COMPARATIVE ANALYSIS OF COATING METHODS ON MORPHOLOGICAL STRUCTURES AND BREATHABILITY OF TIO_2 COATED FABRICS

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Abstract. TiO_2 (titanium dioxide) has found diverse applications in textile products for self-cleaning and antimicrobial. To optimize the adherence of TiO_2 on textiles, several coating methodologies have been implemented on cotton fabric surfaces. However, the effects of these coating techniques on the breathability characteristics of the fabric samples remain largely unexplored. To address this research gap, the present study elucidates the breathability attributes and morphology of TiO_2 coated textiles. The polydimethylsiloxane (PDMS) was used as a binder to increase the adherence of TiO_2 on cotton yarn. The study investigated three coating methods denoted as "after"(A), "before"(B), and "simultaneous"(S) methods, respectively. The analysis reveals that the (A) coating method exhibited strong TiO_2 adherence to yarn surfaces, accompanied by minimal yarn weight loss (0.11%) compared to the (B) and (S) methods. The SEM micrographs showed that the PDMS was seen to coat over the TiO_2 nanoparticles, making the particles trapped and bound to the cotton yarn surface. The presence of TiO_2 and PDMS within the coated fabric was confirmed by EDX analysis. The study also found that TiO_2 can enhance the breathability properties such as air permeability and water vapour permeability. The (A) method exhibited the highest air permeability with approximately (2577.3 mm/s $\pm$ 3.3) compared to the (B) and (S) methods. Moreover, the A method and B methods demonstrated good water vapour permeability at about 503.5 g/m^2/hr and 442.3 g/m^2/hr, respectively. By undertaking this study, an enhanced property of cotton yarn was developed which is suitable for sportswear and casual wear.

Keywords: Coating, titanium dioxide, cotton, morphology, breathability

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Introduction

Recent advancements in nanotechnology have demonstrated that nanomaterials, like photocatalysts composed of nano-sized titanium dioxide, exhibit exceptional photodegradation capabilities against a broad spectrum of organic and inorganic contaminants present in water and land [1].

Titanium dioxide (TiO_2) exhibits various sizes, shapes, and crystalline structures. The most prevalent forms are anatase and rutile, both widely employed in diverse commercial applications such as sunscreens, cosmetics, paints, and surface coatings. TiO_2 possesses key characteristics, including its ability to absorb ultraviolet light, resistance to heat and weathering, and high melting and boiling points [2]. In addition, the antimicrobial agent and a photocatalyst for the removal of organic compounds are also being investigated for textile applications [3].

The typical approach for incorporating TiO_2 into textile materials involves a dip-coating method. In this process, the fabrics are immersed into a TiO_2 slurry, padded, dried, and cured. Subsequently, these processes undergo a rinsing step with water followed by drying [4]. A binder was used to stabilize the distribution of the nanoparticles on the textile materials [5].

In a previous investigation conducted by Sallehudin et al. [6-7], diverse coating methodologies were explored to enhance the adhesion of TiO_2 nanoparticles onto textile substrates. However, the effects of these coating techniques on the breathability characteristics of the coated fabric samples remain largely unexplored. Breathability in textile refers to its ability to allow air and moisture to pass through the material. It is a crucial characteristic of textiles, mainly in the context of clothing and bedding, as it directly affects comfort and overall wearability. Breathable fabrics are designed to provide a comfortable microclimate for the wearer by allowing air and moisture vapor to move through the material [8-9]. As such, the present study aims to conduct a comprehensive study of the breathability attributes of TiO_2 coated textiles. Three distinct coating procedures denoted as "after" (A), "before" (B), and "simultaneous" (S) were employed to coat cotton yarn with TiO_2. The TiO_2 coated cotton yarn was subsequently subjected to flatbed knitting machine to form TiO_2 coated fabrics.

To enhance the adherence of TiO_2 on cotton fibres, polydimethylsiloxane (PDMS) was introduced during the coating process. PDMS encompasses a family of polymers exhibiting a broad spectrum of properties, ranging from liquid to gel-like and elastomeric states. The distinctive characteristics of PDMS are contingent upon the side chains and the extent of cross-linking. Notably, in the context of textile applications, PDMS is predominantly utilized with cotton materials to confer water-repellent properties, as reported by Abidi et al. [10]. Given its compatibility with textile materials, the PDMS has been selected as the binding agent for the experimental investigations in the current study. The fabrics coated with TiO_2-PDMS were subjected to a comprehensive analysis encompassing morphological analysis and evaluations of breathability properties, including air and water vapor permeability.

Materials and Methods

100% cotton yarn with the yarn size of 130 Tex and PDMS from Thermo Scientific Chemicals (molecular weight of 74.15 g/mol) were the main materials used in the study. The TiO_2 nano particles were synthesized using a modified hydrothermal process with the TiO_2 purity of 92%. The TiO_2 particle size was in a range of 20 to 50 nm. The synthesis process of the TiO_2 is described elsewhere [11-12].

Preparation of TiO_2 Suspension

The TiO_2 suspension was prepared by mixing 13.4 g TiO_2 in 2.68 liter of distilled water and was aged overnight at room temperature. Next, all the suspensions were sonicated by using an ultrasonicator (Hielscher Ultrasonics) for 1 hour 30 min with an amplitude of 40% and the frequency was 20 kHz right before the coating process to get an even coating surface on yarn.

Coating Process

The cotton yarn was coated with the TiO_2 nano particles using three different methods, which are after (A), before (B) and simultaneous (S). Details on these methods were discussed by Sallehudin et al. [6]. The after (A) coating method was conducted by immersing cotton yarn into the TiO_2 suspension. The TiO_2 coated yarn was later immersed in the PDMS to bind the TiO_2 on cotton yarn surfaces. The before (B) coating method involves the immersion of cotton yarn into PDMS binder. The PDMS coated yarn was later coated with the TiO_2 suspension. For the (S) coating method, the cotton yarn was immersed in a mixture of PDMS and the TiO_2 suspension. All the coating methods were carried out using an ultrasonicator (Hielscher Ultrasonics) for an hour and 30 minutes with an amplitude of 40% and the frequency was 20 kHz. The coated fabrics were left to rest for a minimum of 24 hours after drying in the oven for 1 hour at 100 °C. This resting period is crucial to ensure consistent results and minimize variations in the fabric's properties. Then, all the coated samples were gone through the fixation process. During the process, the samples were washed with distilled water for 5 minutes to remove the unfixed and excessive TiO_2 nanoparticles. The samples were further dried again in the oven for 1h at 100 °C. The coated yarn was weighed before and after the process to determine the detached TiO_2 nanoparticles. The sample weight loss was calculated using a modified equation (1) reported by a previous study [6].

$$\text{Weight loss (\%)} = \frac{W_1 - W_2}{W_1} \quad (1)$$

where W_1 is the weight of sample before fixation (g) and W_2 is the weight of the sample after fixation.

Fabric Formation Through Knitting Process

Each coated yarn from (A), (B) and (S) methods was knitted to form a 1 x 1 rib knit fabric using a hand driven flat knitting machine (Flying Tiger) of the following parameters (Table 1). The knitted fabric samples as shown in Figure 1(a) to (c) were analyzed for morphological structures, air permeability and water vapour permeability, respectively.

Table 1: Average knitting machine parameters

Parameter	Unit
Machine gauge	7 G
Number of loops	40 courses/cm
Number of needles	40

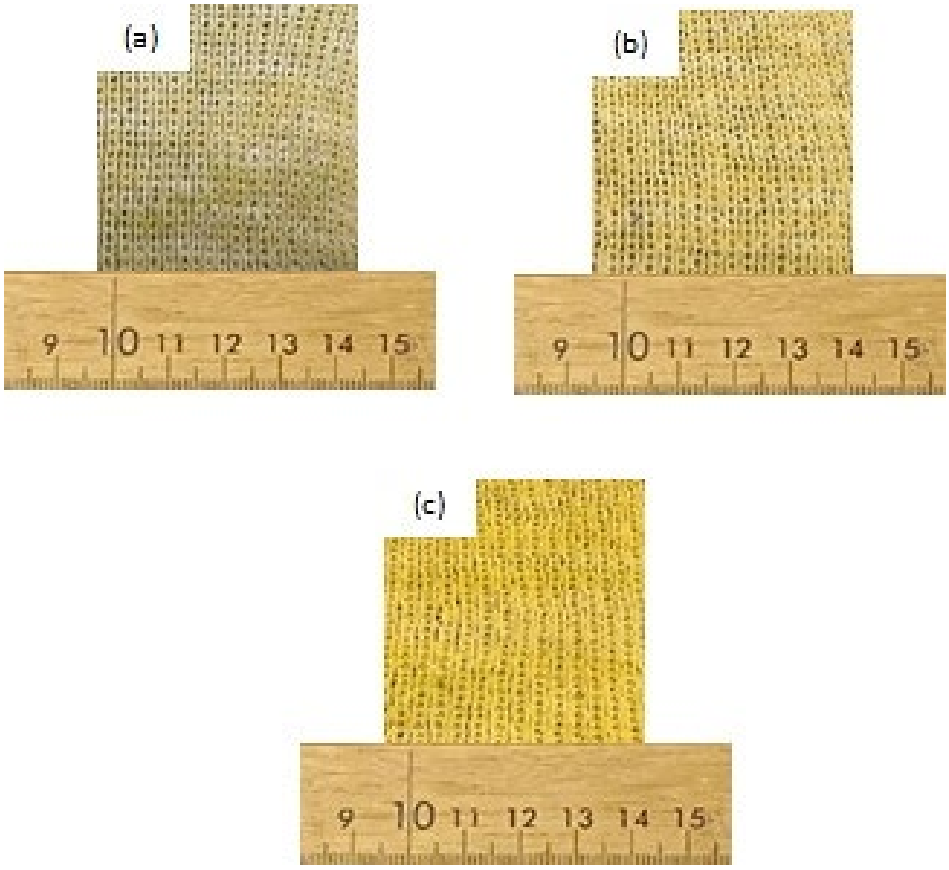

Figure 1: Photographs of (a) TiO_2 Coated Cotton (A method) (b) TiO_2 Coated Cotton (B method), and (c) TiO_2 Coated Cotton (S method)

Morphological Structures and Elemental Analysis of TiO_2 Coated Cotton Knitted Fabrics

The surface morphology and elemental analysis of the TiO_2 coated cotton yarn was observed using scanning electron microscopy (SEM) (Hitachi TM-3000 SEM). All the coated cotton yarn was sputtered with a thin layer of carbon to avoid electrostatic charging during testing. The samples were tested using different magnifications ranging from 100x to 30,000x.

Air Permeability Testing

The air permeability of the knitted fabrics was tested using MESDAN Air-Tronic in accordance with ASTM D737-18(2023) Standard Test Method for Air Permeability of Textile Fabrics. This experiment was performed by applying air pressure 100 Pa per surface area (cm^2)

of the fabric. An average of five measurements was calculated from different areas of the fabrics. The results are expressed in metre per second (m/sec). The air volume is about 10 litre.

Water Vapour Permeability

Water vapour permeability (WVP) is correlated to the fabric sample breathability [13]. The water vapour permeability of samples was evaluated using the SDL Atlas International M261 model and was conducted based on the ISO 8096 standard method. The water vapour permeability was calculated using the equation (2). Five measurements were taken for each fabric sample.

$$\mathrm{WVP} = \frac{24M}{\mathrm{A}t} \tag{2}$$

where M is the water vapour loss (g) in exposed time period t (h), and A is the area of uncovered specimen (m^2).

Results and Discussion

Weight Loss of TiO_2 Coated Cotton Yarn

The purpose of investigating the weight loss is to estimate the amount of detached TiO_2 nanoparticles after fixation process. As tabulated in Table 2, the study shows that coating methods did affect the weight loss of TiO_2 coated cotton yarn. Cotton-TiO_2/PDMS (A method) exhibited the lowest weight loss with approximately 0.11%. The A method was sonicated in TiO_2 suspension and was later treated with PDMS. The PDMS was seen to coat over the TiO_2 nanoparticles, making the particles trapped and bound to the cotton yarn surface. The deposited particles on the cotton yarn after the fixation process have the lowest percentage of detached particles.

The weight loss of coated cotton yarn for the B method was slightly higher than the A method which was approximately 0.25%. By using B method, the TiO_2 nanoparticles were unable to perform strong bonding as compared to the A method. Some of the unfixed particles were drained after the fixation process.

Meanwhile, the TiO_2 coated cotton (S method) had the highest weight loss at about 12.17%. A small amount of TiO_2 nanoparticles were deposited on the cotton yarn. After the fixation process, 12.17% of the unfixed particles were completely detached.

The weight loss analysis indicates that the A method can produce a more durable TiO_2 coating than the B and S methods. Besides coated yarn from A, B and S method, the uncoated yarn also undergone the knitting process to form knitted fabrics. The morphological structures of the coated cotton samples were then analysed by using SEM.

Table 2: The analysis of weight loss coated cotton yarn

Samples	Weight before fixation (g)	Weight after fixation (g)	Weight loss (%)
Cotton – TiO_2/PDMS (A method)	91.80	91.70	0.11
Cotton – TiO_2/PDMS (S method)	97.33	85.49	12.17
Cotton – TiO_2/PDMS (B method)	98.62	98.37	0.25

Morphological Structures and Elemental Analysis of TiO_2 Coated Cotton Knitted Fabrics

Scanning electron microscopy (SEM) was used to observe the effects of coating methods on morphological structures of TiO_2 coated cotton knitted fabrics. All the samples are illustrated in Figure 2(a) to (d). The morphology of A method fabric portrayed smooth yarn surfaces as illustrated in Figure 2(b). It shows the particles were found to be trapped and bound on the yarn surfaces. This is significant with the lowest percentage of detached particles.The B method showed a rough surface as observed in Figure 2(c). This was resulted by the detachment of some TiO_2 nanoparticles from cotton yarn surfaces, hence creating rough surfaces. Meanwhile the S method as illustrated in Figure 2(d) shows the uneven surface of knitted cotton fabric. This was due to the mixture of TiO_2 suspension and PDMS forming an uneven distribution of the TiO_2 particles on the yarn surfaces. This observation indicates that the A method provided good morphology for TiO_2 coated textiles as compared to the S and B methods.

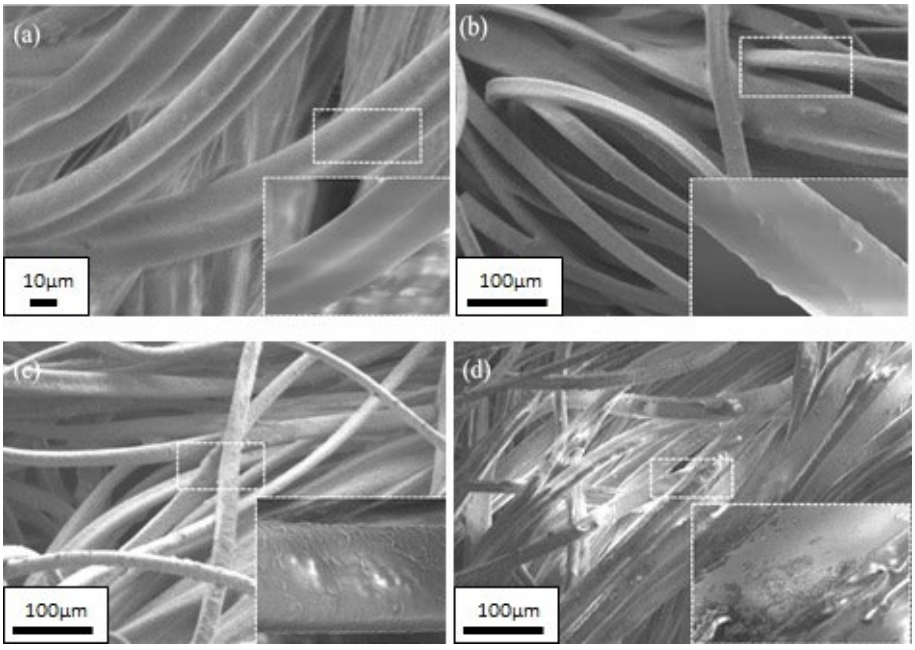

Figure 2: SEM images of (a) uncoated knitted fabric, (b) TiO_2 coated cotton (A method), (c) TiO_2 coated cotton (B method), and (d) TiO_2 coated cotton (S method)

The Energy Dispersive X-ray analysis (EDX) was conducted to estimate the amount of titanium (Ti) and silicon (Si) deposited onto the cotton knitted fabric. Silicone indicates the presence of PDMS in the sample. The EDX spectra for uncoated knitted cotton fabric, TiO_2 coated cotton (A method), TiO_2 coated cotton (S method) and TiO_2 coated cotton (B method) are shown in Figure 3(a) to (d). All the coated samples show the elements of C (carbon), O (oxygen), Ti (titanium) and Si (silicone).

Table 3 demonstrates the presence of carbon and oxygen with a percentage of 88.48% and 11.52%, respectively for the uncoated knitted cotton fabric. The A method has the highest weight percentage of Ti, which was about 76.59% (Figure 3(b)). It is cofirmed that the A method resulted a large deposition of TiO_2 particles onto the knitted fabric sample. In addition, the weight percentages of Ti for the S and B methods were low, at about 0.40% and 15.31%, respectively (Figure 3(c) and (d)), which indicates the small amounts of Ti were deposited on the fabric.

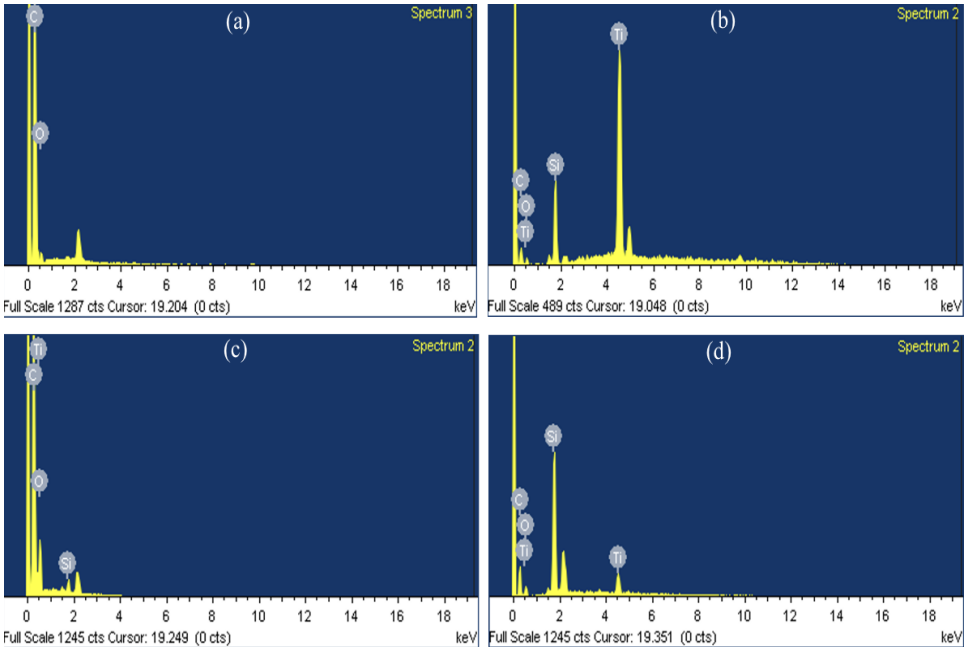

Figure 3: EDX spectra of (a) uncoated knitted fabric, (b) TiO_2 coated cotton (A method), (c) tio_2 coated cotton (S method), and (d) TiO_2 coated cotton (B method).

Table 3: Atomic weight percentage of uncoated and TiO2 coated cotton samples.

	Atomic weight (%)				
Samples	C K	O K	Ti K	Si K	Total
Uncoated knitted fabric	88.48	11.52	-	-	100
Cotton – TiO_2/PDMS (A method)	8.05	6.62	76.59	8.73	100
Cotton – TiO_2/PDMS (S method)	72.95	24.76	0.40	1.90	100
Cotton – TiO_2/PDMS (B method)	42.71	13.42	15.31	28.56	100

Air Permeability of Uncoated and TiO_2 Coated Cotton Samples

Fabric permeability depends on the morphology and distribution of spaces in fabric structures [14]. According to Tandon & Matsudaira [15], the air passes from one side of the fabric to the other mostly through fabric spaces through air diffusion. Due to its distinct morphologies, the current study endeavors to elucidate the effects of the morphological structures on the air permeability of the coated samples. Figure 4 depicts the air permeability of uncoated knitted fabric, A method, S method and B method. The A method (2577.3 mm/s ± 3.3) exhibited the highest air permeability than the S method (2319.4 mm/s ± 22.5) and B method (2474.4 mm/s ± 50).

Fabrics treated using Method A exhibit enhanced air permeability, significant with the observations reported by Manesh et al. [16]. The study demonstrated that the deposition of nanoparticles to fabric has led to an improvement in fabric breathability. This happened due to the changes in fabric structure, where the presence of nanoparticles in the fabric creates more spaces in the fabric [17]. The current study observed that a high amount of TiO_2 nanoparticles was deposited within fibres of the yarn. Due to this factor, the particles were expected to create air gaps between the fibers within the fabric. As a result, it allows more air to pass through the fabric.

Meanwhile, for the S method, the knitted fabric displayed an uneven coating, had contributed to the reduction in air permeability through the fabric. In other condition, the uncoated knitted fabric has the lowest average of air permeability at about 1967.2 mm/s ± 10. This is due to the non-existence of any particles in the fabric, that causes the tight yarns and promotes to the reduction of the air permeability reading.

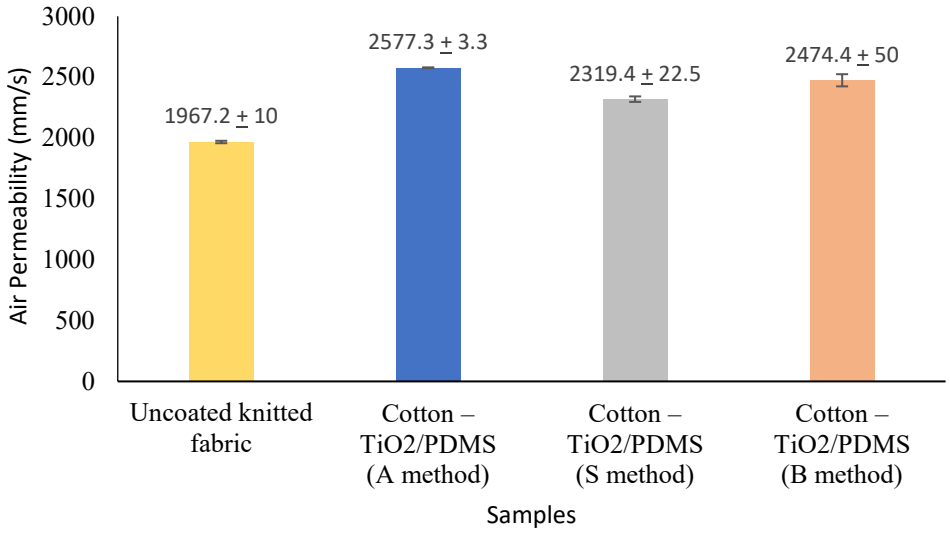

Figure 4: Air permeability of A method, B method, S method and uncoated knitted fabrics.

Water Permeability of Uncoated and TiO_2 Coated Cotton Samples

Water vapour permeability can be described as the transmission of water vapour through textile materials. It identifies the comfort properties of textile materials. The vapour will be discharged in the air from the fabric as soon as the body has quit sweating in order to diminish the skin surface moistness [17].

In the current experimental study, the water vapour permeability test was conducted on the uncoated knitted fabric and TiO_2 coated knitted fabrics with three different methods. In Figure 5, the water vapour permeability for the A method and B method are approximately 503.5 g/m^2/hr and 442.3 g/m^2/hr, respectively. The high value of water vapour permeability is probably due to the high amount of Ti in the fabrics. The Ti absorbs water molecules and releases them through the fabric. From this analysis, the high amount of TiO_2 nanoparticles in the fabric can enhance the comfort properties of the fabric. This phenomenon was also observed by Becenen & Erdogan [18].

In addition, the current study had found that the less amount of TiO_2 nanoparticles make the binder PDMS became dominant which prevents the water vapour from passing through the fabric. This resulted to the S method coated fabrics exhibited 29% and 37% lower than the B and A methods, respectively. Without the presence of TiO_2 nanoparticles, it slows down the water vapour to pass through the fabric. As a result, the uncoated knitted fabric demonstrated the lowest water vapour permeability with approximately 310.3 g/m^2/hr.

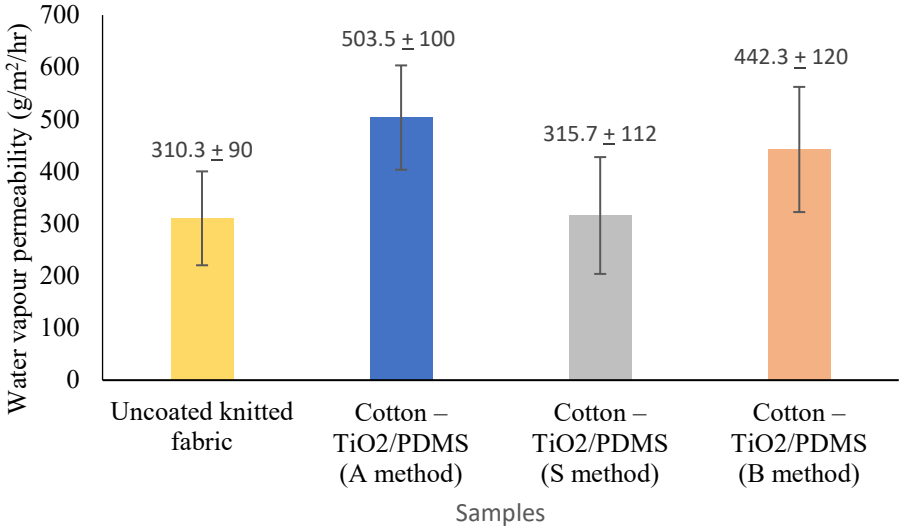

Figure 5: Water vapour permeability of A method, B method, S method and uncoated knitted fabrics.

Conclusions

The study found that each of the coating methods (A method, B method and S method) exhibits distinct morphological structures. The A (after) method exhibited a large amount of TiO_2 deposited onto the cotton knitted fabric and the presence of PDMS in the following process was found to be trapped and bound the TiO_2 particles on the fabric. Meanwhile, the B (before) method demonstrated that some of the TiO_2 particles detached into the solution during the coating process and after the fixation process. For S (simultaneous) method, it resulted to

an uneven surface of the cotton knitted fabric. The EDX result analysis proves the presence of Ti (titanium) and Si (silicone) in the coated knitted fabric. The TiO_2 coated cotton fabric (A method) showed the highest weight percentage of titanium (Ti) with approximately 76.59%, which portrayed the large deposition of TiO_2 particles onto the knitted fabric sample. The air permeability and water vapour permeability determine the breathability of the TiO_2 coated knitted cotton fabric samples with three different methods. Based on the analysis, the A method exhibited a higher air permeability than the B and S methods, primarily attributed to the high amount of TiO_2 deposited on the yarn. This deposition led to the formation of spaces between fibres, facilitating more air to pass through the fabric. Meanwhile, the water vapour permeability is identified to allow water vapour to pass through the textile material. This study proved that the A method also had higher water vapour permeability due to its high amount of TiO_2 nanoparticles in the fabric. In a nutshell, this study has identified the A method gives the optimal coating condition for the TiO_2 coated cotton fabric due to its smooth morphological structures, high air permeability and water vapour permeability.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work does not require any ethical standards.

References

[1] Nyamukamba, P., Okoh, O., Mungondori, H., Taziwa, R. & Zinya, S. (2018). Synthetic Methods for Titanium Dioxide Nanoparticles: A Review. In *Titanium Dioxide Material for a Sustainable Environment*, vol.1. Ed. Yang, D. (Intech Open, London.), pp. 151-175.

[2] Sayes, C. M., Wahi, R., Kurian, P. A., Liu, Y., West, J. L., Ausman, K. D., Warheit, D. B. & Colvin, V. L. (2006). Correlating Nanoscale Titania Structure with Toxicity; a Cytotoxicity and Inflammatory Response Study with Human Dermal Fibroblasts and Human Lung Ephithelial Cells. *Toxicological Sciences*. 92(1), 174-185.

[3] Calero, J. L., Berrios, Z. O. & Suarez, O. M. (2019). Biodegradable Chitosan Matrix Composite Reinforced with Titanium Dioxide for Biocidal Applications. In *Renewable and Sustainable Composites*, vol. 1. Ed. Pereira, A. B. & Fernandes, F. A. O. (Intech Open, London), pp. 73-94.

[4] Radetic, M. (2013). Functionalization of Textile Materials with TiO_2 Nanoparticles. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* 16, 62-76.

[5] Dastjerdi, R. & Montazer, M. (2010). A Review on the Application of Inorganic Nanostructured Materials in the Modification of Textiles: Focus on Anti-microbial Properties. *Colloids and Surfaces B: Biointerfaces.* 79(1), 5-18.

[6] Sallehudin, M. E., Affandi, N. D. N. & Bonnia, N. N. (2019). Preparation and Characterization of TiO_2-Polysiloxane Coated Cotton Yarn at Different Coating Methods. *Materials Today Proceedings*. 51(2), 1303-1308.

[7] Sallehudin, M. E., Affandi, N. D. N., Harun, A. M., Alam, M. K. & Indrie, L. (2023). Morphological Structures and Self-Cleaning Properties of Nano-TiO_2 Coated Cotton Yarn at Different Washing Cycles. *Nanomaterials.* 13(1), 31.

[8] Chang, Y. & Liu, F. (2023). Review of Waterproof Breathable Membranes: Preparation, Performance and Applications in the Textile Field. *Materials*. 16(15), 1-23.

[9] Rajendran, S. (2018). *Advanced Textiles for Wound Care*. 2nd edition (Woodhead Publishing) pp. 184-188.

[10] Abidi, N., Hequet, E. & Tarimala, S. (2007). Functionalization of Cotton Fabric with vinyltrimethoxysilane. *Textile Research Journal*. 77(9), 668–674.

[11] Harun, A. M., Ghani, N. B. A., Noor, N. F. M., Abas, R. & Alam, M. K. (2020). Mutagenic Properties of Modified Hydrothermal Nanotitania Extract. *Bangladesh Journal Medical Science*. 19(1), 159–162.

[12] Harun, A. M., Noor, N. F. M., Shaari, R., Ying, L. X., Yusof, M. E. & Alam, M. K. (2022). The Toxicology Properties of Modified Hydrothermal Nanotitania Extraction. *Archives Medical Science.* 18(5), 1338–1341.

[13] Das, S. & Kothari, V. K. (2012). Moisture Vapour Transmission Behaviour of Cotton Fabrics. *Indian Journal of Fibre & Textile Research*. 37(2), 151-156.

[14] Ogulata, R. T. (2006). Air Permeability of Woven Fabrics. *Journal of Textile and Apparel, Technology and Management*. 5(2), 1-10.

[15] Tandon, S. & Matsudaira, M. (2010). Improved Discrimination and Prediction of Drapability of Fabrics. *Research Journal of Textile and Apparel*. 14(3), 62-76.

[16] Manesh, E. E., Ajeli, S. & Zarrebini, M. (2014). Crease Recovery Angle of Weft Knitted Fabrics Produced by Shape Memory Polymer-Coated Yarn. *Journal of Apparel and Textile Science and Technology*. 3(4), 9-12.

[17] Skenderi, Z., Cubric, S. & Srdjak, M. (2009). Water Vapour Resistance of Knitted Fabrics Under Different Environmental Conditions. *Fibres & Textiles in Eastern Europe*. 73(2), 72-75.

[18] Becenen, N. & Erdogan, S. (2022). Chitosan and Nano-TiO_2 Coating Improves the Flame Retardancy of Dyed and Undyed Denim Fabrics by Increasing the Charring. *Journal of Industrial Textiles*. 51(15), 1252–1278.