in 1-Butanol ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$) from JUNSEI Chemical Co., Ltd. Lot No. 5E5810 with acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) from JUNSEI Chemical Co., Ltd. Lot No. 2017D2026 used as a chelating agent to stabilize the zirconium nanoparticle ($\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$).

2.1 Digital printing and fixation of pigment

The original cotton fabric was pre-treated by dissolving sodium alginate in 50 grams of deionized water -0.95 dm^3 , sodium bicarbonate of 8 grams, and urea -10 grams [12,13,14]. The weight of the paste was 200 grams of deionized water [12,13,14], which was mixed thoroughly. The paste used to treat the original fabric before printing was applied to the original cotton fabric by the use of a 'padding machine'. The pressure used was even and at 2.6 kg/m^2 with a 'padding speed' at 2.5rpm. This continued until the original fabric being treated reached a percentage of 80% of 'pick-up' of the solution mixed after which the coated pre-treated cotton fabric was dried at 80°C in an oven. Before digital printing, the pre-treated cotton fabric underwent a conditioning treatment [12,13,14].

Digital printing was done using the digital printing machine- UJET MC3 Premium by Yuhan Kimberly with Reactive LT CMYK digital textiles printing pigment in figure 8a with additional pigments used which were light magenta, orange, gray and blue. The printing resolution was set at 300dpi. After printing, the digital-printed fabric was steamed twice to wash off excess printing pigments and to fix the printing pigment into the fabric structure at 95°C for 40 minutes. Steamed digital-printed fabrics were dried under room temperature overnight shown in figure 3. Figure 4 shows the overall process of treating the original cotton and finally printing the digital-printed fabric.

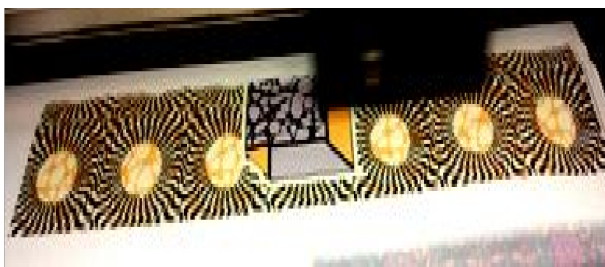


Fig. 2. Digital Textile Printing of pre-treated fabric.



Fig. 3. Steamed digital-printed fabric.

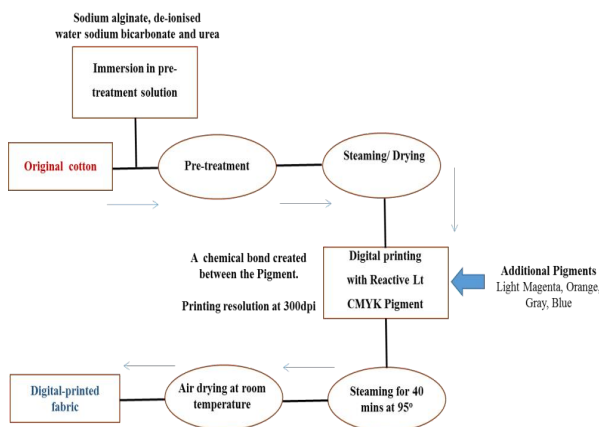


Fig. 4. Digital textile printing of original cotton fabric from the pre-treatment stage to the final digital-printed fabric.

2.2 Preparation of cotton fabric

Prior to superhydrophobic treatment, the original cotton fabric and digitally printed fabric samples were treated with deionized water and Ethyl alcohol anhydrous 99.9% - (C_2H_5OH) [14]. Fabrics were dried at room temperature and 3 digital-printed fabric samples were cured at $100^{\circ}C$, $120^{\circ}C$ and at $140^{\circ}C$ without the use of water due to the high temperature required in fixing reactive dyes into the fibre structure of cotton fabric during printing; whereby dye fixation was done by heat-treatments based on the following techniques [15]:

- i. Steaming by saturated vapour ($100^{\circ}C$).
- ii. High-temperature steaming by super-heated vapour at temperature conditions from $120-150^{\circ}$.
- iii. Dry

Table 1 shows the sample codes used in this study with the original fabric sample names.

Table 1. Samples used and their respective sample codes.

Samples of fabrics used	Sample codes
Original fabric	O
Digital-printed fabric	P
Digital-printed cured fabric	PC
Digital-printed and superhydrophobic treated fabric	PCS
Original superhydrophobic treated fabric	S
Superhydrophobic heat-treated samples after coating durability test	SH, PCSH

2.3 Fabrication of superhydrophobic digital-printed fabric

To lower the surface energy, silane sol was first prepared by dissolving 20ml dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) in 10ml of methyl alcohol - ($CH_3 OH$) in the ratio 2:1 with a dropwise addition of 10ml deionized water in table 2 and stirred magnetically for 1 hour at 400 rpm. Dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) was used to increase the bonding mechanism with zirconium as silane coupling agents improve the resin zirconia bonding significantly [16]. The percentage volumes of each material used in synthesizing the sol for the superhydrophobic treatment of the digital-printed fabric have been shown in table 3. To add to the above, dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) was used because the more the 'hydroxyl groups on the surfaces of the 'silane-coated' zirconium, the higher the level of bonding in-between the 'silane primer and the zirconium-coated surface where a lot of energy would be needed to interrupt the 'interfacial' layer [17].

To produce a superhydrophobic digital-printed fabric with hierarchical roughness, zirconium sol was synthesized according to the previous report [11] and modified to suit the current study without the use of fluorinated materials because; zirconium exhibited a very good mechanical strength which possesses a high relationship with energy that does not dissociate at ~ 753 KJ mole⁻¹ [18] and as well; a strong covalent character of which it has been noted for Zirconium has also been well known for its stability thermally [19] as well as the ability to withstand strong alkali and acid when compared with other particles also of the ceramic origin [20].

A 10ml of zirconium nanoparticle ($Zr (OCH_2CH_2CH_3)_4$) was dissolved in 10ml 1-Butanol ($CH_3 (CH_2)_2CH_2OH$) in the ratio of 1:1. Stirring was done for 1 hour at 400 rpm magnetically after which 2ml acetylacetone ($CH_3COCH_2COCH_3$) was added by dropwise addition as a chelating agent to remove toxins and stabilize the zirconium nanoparticle ($Zr (OCH_2CH_2CH_3)_4$). The

synthesized sol was stirred again magnetically for one hour all under cold temperature.

Table 2. Concentration of materials for the fabrication of the superhydrophobic digital-printed fabric

Materials	Concentration (ml)
Methyl alcohol	10
Dodecyltriethoxysilane (Silane Hydrophobes)	20
Deionized Water	10
1-Butanol	10
Zirconium (IV) propoxide solution 70 wt. % in 1-propanol	10
Acetyl Acetone	2

Table 3. The percentage volume of materials used for treating the digital-printed fabric

Materials	Vol %
Methyl alcohol	$10/62 = 0.16$
Dodecyltriethoxysilane (Silane Hydrophobes)	$20/62 = 0.32$
Deionized Water	$10/62 = 0.16$
1-Butanol	$10/62 = 0.16$
Zirconium (IV) propoxide solution 70 wt. % in 1-propanol	$10/62 = 0.16$
Acetyl Acetone	$2/62 = 0.03$

The silane sol was added to the zirconium sol and stirred magnetically for 1 hour at 400rpm. Samples were dipped into the sols for one hour and heat-treated under different temperature degrees to ascertain the temperature condition suitable for superhydrophobic development on digital-printed surfaces as reactive pigments require a set temperature condition to adhere to the fabric structure [15]. In figure 4, the schematic structure has been represented showing the preparation for fabrication. Figure 5 shows the overall treatment procedure for the fabrication of the superhydrophobic digital-printed fabric has been outlined. After washing off excess nanoparticles, the samples were then re-coded as sample S being the original fabric O before superhydrophobic treatment; heat treated at 120°C before superhydrophobic treatment, sample PS- the superhydrophobic treated digitally printed fabric P heat treated at 120 °C, sample PCS/100- the treated superhydrophobic digital-printed fabric cured at 100 °C; sample PC/100 before superhydrophobic treatment which was heat-treated after superhydrophobic treatment at 100 °C, sample PCS/120- the treated superhydrophobic digital-printed fabric cured at 120°C before superhydrophobic treatment- PC/120 which was heat-treated after superhydrophobic treatment at 120 °C and sample PCS/140 - the treated superhydrophobic digital-printed fabric cured at 140°C before superhydrophobic treatment- PC/140 heat-

treated after superhydrophobic treatment at 140°C. All heat treatments lasted for one hour for all samples.

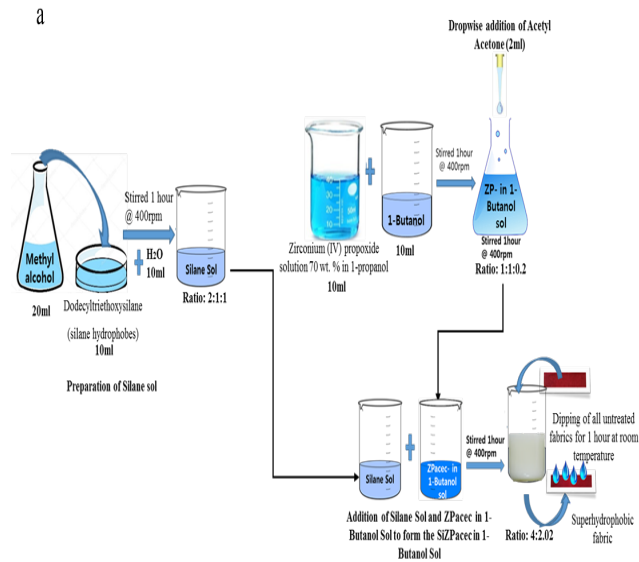


Fig. 4. A diagrammatic representation of the preparation of sol and fabrication of superhydrophobic digital-printed fabric.

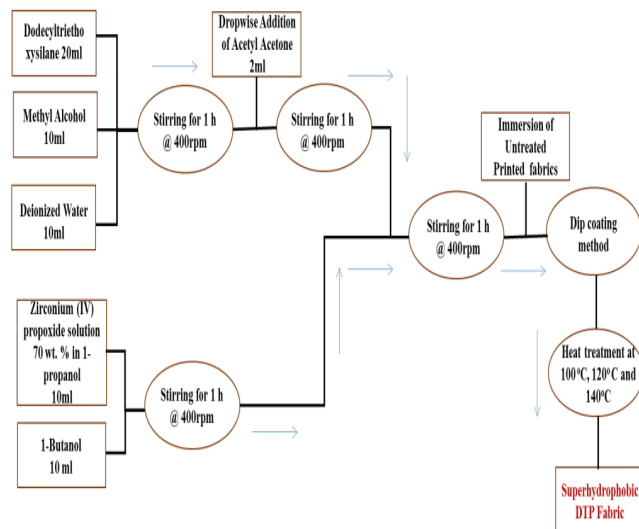


Fig. 5. The overall treatment procedure for the treatment of the digital-printed fabric.

2.4 Characterization

The surface morphology of untreated fabric samples O, P, PC/100, PC/120, PC/140 and superhydrophobic treated samples S, PS, PCS/100, PCS/120, and PCS/140 was monitored using the ESC 7900 scanning electron microscopy. Water contact angle and water shedding angle measurements were conducted with the water contact angle goniometer 'Theta lite optical tensiometer, KSV Instruments, Finland' and the shedding angle adjustment by using the 'cradle (Attention theta lite)' on treated and

untreated samples The colour difference was tested with the colour spectrophotometer ELECOM U2H-M4BGT S/N003090. An air permeability test was done with the Testing Instruments for Quality Control. Zurich, Switzerland TEXTESTAG (FX 3300).

2.5 Evaluation of surface morphology

The fundamental composition and surface morphology of developed digital printed cotton fabric samples and undeveloped digital-printed cotton fabric samples was examined by scanning electron microscopy ESC 7900. Before the examination of the surface morphology, a sputtering coater was used by depositing a thin layer of gold film to cover all sample surfaces to aid in increasing the conductivity of the structures during the main experiment.

2.6 Evaluation of water contact angle and shedding angle

The water contact angle measurement and shedding angle measurement tests have been done using the contact angle goniometer. Both treated and untreated sample surfaces were measured and compared by using a sessile water drop method with water droplets of distilled water up to 10-15 μ l on all fabric samples without any set temperature conditions. The results of the water contact angles and shedding angles were measured on two different samples at five separate points. The mean values of the contact angles were recorded. The photographs of the water droplets on the surfaces of the fabric samples were captured with the use of a digital camera between 10-20 seconds. This was done without changing the temperature and the airflow of the testing environment The measurement of the shedding angle was also done by dropping the liquids on the surfaces of the untreated and treated fabric samples which were very difficult to record due to the stickiness of the surfaces of the treated digital-printed fabrics and the hydrophilic nature of the untreated fabric samples. This was based on the roll-off angles of the various samples to be proven as a superhydrophobic substrate.

2.7 Evaluation of colour difference

The colour difference of the steamed digital-printed fabric, digital-printed fabric washed with ethyl alcohol and deionized water; zirconium-treated digital-printed cotton fabric and treated digital-printed cotton fabric that had undergone five washing cycles were tested. The same colour points were cut out and measured for the colour difference since the digital-printed fabric sample used in this study was a patterned digital-printed fabric. The samples were measured with the colour spectrophotometer ELECOM U2H-M4BGT S/N003090 to find out the effect of treatment on colour based on the colour difference at observer 10° (Primary: D65). Results of the L* values at D65 were recorded since the colour brightness results were used to assess the colour difference

2.8 Evaluation of air permeability

An air permeability test was performed on the various samples to evaluate the air passage of the treated surfaces which could affect the air pores of the treated fabric samples. The untreated and treated fabric samples were tested with the Testing Instruments for Quality Control Zurich, Switzerland TEXTESTAG (FX 3300).

2.9 Various liquids'-repellency tests

The repellency of other liquids was tested with various liquids by comparing all fabric samples- both the treated and the untreated. This was executed by dropping droplets of various liquids on the sample surfaces. The various liquids used to test the surface repellence of the treated fabrics were coloured water, cocoa drink, black tea, cranberry juice and coffee. These liquids were selected to evaluate the surface repellency of the treated surface to ascertain the repellency of the treated surface to other liquids apart from water.

2.10 Evaluation of coating durability

All superhydrophobic treated fabrics underwent five washing cycles at 40°C for 39 mins in a commercial washing machine. This was to compare the durability of the superhydrophobic digital-printed fabrics with the superhydrophobic original cotton fabric for a better assessment of the printing pigment based on the water contact angles, and the colour difference.

After the first, third and fifth laundry cycles before and after healing treatment water contact angle measurements were taken. During the healing treatment, fabric samples were subjected to heat treatment for 5 minutes. Measurement of the water contact angles was also to find out if all treated fabric samples maintained their superhydrophobicity after the five laundry cycles and could possess self-healing properties after being washed five times. After each washing cycle, the state of firmness and strength of treatment on the samples was determined by measuring the water contact angles.

2.11 Self-cleaning property of fabricated digital-printed fabrics

The self-cleaning ability test was conducted with silicon carbide to find out if treated samples had the ability to self-clean without any external force on the surfaces. This was recorded with the use of a digital camera to find out the self-cleaning performance of all samples used in the experiment.

3. Results and Discussion

3.1 Surface morphology of treated and untreated fabrics

Surface morphology results confirmed the original cotton fabric in figure 6, (a) with a smooth surface structure of the fibre with fine terraces visible features on its fibre cuticle at low magnification, while (b) shows a low magnification of the superhydrophobic developed original fabric - S with roughened surface structures indicating the deposition of the nanoparticles employed in this study on the surface of the fibre thereby altering the fibre structure and surface. The (c) shows the high magnification of (b)

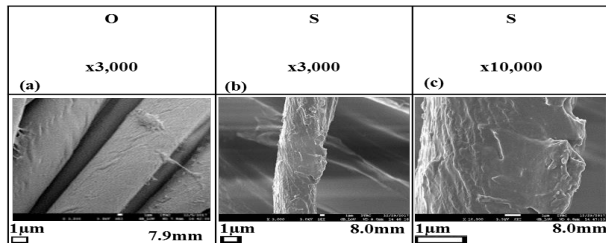


Fig. 6. The surface morphology of the original cotton fabric O in (a), S in (b) at low magnification and S at higher magnification in (c).

The surface morphology of the digital-printed fabric -P in figure 7 where (a) shows very slight rough surfaces on the cotton substrate due to the deposition of the printing pigment. In (b), the treated digital-printed fabric PS shown at low magnification after heat-treatment at 120°C had more roughened surfaces owing to the changing of the fibre surface and structure showing deposition of the nanoparticles used thereby recording the highest at 162° due to the change in morphology of the coated surface. The higher magnification in (c) clearly demonstrated the structure after treatment, by becoming rougher and uneven

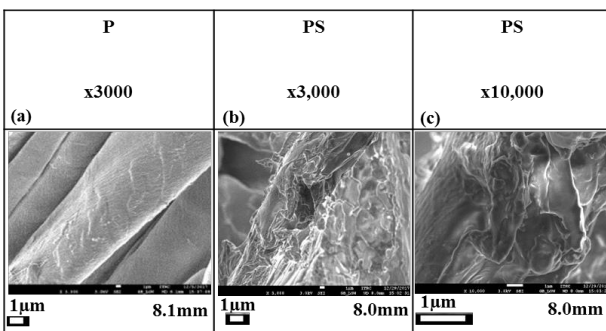


Fig.7. The surface morphology of the digital-printed fabric -P in (a), PS in (b) at low magnification and PS at higher magnification in (c).

The digital-printed fabric cured at 100° before superhydrophobic treatment- PC/100 in figure 8, (a) had a smooth surface with slight rough patches while (b) shows the superhydrophobic digital-printed fabric -PCS/100 with some kind of rough surface and a meandering glossy effect which could be due to the curing before superhydrophobic treatment in low magnification. The higher magnification of (b) is shown in (c).

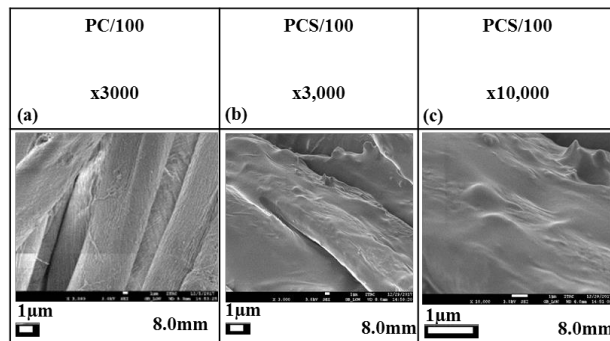


Fig.8. The surface morphology of the digital-printed fabric PC/100 in (a), PCS/100 in (b) at low magnification and PCS/100 at higher magnification in (c).

The digital-printed fabric was cured at 120° before superhydrophobic treatment PC/120 in figure 9, (a) also shows a smooth surface with slight rough patches which could be due to the printing pigment and the temperature at which the digital-printed fabric was cured before superhydrophobic treatment. The (b) shows the superhydrophobic digital-printed fabric PCS/120 with a more roughened surface than (a) and some glossy effects in low magnification. The higher magnification of (b) is shown in (c).

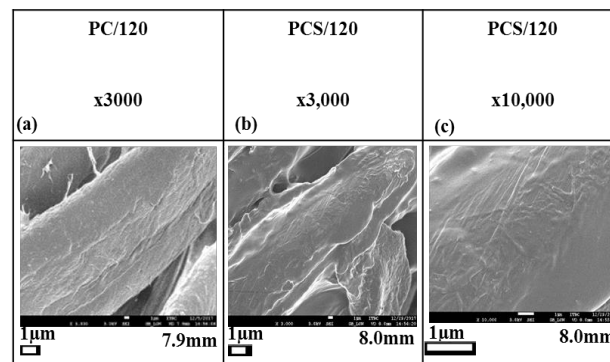


Fig. 9. The surface morphology of the digital-printed fabric PC/120 in (a), PCS/120 in (b) at low magnification and PCS/120 at higher magnification in (c).

The digital-printed fabric cured at 140° before superhydrophobic treatment PC/140 in figure 10 where (a) shows a smooth surface of the untreated digital-printed fibre structure while (b) shows the superhydrophobic digital printed fabric -PCS/140 with rougher surface and less glossy effect than in figures 12 and 13 which could also be due to the curing before superhydrophobic treatment and deposition of the superhydrophobic particles in low magnification. The higher magnification of (b) is shown in (c).

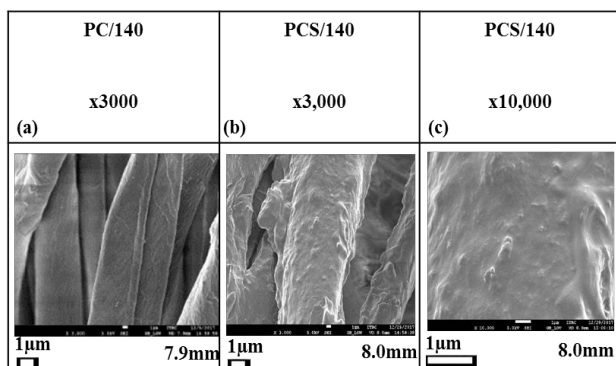


Fig. 10. The surface morphology of the digital printed fabric PC/140 in (a), PCS/140 in (b) at low magnification and PCS/140 at higher magnification in (c).

3.2 Water contact angle and shedding angle

Based on the ‘ASTM D7334-08(2013)-Standard Practice for Surface Wettability of Coatings, Substrates and Pigments’, the results of the water contact angle confirmed complete wetting for all fabric samples. The wettability of the original cotton sample after contact angle measurements exhibited the typical cotton fabric, due to the wetting group called the ‘hydrophilic groups’ in the fabric structure made up of cellulose that absorbed all the water.

After the steaming process, the pre-treatment elements were lost in the untreated digital-printed fabric by rendering it hydrophilic thereby losing the hydrophobic property. Further results of the water contact angle confirmed the digital-printed fabric - PS with the highest water contact angle at 162° while PCS/100 recorded the lowest water contact angle at 150°. PCS/120 recorded an average water contact angle at 153°. The PCS/140 recorded an average water contact angle at 154° in table 4.

Table 4. Water contact angle and shedding angle of untreated samples and treated samples with the contact angle images of superhydrophobic treated samples.

	UNTREATED SAMPLES					SUPERHYDROPHOBIC TREATED SAMPLES				
	O	P	PC/100	PC/120	PC/140	S	PS	PCS/100	PCS/120	PCS/140
Water Contact Angle (°)	0 (Complete wetting in less than 5 sec)	0 (Complete wetting in less than 5 sec)	0 (Complete wetting in less than 5 sec)	0 (Complete wetting in less than 5 sec)	0 (Complete wetting in less than 5 sec)	161	162	150	153	154
Shedding Angle (°)						20	14	19	20	30

The results concluded that printing before superhydrophobic treatment had no effect on the superhydrophobicity but rather on the temperature condition of heat treatment. Curing before superhydrophobic treatment at various temperature degrees also confirmed the temperature conditions interfered with the pigment by exposure to excessive heat after steaming twice at 95° for 40 minutes by breaking down the chemical structures of the cured digital-printed fabrics before treatment. On the other hand, the untreated samples had complete wetting based on the water contact angle results and water could not roll off the surfaces. Therefore, it was impossible when taking measurements of the shedding angle of the untreated samples.

The shedding angles of the superhydrophobic treated samples recorded were higher than 10° due to the sticky surface of the treated fabrics. In figure 11, the water contact angle and shedding angle results of the treated fabric samples have been shown in detail.

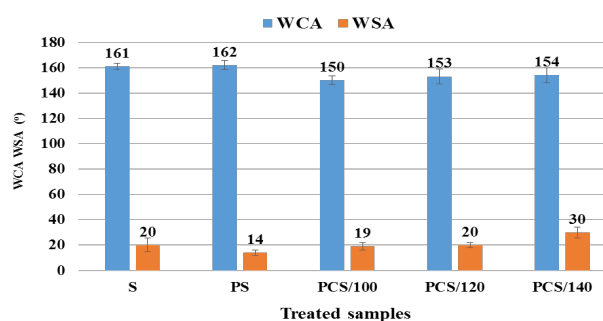


Fig. 11. Graph showing the water contact angle and water shedding angle of treated fabric samples.

3.3 Repellency

Observation of the surface repellency to water by visual examination with various liquids (coloured water, cocoa drink, black tea cranberry juice and coffee) dropped on the surfaces showed that the original cotton sample -O absorbed completely in less than 3 seconds. Also, the untreated digital printed cotton sample -P absorbed all liquids completely.

The superhydrophobic treated digital-printed fabric -PS showed much repellency when the various liquids were dropped on the surface to other liquids apart from water which could be because of the air layer trapped on the digital-printed cotton surface. Likewise, the superhydrophobic treated original cotton fabric -S did not absorb any of the aforementioned liquids compared to the original cotton fabric which is a phenomenon that proves the ‘Cassie-Baxter state’ of the finished treated fabric samples [1] in figure 12.



Fig.12. Images of various liquid droplets on the surfaces of untreated fabrics, and treated fabrics with coloured water, cocoa drink, black tea, cranberry juice and coffee.

3.4 The durability of coating before heat treatment

A very significant factor for the functionality of the prepared fabric is the durability test by subjecting treated fabric samples to a number of washing cycles based on the fact that the superhydrophobic digital-printed cotton fabrics would be in the future subject to washing in the environment. The water contact angle of treated samples is shown in figure 13 before heat treatment. Water contact angle results before washed samples were subjected to heat treatment confirmed the superhydrophobic digital-printed fabric -PS recorded the highest water contact angle at 159° compared to the water contact angle result before the first washing cycle at 162° in figure 27. The superhydrophobic digital-printed fabric -PCS/100 increased in water contact angle before heat treatment from 150° to 153° which could be due to uneven heat treatment before evaluation of the coating durability. Only the superhydrophobic digital-printed fabric PCS/140 recorded the lowest water contact angle at 122° after all washing cycles before heat treatment.

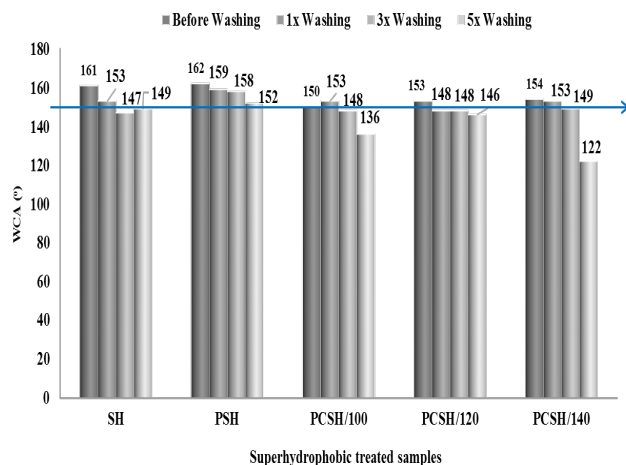


Fig. 13. Water contact angle after all washing cycles before heat treatment in comparison with water contact angles before washing cycles.

3.5 The durability of the coating after heat treatment

After heat treatment for 5 minutes at various temperature conditions, the superhydrophobic digital-printed fabric -PS recorded the highest water contact angle at 156° after all washing cycles compared to the water contact angle at 162° before coating evaluation, and at 152° before heat treatment, after all, washing cycles. The superhydrophobic digital-printed fabric -PCS/120 recorded a water contact angle slightly below 150° at 148° making it hydrophobic after all washing cycles which could be due to excessive exposure to heat since the superhydrophobic digital-printed fabric -PCS/120 was cured before superhydrophobic treatment at 120°. This could also break down the fibre structure of the treated superhydrophobic digital-printed fabric PCS/120 based on the water contact angle results in figure 14.

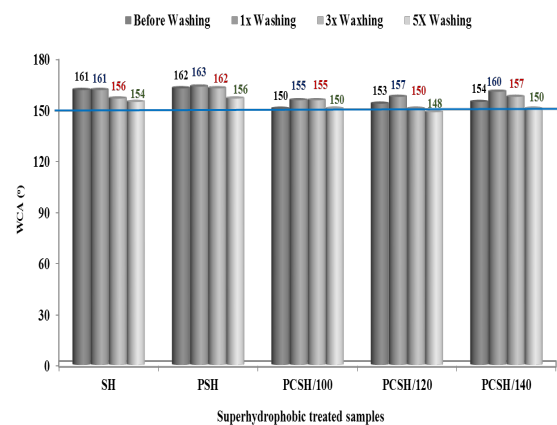


Fig. 14. Water contact angle after heat treatment in comparison with water contact angles before washing cycles.

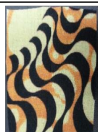



3.6 Effect of treatment on colour

The outcome values from the spectrophotometer and images for the visual examination have been shown in table 5 where the digital-printed fabric had a decrease in the light-shaded colour tested after cleansing with deionized water and ethanol based on the results from the colour spectrophotometer with L* value of 84.4 at D65 After superhydrophobic treatment, the light-shaded colour decreased and became shady with the lowest result at L* value of 63.4 at D65 which could be due to the deposition of the superhydrophobic particles on the surface of the digital-printed fabric because; the results recorded after five washing cycles rather increased to L* value of 76.6. at D65.

Visually, the difference could have amounted to the removal of some of the superhydrophobic particles deposited after all washing cycles with little effect on the

shade. The outcome values based on the results of the colour spectrophotometer also show the difference in the brightness in figure 15.

Table 5. The colour difference of the effect of treatment on colour with images of digital-printed fabric samples - (after steaming, after cleaning with deionized water and ethanol, after superhydrophobic treatment and after 5 washing cycles).

Steamed digital-printed fabric	After cleaning with deionized water and ethanol	After superhydrophobic treatment	After 5 washing cycles
			
L* (D65) = 85.6	L* (D65) = 84.4	L* (D65) = 63.4	L* (D65) = 76.6

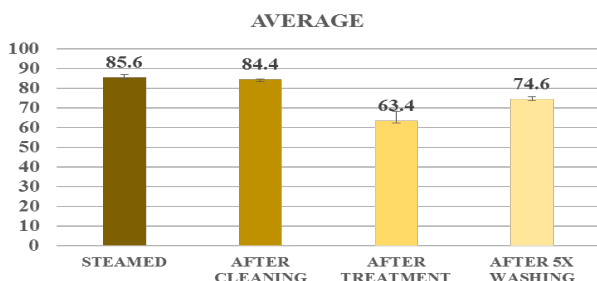


Fig. 15. Graph showing the effect of treatment on the colour of digital-printed samples - (after steaming, after cleaning with deionized water and ethanol, after treatment and after 5 washing cycles).

3.7 Air permeability

Superhydrophobic digital-printed fabric cured at 100° - PCS/100 recorded the highest air permeability at 52.4 (cm³/cm²/s) and proved more breathable than the other samples. The other superhydrophobic treated fabric samples because of their ‘high-density’ nature of how packed the yarns became in the various structures produced rather a low flow of air at an average of 32.3 (cm³/cm²/s) in figure 16.

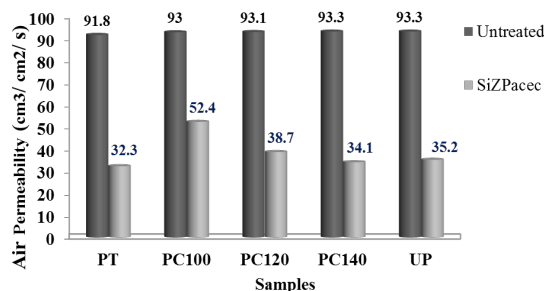


Fig. 16. Air permeability of samples before and after treatment.

3.8 Self-cleaning Ability

The self-cleaning ability confirmed the original cotton fabric was not able to self-clean in figure 17. The untreated digital-printed fabric was also not able to self-clean the dirt used to test the self-cleaning ability. Meanwhile, the superhydrophobic original fabric- S and the digital-printed superhydrophobic fabric-PS had the water droplets on the silicon carbide collected in the droplets and trapped the dirt in the droplets. When the surface was agitated, the droplets rolled off from the surfaces leaving very minute particles of the dirt on the surfaces proving more room for improvement in self-cleaning abilities.

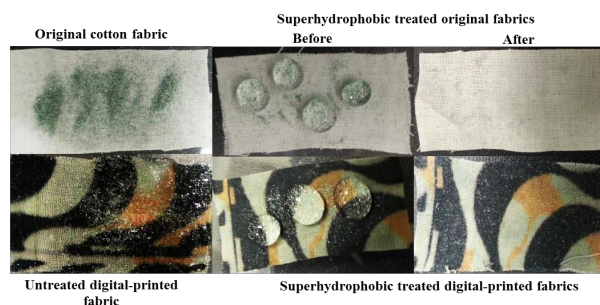


Fig. 17. Images showing the self-cleaning abilities of untreated and treated printed fabrics.

4 Conclusion

In conclusion, the morphology of the superhydrophobic treated digital printed fabric samples proved that the nanoparticles employed in this study are good hydrophobisation agents for excellent surface roughness and wettability with WCA at 162°. Digital-printed fabric with temperature condition at 120°C only after superhydrophobic treatment as the plain cotton fabrics according to the previous report had a great effect on the water contact angle recorded. Therefore, the breathable, durable, self-healing and superhydrophobic digital-printed cotton fabric could be applicable in the textile industry that needs functional and dyed fabrics. But it could not meet the criteria as a superhydrophobic surface because of the water shedding angle greater than 10°. This needs to be improved by optimizing the surface roughness and surface energy for more diverse applications in subsequent research to be conducted.

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Conflict of interest

The authors declare that there is no conflict regarding the publication of this paper.

References

- [1] Xing, L., Zhou, O., Chen, G. Sun, G. & Xing, T. (2015). *Recent developments in preparation, properties, and applications of superhydrophobic textiles*. SAGE.
- [2] Singh, K. & Singh, J.K. (2016). Fabrication of zirconia-based durable: Superhydrophobic-superoleophilic fabrics using non-fluorinated materials for oil-water separation and water purification. *RSC Advances*,1-9.
- [3] Saleemi, S. (2013). Sol-gel treatment of direct dyed cotton fabric with Aerosil®200 to enhance water repellency and fastness properties. *Science International*, 4. 823-827.
- [4] Feng, X.J. & Jiang, L. (2006). *Adv. Mater*, 18, 3063.
- [5] Chapman, I.K. (2002). Printing: A digital odyssey. *Am Assoc Text Chem Color Rev.*, 2, 12-15.
- [6] Furstner, R.; Barthlott, W.; Neinhuis, C.; Wallzel, P. (2005). Wetting and self-cleaning properties of artificial superhydrophobic surfaces. *Langmuir*, 21, 956–961.
- [7] Wang, S. & Jiang, L. (2007). Definition of superhydrophobic state. *Advanced Materials*,19 (21),3423–3424.
- [8] Sidra,S., Samander, A.M. & Uzma, S. (2014). Investigation of wash durability of silica nanoparticle coated 100% cotton reactive dyed fabric treated by sol-gel technique. *Journal of Engineered Fibers and Fabrics*, 9 (4), 16-23.
- [9] Sidra, S. & Nadir, A. (2012). Nano-silica based sol gel coating of direct dyed cotton fabric to improve the colour fastness properties. *Advanced Materials Research* 538-541, 2251- 2255.
- [10] Hoefnagels, H. F., Wu, D., de With, G. & Ming, W. (2007). Biomimetic superhydrophobic and highly oleophobic cotton textiles. *Langmuir*, 23, 13158-13163.
- [11] Das, I. & Goutam, D. (2015). Scientific Reports 5, Article number: 1850 doi: 10.1038/srep18503.
- [12] Yuen, C.W.M., Ku, S.K.A., Kan, C.W. & Choin, P.S.R. (2007). Enhancing textile ink-jet printing with chitosan. *Colour Technol.*, 123,267-270.
- [13] Fan,Q., Kim,Y.K. Lewis, A.F. & Perruzi, M.K. (2003). Fabric pretreatments and digital textile print quality. *J. Imaging Sci. Technol.*, 47, 400-407.
- [14] Kyuchul, L., Jisu H., & Yonghyun, A. (2014). Fabrication of superhydrophobic surface on a cellulose-based material via chemical modification. *Korean Chem. Soc.* 35, (5),1545-1548.
- [15] Yasukawa, R., Higashitani, H. & Yasunaga, H. & Urakawa, H. (2008). Dye fixation process in ink-jet printing of cotton fabric by reactive dye, Sen-I Gakkaishi. 64. 113-117.
- [16] Aboushelib, M.N, Matinlinna, J.P., Salameh. Z. & Ounsi, H. (2008). Innovations in bonding to zirconia-based materials. *Part I. Dent Mater*, 24, 1268–72.
- [17] Lung, C. Y. K. (2010). *Aspects of silane coupling agents and surface conditioning in dentistry: An overview of Jukka Pekka Matinlinna*. Dental Materials Science, Faculty of Dentistry, The University of Hong Kong.
- [18] Ramesh, T. R., Gangaiah, M., Harish, P. V., Krishnakumar, U. & Nanandakishore, B. (2012). Zirconia ceramics as a dental biomaterial-an over view. *Trends Biomater. Artif. Organs* 26, 154– 160.
- [19] Family, R., Solati-Hashjin, M., Nik, S. N. & Nemati, A. (2012). Surface modification for titanium implants by hydroxyapatite nanocomposite. *Caspian J. Intern. Med. Summer*,3(3) 460-465.
- [20] Masheder, B., Urata, C. & Hozumi, A. (2013). Transparent and hard zirconia-based: Hybrid coatings with excellent dynamic/ thermoresponsive oleophobicity, thermal durability, and hydrolytic stability. *ACS Appl. Mater. Interfaces* 5, 7899–7905.