(REFEREED RESEARCH)

DEVELOPMENT OF WATER REPELLENT COTTON FABRIC WITH APPLICATION OF ZnO, Al2O3, TiO2 and ZrO2 NANOPARTICLES MODIFIED WITH ORMOSILS

ORMOSİL'LER İLE MODİFİYE EDİLEN ZnO, Al_2O_3, TiO_2 and ZrO_2 NANOPARTİKÜLLERİNİN APLİKASYONU İLE SU İTİCİ PAMUKLU KUMAŞLARIN GELİŞTİRİLMESİ

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ABSTRACT

The study aimed to achieve durable water repellent properties in cotton fabric by creating roughness on its surface using zinc acetate, aluminium sulphate, aluminium isopropoxide, zirconium acetylacetonate and titanium isopropoxide as the inorganic precursors with subsequent hydrophobic modification with ORMOSILs (ORganic MOdified SILanes) consisting of long-chain alkyl silanes. The contact angle values before and after washing treatment, whiteness values, tear strength and bending length values of the fabric samples treated with these organic–inorganic hybrid materials were measured. Moreover, the microstructural properties of the cotton fabric were analysed by scanning electron microscopy and Fourier transform infrared-attenuated total reflectance spectroscopy. It was concluded that the fabric samples treated with zinc- and zirconium-based inorganic precursors have durable water repellent properties. The results were successful for the fabric samples when the wet chemical route contained three steps: nanocrystal preparation, nanoparticle growth and hydrophobic modification. Moreover, the process has the advantages of simplicity, low cost, low temperature and environmental friendliness without being based on perfluorination.

Keywords: Wet chemical route, Hydrothermal nanoparticle growing, Water repellency, Ormosil, Washing durability, Cotton fabric.

ÖZET

Bu çalışma, uzun zincirli alkil silanları içeren ORMOSİL'ler (ORganik MOdifiye SİLanlar) ile ard hidrofob modifikasyon işlemi gören çinko asetat, alüminyum sülfat, alüminyum izopropoksit, zirkonyum asetilasetonat ve titanyum izopropoksit gibi inorganik başlatıcılarla pamuklu kumaş yüzeyinde pürüzlülük yaratarak yıkamaya dayanıklı su iticilik özelliği kazandırmayı amaçlamaktadır. Bu organik-inorganik hibrid materyaller ile işlem gören kumaş numunelerinin yıkama işleminden önce ve sonra temas açısı değerleri, beyazlık değerleri, yırtılma mukavemeti ve eğilme uzunluğu değerleri ölçülmüştür. Ayrıca pamuklu kumaşların mikroyapısal özellikleri tarama elektron mikroskobu ve Fourier transform kızılötesi spektroskopisi ile analiz edilmiştir. Çinko- ve zirkonyum-esaslı inorganik başlatıcılar ile işlem gören kumaş numunelerinin yıkamaya dayanıklı su itici özelliğe sahip olduğu bulunmuştur. Nanokristal hazırlanması, nanopartikül büyümesi ve hidrofob modifikasyon olmak üzere üç adımlı yaş kimyasal yöntem kullanıldığında başarılı sonuçlar elde edilmiştir. Ayrıca bu proses basitlik, düşük ücret, düşük sıcaklık ve florokarbon kimyasına dayanmayan çevre dostu uygulama olması avantajlarına sahiptir.

Anahtar Kelimeler: Yaş kimyasal yöntem, Hidrotermal nanopartikül büyümesi, Su iticilik, Ormosil, Yıkama dayanımı, Pamuklu kumaş.

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1. INTRODUCTION

Recently, super-hydrophobic fabrics have been widely investigated due to their importance in industrial applications [1]. Many methods are based on surface roughening and perfluorination, and modification with a material of low surface energy using lithographic processes, electrospinning, templating, electrodeposition, layer-by-layer deposition and sol-gel methods [2, 3], so that the fabrics achieve super-hydrophobic properties. In recent decade, much research has been undertaken on developing super-hydrophobic textiles by the sol-gel process [4–17]. Producing different nanostructures with surface roughening is a useful method in creating super-hydrophobic surfaces. Nanoparticles, such as ZnO [18], SiO_2 [19], TiO_2 [11, 13], ZrO_2 [20] and Al_2O_3 [1, 21, 22] have been used in the sol-gel process to obtain surface roughness. The production of micro-structured ZnO surfaces has also been carried out using various methods, such as chemodeposition and electrodeposition. The hydrothermal method or the wet chemical route is the most preferred due to its simplicity, low cost and low temperature application [18, 23]. Wu et al. developed a wet chemical method consisting of preparing ZnO micro-structured surfaces in a Zn^{+2} solution at a mild temperature on silicone substrate [1]. Xu and Cai applied the wet chemical route to create a super-hydrophobic surface on cotton fabric. First, the fibres were coated with ZnO nanocrystals. Oriented ZnO nanorod arrays were subsequently produced on the fibres by growing nanoparticles to provide nanosized roughness. Then, the fabric samples were modified with n-dodecyltrimethoxy silanes to produce a super-hydrophobic surface using the sol-gel process [18]. In this way, the effects of surface roughening and the bonding of long-chain alkyl groups on the surface were combined to create super-hydrophobicity on the substrates. Moreover, paraffin repellents, which are emulsions containing zirconium or aluminium salts of fatty acids, were conventionally used to produce hydrophobic textile surfaces. However, they have low oil repellency and low durability to washing [24]. Masheder et al. produced hybrid films by a simple combination of zirconium tetrapropoxide and stearic acid without perfluorination and surface roughening. These transparent films have excellent dynamic oleophobicity, thermal durability, and hydrolytic stability [25]. Masheder et al. prepared organic–inorganic hybrid materials with dewetting ability towards different alkane liquids. The hybrid materials were created by bonding carboxylic acids with long alkyl chains into zirconium [26]. We have also studied using Al_2O_3 and TiO_2 nanoparticles to produce super-hydrophobic properties. Al_2O_3 coatings have some advantages such as high transparency, strong mechanical properties and good abrasion resistance [1] and TiO_2 coatings have self-cleaning properties.

In this study, producing a water repellent surface on cotton fabric was investigated following the method in Ref. [18]. With this aim, we used aluminium isopropoxide, aluminium sulphate, zirconium acetylacetonate, titanium isopropoxide and zinc acetate as the precursor to create the rough surface and hexadecyltrimethoxysilane as the modifying agent for hydrophobicity. It was found that zirconium and zinc based precursors are promising in creating durable super-hydrophobic surfaces on cotton fabric. In the literature, there is a gap in the research into using zirconium based precursors to produce durable super-hydrophobic textile surfaces. This study, including combining the roughening of surfaces by means of using inorganic precursors and the hydrophobic modification of the surfaces with a long-chain alkyl silane, fills that gap.

2. MATERIALS AND METHODS

2.1 Materials

In the study, all the chemicals were supplied as reagent grade. Zinc acetate dehydrate (97+%, Alfa Aesar, Germany), aluminium isopropoxide (98+%, Alfa Aesar, Germany), aluminium sulphate hydrate (97+%, Alfa Aesar, Germany), titanium (IV) isopropoxide (VERTEC|r TIPT, 97+%, Germany) and zirconium (IV) acetylacetonate (Merck, Germany) were used as the precursors; ethanol (96%, Merck, Germany) as the solvent; 0.15 M NaOH solution (pellets, puriss, Sigma-Aldrich, Germany) was used to adjust the pH in the nanocrystal preparation stage, while zinc nitrate hexahydrate (98%, Sigma-Aldrich, Germany), aluminium isopropoxide, aluminium sulphate and zirconium acetylacetonate as precursors, hexamethylene tetramine (HMTA, 99+%, Alfa Aesar, Germany) as a stabilizer and distilled water as solvent were used in the hydrothermal nanoparticle growing stage. In the last stage of the hydrophobic modification, hexadecyltrimethoxy silane (HDMS, Dynasylan 9116, Evonik Degussa GmbH, Germany) as precursor for its water repellent properties and ethanol as the solvent were utilized. Scoured and bleached 100% plain-weave cotton fabrics (weight 110 g/m^2, 22 picks/cm, 32 ends/cm) as the substrate were cut into strips 30 cm x 20 cm and used to produce water repellent surfaces. All experiments were carried out twice.

2.2 Methods

2.2.1 Sol-Gel Processing

Nanocrystal Preparation (Step P)

Zinc acetate dehydrate, aluminium isopropoxide, aluminium sulphate, zirconium acetylacetonate and titanium isopropoxide (0.05 M) as precursors were separately dissolved in ethanol at 60^{o}C. NaOH solution (0.15 M) in ethanol was slowly added to these solutions. Then the solutions were stirred at 60 ^{o}C for 2 hours to prepare Zn, Al, Ti and Zr based nanocrystals. The fabric samples were dipped in the nanocrystal solution and padded, dried at room temperature for 20 min and cured at 170 ^{o}C for 3 min. The pad–dry–cure process was applied to the fabric samples three times.

Nanoparticle Growth (Step G)

Aqueous solutions (25 ml) of zinc nitrate hexahydrate, aluminium isopropoxide, aluminium sulphate, zirconium acetylacetonate and titanium isopropoxide (0.03M) were separately prepared for the hydrothermal nanoparticle growing step of ZnO, Al_2O_3, TiO_2 and ZrO_2. Aqueous hexamethylene tetramine (HMTA) solutions (0.03 M) (25 ml) were separately added to these solutions. Then the fabric samples were treated with the nanocrystal preparation and dipped in the solutions prepared in the nanoparticle growth stage and treated at 90 ^{o}C for 3 h in a water bath. The samples were rinsed and dried at 70 ^{o}C for 20 min.

Hydrophobic Modification (Step M)

The fabric samples, with and without the applied nanoparticle growing step, were separately immersed in HDMS solution (wt. 3.5%) in ethanol and stored at room temperature for 24 h. The fabric samples were washed in ethanol to remove chemical residues and dried at room temperature and cured in oven at 120 ^{o}C for 1 h. The formulas used and a flow chart of the wet chemical route are given in Table 1 and Figure 1.

3. CHARACTERIZATION

The add-on values of the treated fabric were calculated according to [27]. The contact angle of the fabrics was determined using a KSV Cam 100 Instruments Contact Angle Goniometer to determine the water repellent properties of the fabrics. The fastness of their water repellent properties when washing was evaluated using the washing conditions according to TS EN ISO 105- C06- A1S at 40 ^{o}C without balls using a Rotawash washing machine (Etki Company, Istanbul, Turkey). The washing process was repeated five times. After the washing process, the samples were dried at 100 ^{o}C. Oil repellency tests on the fabric samples were carried out using hydrocarbon compounds as in the AATCC Test Method 118 Standard. The whiteness (Stensby) of the treated and untreated fabric samples was measured using a Datacolor 600 spectrophotometer (Datacolor Applied Color Systems, Inc., USA) in UV-included, specular excluded, USAV mode with fourfold fabric samples in D65 (daylight source) at a 10^{o} measurement angle. The tear strength values of the treated and untreated fabric samples were measured using an Elmatear Digital Tear Tester (James H. Heal Co. Ltd. Halifax, England) in accordance with the ASTM D5035 Standard. The bending length values of the fabric samples were analysed using a Shirley Stiffness Tester (SDL Atlas Textile Testing Solutions, England) in accordance with the BS 3356 Standard. The Fourier transform infrared spectroscopy-Attenuated total reflection (FTIR-ATR) (PerkinElmer Inc., Beaconsfield UK) absorption spectra of the treated and untreated fabric samples were measured over the range of 4000 to 650 cm^{-1} at room temperature. The surface topographies of the treated and untreated fabrics were examined using a JEOL JSM 6060 scanning electron microscope (JEOL Ltd., Tokyo, Japan) operating at 3 kV with X2000 and X1000 magnification.

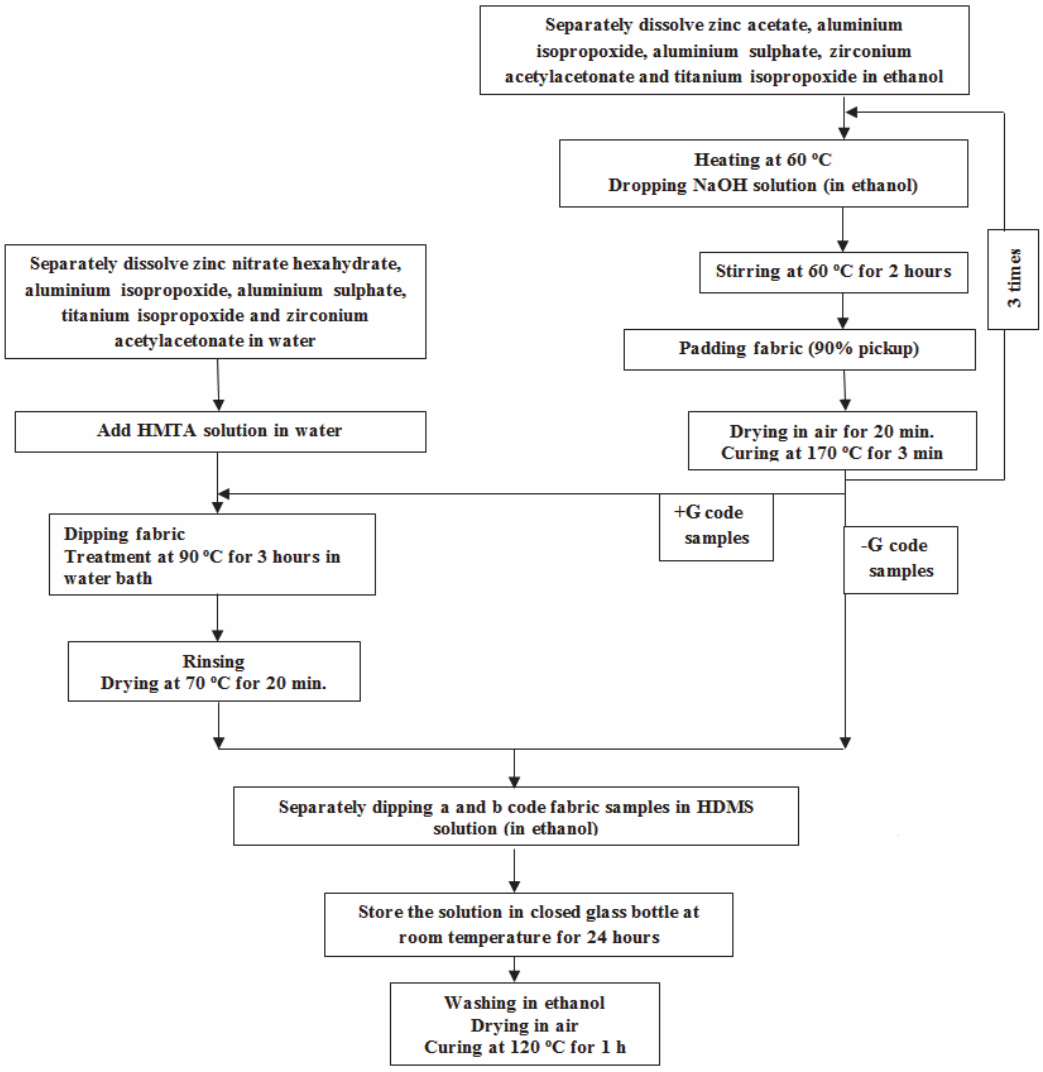

Figure 1. Flow chart for wet chemical route

Table 1. Recipes for sol-gel process

Steps	Zn			AlC			AlS			Zr			Ti		
	P	G	M	P	G	M	P	G	M	P	G	M	P	G	M
NaOH (gr)	6	-	-	6	-	-	6	-	-	6	-	-	6	-	-
Zinc acetate (gr)	10.97	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ethanol (l)	1	-	0.1	1	-	0.1	1	-	0.1	1	-	0.1	1	-	0.1
Zinc nitrate hexahydrate (gr)	-	8.92	-	-	-	-	-	-	-	-	-	-	-	-	-
Aluminium isopropoxide (gr)	-	-	-	10.42	6.25	-	-	-	-	-	-	-	-	-	-
Aluminium sulphate (gr)	-	-	-	-	-	-	17.64	10.58	-	-	-	-	-	-	-
Zirconium acetylacetonate (gr)	-	-	-	-	-	-	-	-	-	24.88	14.93	-	-	-	-
Titanium isopropoxide (gr)	-	-	-	-	-	-	-	-	-	-	-	-	14.65	8.79	-
Hexametylene tetramine (gr)	-	4.20	-	-	4.20	-	-	4.20	-	-	4.20	-	-	4.2	-
H_2O (lt)	-	1	-	-	1	-	-	1	-	-	1	-	-	1	-
HDMS (gr)	-	-	3.5	-	-	3.5	-	-	3.5	-	-	3.5	-	-	3.5

P: Nanocrystal **P**reparation, G: Nanoparticle **G**rowing, M: Hydrophobic Modification

4. RESULTS AND DISCUSSION

Contact angle values before and after the washing treatment, the add-on, whiteness, tear strength and bending length values of the fabric samples are given in Table 2.

Table 2. Add-on, contact angle, whiteness, tear strength, bending length values of fabric samples

	Add on (%)	Oil repellency	Contact angle (°)		Whiteness (Stensby)	Tear Strength (N)	Bending Length (cms)
			B	A			
UT	-	0	-	-	80.92	8.05	2.30
Zn-G	8.53	0	144	132	38.94	6.24	2.75
Zn+G	3.55	0	149	135	48.86	6.94	1.67
AlC-G	10.63	0	123	114	36.15	6.38	3.22
AlC+G	0.15	0	152	101	62.07	7.22	1.87
AlS-G	10.24	0	121	H	76.76	6.52	1.97
AlS+G	8.78	0	121	126	74.59	6.8	2.10
Zr-G	7.96	0	136	110	30.41	6.66	2.67
Zr+G	3.45	0	147	130	32.19	6.24	2.15
Ti-G	3.38	0	143	88	32.56	5.96	2.47
Ti+G	1.17	0	145	116	44.35	5.82	2.02

-G: not contaning nanoparticle growing step, +G: contaning nanoparticle growing step, B: Before washing, A: After washing, H:Hydrophilic, UT: Untreated fabric

4.1 Contact Angle Values and Oil Repellent Properties

Production of super-hydrophobic surfaces with surface roughening with ZnO, Al_2O_3, TiO_2 and ZrO_2 nanoparticles and hydrophobic modification using HDMS with long alkyl chains groups was investigated. The fabric samples without the nanoparticle growing step (-G code) (121–144°) had lower contact angle values than the fabric samples containing the nanoparticle growing step (+G code) (121–152°) both before and after the washing treatment. Thus the hydrothermal nanoparticle growing step containing HMTA as the stabilizer was important to the fabric gaining the water repellent properties. However, an explanation for the differences in the structures of the grown nanoparticles needs further investigation. The differences in their durability and hydrophobicity could be based on the structural changes in these grown nanoparticles. The contact angle values of the +G code fabric samples are higher than 145°, except for the AlS+G samples using aluminium sulphate as the precursor. They exhibited water repellent properties. The highest contact angle values at 152° were obtained for the AlC+G samples using aluminium sulphate as the precursor before the washing treatment. After the washing treatment, the contact angle values generally decreased and some samples indicated hydrophilic properties. Durable water repellent properties were provided for the Zn+G and Zr+G samples using zinc acetate-zinc nitrate and zirconium acetyacetonate as the precursors, respectively. The contact angle values of the Zn+G and Zr+G samples were 149° and 147° before the washing treatment, and 135° and 130° after the washing treatment, respectively (Table 2, Figure 2). Super-hydrophobic textiles present a contact angle higher than 150° and thus repel water [2, 28]. Thus, our fabric samples have high contact angle values and almost super-hydrophobic properties before and after the washing process. Figure 3 illustrates the image of the contact angle for the AlC+G fabric sample. None of the treated fabric samples showed oil repellent properties (Table 2).

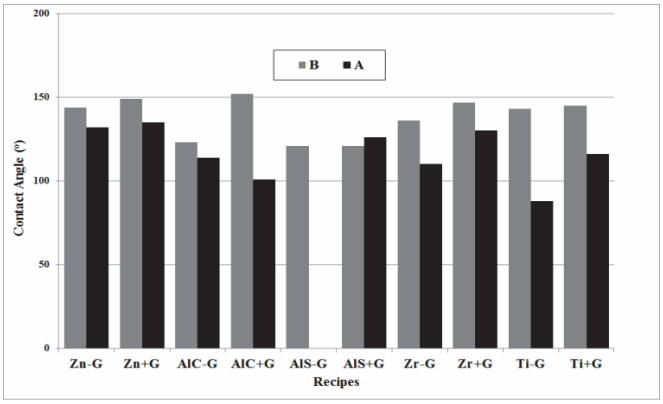

Figure 2. Contact angle results of treated fabric samples before and after washing treatment.

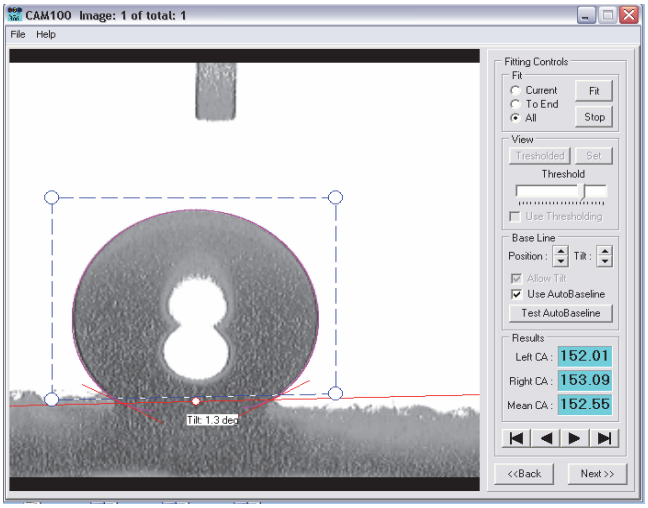

Figure 3. The image of contact angle of AlC+G fabric sample

4.2 Add-on Values

High add-on values of 10.63% and 10.24% for the AlC-G and AlS-G fabric samples, respectively, were obtained (Table 2, Figure 4). The add-on values indicated that the hydrothermal nanoparticle growing step (Step G) caused weight loss from the fabric samples due to the transfer of unreacted precursors on the fabric samples to the solution prepared in the nanoparticle growing step. Thus, the add-on values of the +G code fabric samples were lower than those of the -G code samples. The add-on values of the Zn+G and Zr+G fabric samples with good and relatively durable water repellent properties were not very high at 3.55% and 3.45%, respectively.

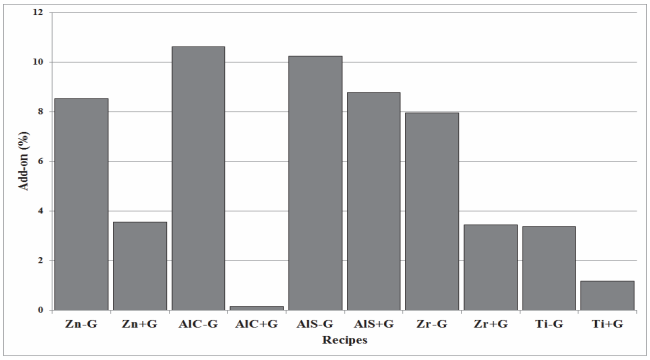

Figure 4. Add-on results of treated fabric samples

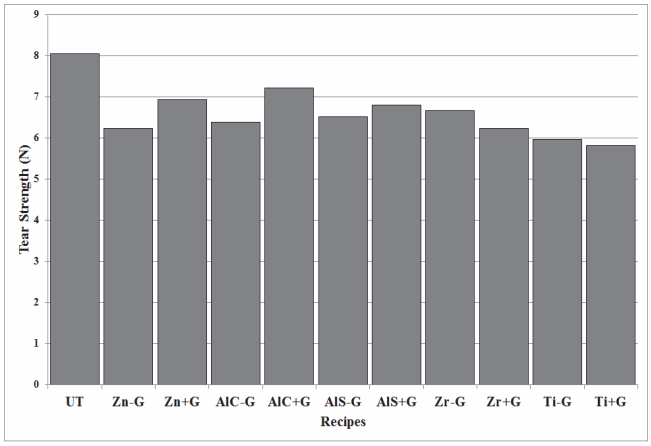

Figure 5. Tear strength results of treated and untreated fabric samples

4.3 Tear Strength

It was observed that the tear strength values of the treated fabric samples changed from 5.82 N for the Ti+G samples to 7.22 N for AlC+G samples, while the tear strength value of untreated fabric was 8.05 N. After treatment, the tear strength values slightly decreased as compared with that of the untreated fabric. The tear strength values of the Zn+G and Zr+G samples, which have good and relatively durable water repellency, were not significantly low compared with those of the untreated fabric samples. It could be said that significant damage did not occur to fabric samples by this treatment and the inherent properties of the fabric samples could be considered to have been protected after the treatment (Figure 5).

4.4 Whiteness Values

The whiteness values of the fabric samples significantly decreased as compared with that of untreated fabric at 80.92, except for the AlS-G and AlS+G samples. The lowest whiteness values were determined for the Zr-G samples at 30.41. It was observed that the whiteness values of the Zn+G and Zr+G fabric samples, which have good and durable water repellent properties, significantly decreased in comparison with those of the untreated fabric (Figure 6). The decrease in the whiteness values could have arisen from the nitrogen atoms content of HMTA.

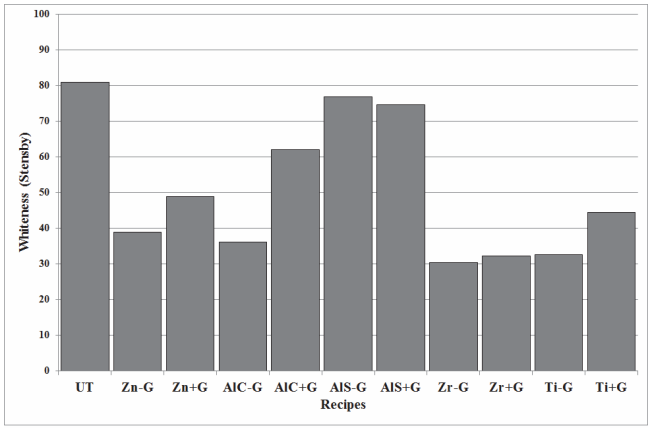

Figure 6. Whiteness results of treated and untreated fabric samples

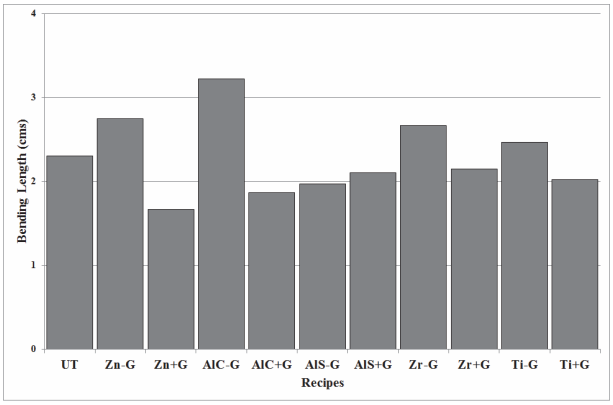

Figure 7. Bending length results of treated and untreated fabric samples

4.5 Bending Length

The highest bending length values were 3.22 cm for the AlC-G samples and the lowest were 1.67 cm for the Zn+G samples. The bending length values of the fabric samples exposed to the nanoparticle growing step (+G codes**)** were lower than those of the fabric samples without the nanoparticle growing step (-G codes). It could be said that the application of the nanoparticle growing step containing organic HMTA agents (+G codes) could produce softer fabric samples, while the hydrophobic modification step with inorganic HDMS (especially –G codes) gave rise to stiffer fabric samples (Figure 7). The fabric samples with lower bending length values exhibited a softer form [29].

4.6 Scanning Electron Microscopy Analysis

SEM images of the treated and untreated fabric samples are illustrated in Figure 8. In the SEM images, we observed some deposited particles on the fibres' surfaces creating roughness. Characteristic film cracks of the titania thin films were found on the fibre surfaces for the Ti+G samples. When the SEM images of the Zn+G and Zr+G samples, which have good and durable water repellent properties, were evaluated, the Zn+G samples had dense particle deposition on their surfaces while the Zr+G samples had a dense film layer, providing fillings and interconnections between the fibres, together with lower particle deposition on the surface. The difference in the contact angle values and durability properties of the fabric samples could result from the structural forms of the grown nanoparticles. However, their growth structures could not be clearly observed in the SEM images at 3 kV with X2000 and X1000 magnification. At a higher voltage and magnification, the fabric samples burned. Thus the structures need more detailed investigation.

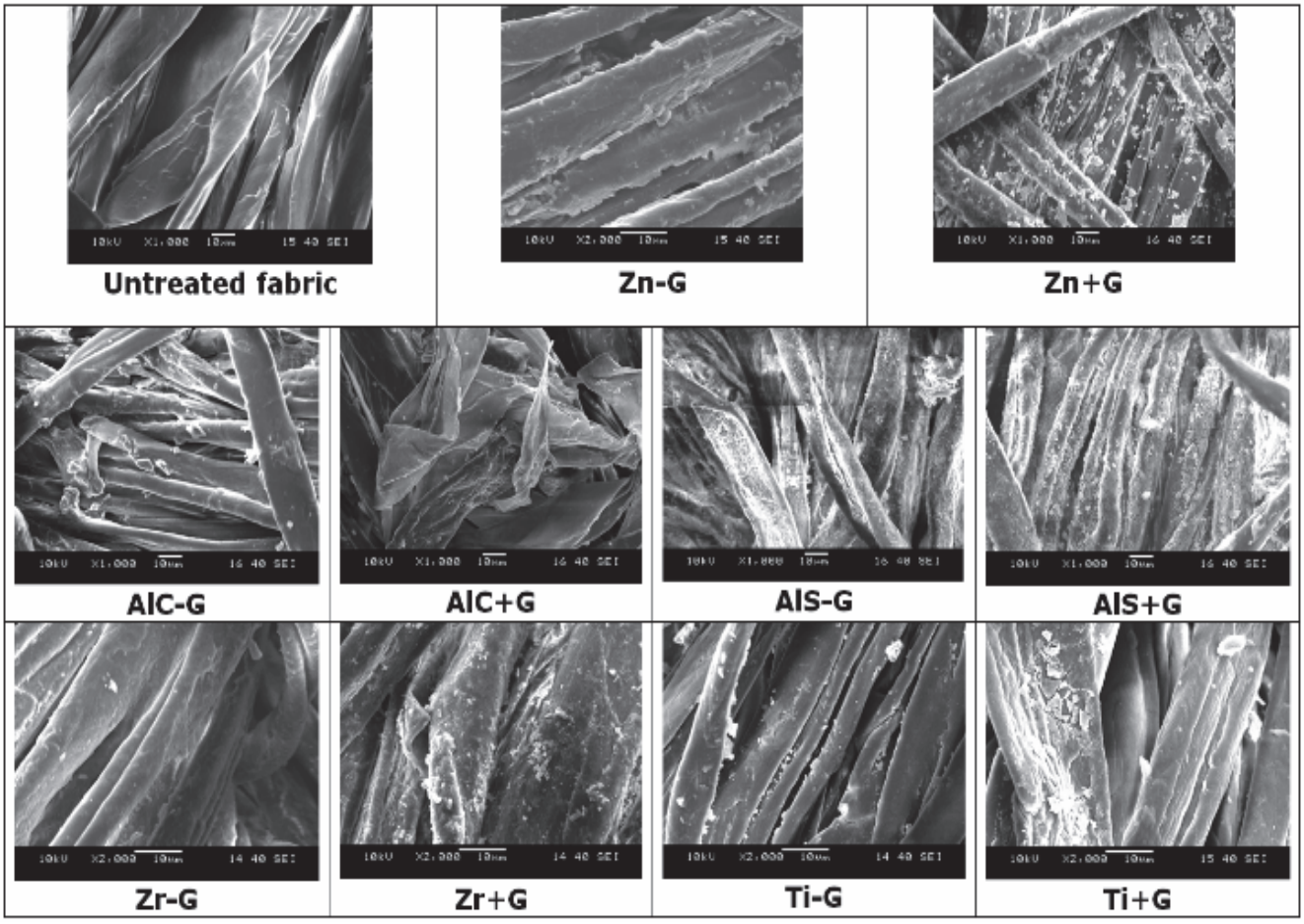

Figure 8. SEM images of treated and untreated fabric samples

4.7 FTIR-ATR Analysis

The FTIR-ATR spectra of the fabric samples are shown in Figure 9. O-H stretching could be the cause of the band at 3200–3600 cm^{-1}. The absorbance peak at almost 3284 cm^{-1} is assignable to the -OH groups [30]. The presence of the CH_2 and CH_3 groups could be observed as the vibration mode in the 2400–2900 cm^{-1} range. The 1000–1110 cm^{-1} bands could be attributed to the Si-O bonds [31]. In all these ranges, all spectra resembled each other and these peaks overlapped with the peaks of the cotton. Two strong peaks at 2848 cm^{-1} and 2916 cm^{-1} demonstrated the existence of the long-chain aliphatic groups on the surface [23]. Moreover, two peaks are evident at 2920 and 2849 cm^{-1} due to C–H groups in the spectrum of the sample treated with HDMS (C16) modified nanosols, while the same peaks are lower in the spectra of untreated cotton [31]. However, the most significant peaks of the coating overlapped with those typical of the cellulose substrate. The stretching mode of the vibration of C=O for the Zn and Zr fabric samples with and without the applied nanoparticle growing step is observed at 1400–1600cm^{-1}. The absorption peaks at 2854 cm^{-1} and 2924 cm^{-1} correspond to the stretching modes of the methylene groups, which confirm the presence of HMTA [32]. The peak at 2929 cm^{-1} is due to the C–H stretching vibration of HMTA. The peak at 1053 cm^{-1} corresponds to C–H bending vibrations, and should have arisen from the coordination between the N of the HMTA and Zn^{2+} [33].

Three main bands concerning metal–oxygen (M–O) bonding between 400 and 800 cm^{-1} are obvious for the Zr-G and Zr+G samples [34]. Two broad bands, located between 800 cm^{-1} and 600 cm^{-1}, could have been ascribed to the oxide network belonging to the formation of the Ti-O-Ti bands in the film on the surface [35]. The Al-O vibration band is observed at the characteristic 1023 cm^{-1}. The S-O and S=O vibrations would be found at 985 cm^{-1} [36].

5. CONCLUSION

In our study, cotton fabric samples were first treated using the wet chemical route containing the hydrothermal growing step on ZnO, Al_2O_3, TiO_2 and ZrO_2. Then the surface roughening and hydrophobic modification step was applied with long alkyl chain silanes to achieve durable super-hydrophobic properties. The advantages of the process are its simplicity, low cost, low temperature and environmental friendliness without perfluorination. It was found that the contact angle values of the +G code fabric samples, before and after the washing treatment, were higher than those of the -G code fabric samples. Thus, it was concluded that the hydrothermal nanoparticle growing step has remarkable importance for the water repellent properties of treated fabric samples. The Zn+G and Zr+G fabric samples did not completely lose their hydrophobic properties after the washing treatment. Thus, it was determined that durable water repellent properties could be obtained on cotton fabric with the combination of surface roughening using zinc acetate-zinc nitrate and zirconium acetyl acetonate as the precursor and hydrophobic modification using HDMS.

In the literature, super-hydrophobic cotton fabrics using zinc salts under the wet chemical route have been investigated, but their durable properties with regard to washing were not examined. In our study, aluminium sulphate, aluminium isopropoxide, zirconium acetylacetonate and titanium isopropoxide as the precursor were first used in the wet chemical route to achieve durable super-hydrophobic properties for the cotton fabric. It was deduced that durable water repellent properties could be obtained for cotton fabric samples treated with zirconium acetylacetonate as the precursor using the wet chemical route.

It was determined that the inherent properties, such as tear strength and bending length, of the Zn+G and Zr+G fabric samples with good and durable water repellent properties, did not significantly change. Moreover, the presence of chemical bonds and film layers with deposited particles on the fibre surfaces was proved with SEM images and FTIR-ATR analysis.

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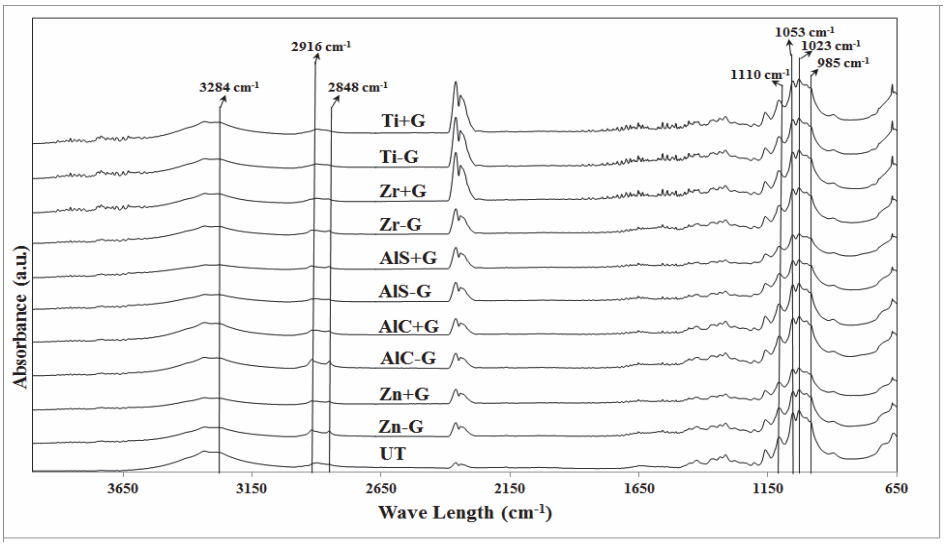

Figure 9. FTIR-ATR spectras of treated and untreated fabric samples

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