The finished polyester fabric with hot NH4OH pretreatment and mixed ZnO-Zn(OH)2 nanoparticles for hydrophobic property

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Abstract

This work aims to modify the hydrophobic coated polyester fabrics using 2%w/v ammonium hydroxide (NH4OH) at 90°C prior and subsequently dipped in two difference aqueous zinc solution batchs containing 0.6%w/v zinc precursors with/without starch and NH4OH, finally dehydration, and characterized by the attenuated total reflection - Fourier transform Infrared *(ATR-FTIR)* and Raman spectroscopy (Raman), X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM), Energy dipersive spectrometry (EDX), and Water contact angle (WCA) of 10 µL dropping at 23°C and humidity of 63%. Raman spectra and XRD patterns results showed ε-zinc hydroxide (ε-Zn(OH)2), zinc oxide nanoparticle (ZnO NP) and ZnO-starch nanocomposite crystallized in the orthorhombic and hexagonol wurzite structure, respectively. The increasing intensities of Raman vibrational modes at 369 cm^{-1} and 750 cm^{-1} confirmed the increased of ε-Zn(OH)2 content with additional starch, therefore, WCA trend of those finished fabric surfaces decreased. WCA optimum of 138° before washing and 136° after 5 washing cycles of the treated fabric which was activated by NH4OH acts as scourer and also as promoter of ε-Zn(OH)2/ZnO NPs as revealed from ATR-FTIR result. While, other observed lower hydrophobic property after 5 washing cycles due to the hydroplilic ZnO-starch nanocomposite.

1. Introduction

The fabric materials with more proper properties are growing attempts to develop for fabric industry [1] such as self-cleaning, hydrophobic, and antibacterial properties are an essential requirement for our daily life and healthcare. Those fabric materials have hydrophilic and hydrophobic properties, especially synthetic polyester fiber or polyethylene terephthalate (PET) as shown in Figure 1 that is known to be hydrophobic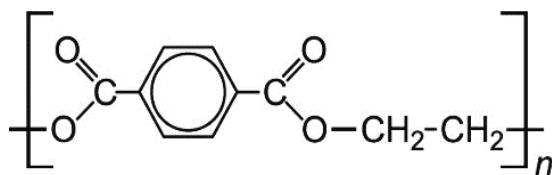 property, but fabrics manufactured thereof have an intricate capillary-porous structure and do not possess hydrophobic properties: Fluid droplets getting thereon are instantly absorbed by inter-fiber spaces. Hence, it seems appropriate that a woven material, rather than an individual fiber, be subjected to modification hydrophobic treatment [2] for the suitable outdoor and indoor uniform, help fabric care by protecting from dirty or stain with especially any type of liquid with dissolved in water or oil, and reduced the washing cycles as well.

Several methods for modified water-repellent fabric in such of the modified fiber scales into nano-or submicrometer, the selected hydrophobic agents; pyridine, silicone and fluorocarbons; however, later coating agent that consisting of eight carbon atoms, C8, is rejected with toxic agent, and also other is preferred, nanomaterial coated fabric with enhanced the roughness fabric surface is similar to water-repellent on the natural lotus leaf or hydrophobic coating. In 2012, S.S. Latthe and coworkers [3] reviewed the various methods for the preparation of hydrophobic coated fabric with the nanometer-or-micrometer scales such as phase separation [4], electrochemical deposition [5], template

Figure 1. Chemical structure of polyester (namely polyethylene terephthalate, PET).

method [6,7], emulsion [8], plasma method [9], crystallization control [10], chemical vapor deposition [11], wet chemical reaction [12], sol-gel processing [13-16], lithography [17], electrospinning [18], solution immersion [19] and so on.

The nanomaterial coated fabric have been considered and interested especially of ZnO NP because of its excellence in UV blocking and self-cleaning [20], and antibacterial [21], and hydrophobic properties [22]. ZnO has generally bandgap at around 3.37 eV corresponding to 376 nm and thus it absorbs light that matches or exceeds this band gap energy, and other advantages of chemical uniform, non-toxic, low cost, and observed in both of natural or synthesis from zinc salts precursor. Many coated fabrics processes can be prepared by dip-coating, sol-gel, dip-pad, deposited electrochemistry and batch of ZnO colloidal nanoparticles or zinc ion solution or in situ on fabric with hydrothermal, solvothermal, precipitation, ultrasonic, mechanicochemistry, microwave and sol-gel techniques [3-22]. For example, S. Nourbakhsh and coworkers [20] had successfully prepared ZnO NP modified polyester textiles functionalized UV blocking and self-cleaning properties, and also two years next, P. Kampeerapappun [21], reported excellent ZnO antimicrobial agent, which is attributed to the generation of reactive oxygen species on the surface of these oxides. In 2019, M. Wang *et al.* [22] prepared highly durable polysiloxane-ZnO coated polyester fabric improved ultraviolet resistance, hydrophobicity, and thermal resistance via radiation-induced graft polymerization (RIGP) of γ-methacryloxypropyltrimethoxysilane (MAPS) and the subsequent sol-gel in situ mineralization with zinc acetate. However, surface modification of highly hydrophobic polyester fabric coated with octadecylamine functionalized graphene nanosheets was reported in currently [23].

From above, the fabric materials were generally cleaned and scoured prior with hot the approximated 2% to 5% alkaline aqueous solutions or the other suitable solvents for eliminated the several amounts and kinds of impurities contained in various cuts and pieces of fabric in such of oily substances acquired during spinning, weaving, finishing, storage and transportation [24] must be done before the coated fabric process. The highly alkaline sodium hydroxide (NaOH) is commonly selected as scoured agent; however, it has the disadvantage of which attacks the textile material if not properly handled leading to reduction in mechanical and poor finishing properties of the fabric. The effluents of these processes are corrosive and harmful to the environment too. Boryo D.E.A. and their groups [24] reported alternative scouring agents on mechanical properties of cotton/polyester blend fabric. Ammonium hydroxide (NH₄OH) at the various concentrations of 5% and 2% are best for the breaking load and extension of cotton/polyester blend fabric compared with NaOH (control) and other alternative scouring agents of ammonium oxalate monohydrate ($(NH_4)_2C_2O_4$), acetic acid (CH_3COOH), liquid NH_3 and ethanol (CH_3CH_2OH). Since as scouring progressed, the impurities absorbed and reacted for the cleansing process leading to a decline in pH value up to a range of 7.50 to 8.45 for the various concentrations of NH₄OH. These pH value, although slightly alkaline is within the optimal range of a suitable soil pH (7 to 8) for plant growth and streams/lakes pH (6 to 9) for aquatic lives, thus NH₄OH is more friendly than NaOH as far as environmental activities are concerned [24]. However, the PET fabrics were scoured in only a bath containing 1 g·L⁻¹ nonionic detergent before the situ synthesis of ZnO nanoparticles which were prepared by wet chemical

method using triethanol amine (0.06% v/v to 0.12% v/v) as reducing and stabilizing agent and zinc acetate (0.05% v/v to 0.20% v/v) as zinc source through the aminolysis reaction as published in [25].

Moreover, the softly basicity of NH₄OH can be helped to control the morphology of $Zn(OH)_2$ and ZnO as reported of [26]. In addition, the fabric can be absorbed more nanomaterial and reduced agglomeration of ZnO NP through biopolymer structure of starch which consisting of more OH functional group as observed in [27]. Along with these background, the hydrophobic modification of mixed $Zn(OH)_2$-ZnO NPs coated woven polyester fabrics by using the pretreatment of hot NH₄OH, with are unreported yet from literature reviews.

In the present work, the preparation of hydrophobic polyester fabric was prior pretreated with hot NH₄OH scourer with hydrolysis reaction of ester is included, and the deposited the zinc precursors by comparison of two different preparation routs; only zinc aqueous solution and another one included starch acts as stabilizer and also binder agent, at ambient temperature. Finally, all treated fabrics are converted $Zn(OH)_2$ precursor to ZnO NP by dehydration at 100°C. The obtained water-repellent fabrics were compared with the control fabric.

2. Experimental

2.1 Materials

The white plain weave polyester fabric with 17 warps and 17 wefts in centimeter which was ordered from Sonibrazar shop, Lampang, Thailand. Zinc chloride ($ZnCl_2$) was purchased from J.T. Baker. NH₄OH was ordered from Qrec, New Zealand. Sticky rice starch was derived from Thai commercial shop. SDCE ECE type A non-phosphate standard reference detergent acts as nonionic soap was purchased from Union TSL Ltd, and distilled water was used.

2.2 General procedure

The 10 cm × 10 cm white plain weave polyester fabrics were washed with detergent and distilled water. Next, it was immersed in 2% w/v NH₄OH at 90°C for 30 min. After that, it was dipped in 0.6% w/v $ZnCl_2$ solution for 1 min and dried at 100°C for 1 h (sample code: C1). Another two conditions, first one as followed of C1 method but added 0.2% w/v starch into the zinc solution batch (sample code: C2). The controlled fabric is no added any chemical solution (sample code: C0) and those process using liquor to a material ratio of 50:1 as shown in Table 1.

2.3 Durability of hydrophobic property

The durability of hydrophobicity was measured using washing conditions as per test method ISO 105 C01:2006 which is designed to determine the effect of washing only on the metal oxide coating fastness of the textile. 5 g·L⁻¹ nonionic soap solution was used as washing liquor. The untreated and treated fabric samples were washed using liquor to a material ratio of 50:1 at 40 ± 2°C for 30 min. After that, fabric sample was removed from washed cylinder, take to 4 L container with 2 L water at ambient temperature, softly stirred for 1 min, rinsed with water for 1 min, pressed out the excess water by hand, and continuously pressed on the filter paper, and air dried at ambient temperature. The durability of hydrophobic property was studied to 20 washing cycles.

Table 1. The preparation routes of as-prepared hydrophobic fabrics.

Conditions	Wet chemical batch and process			Dried at 100°C
	2%w/v NH₄OH at 90°C	0.6%w/v ZnCl₂	0.6%w/v ZnCl₂ and 0.2%w/v starch	
C0	-	-	-	-
C1	30 min	1 min	-	1 h
C2	30 min	-	1 min	1 h

2.4 Characterization methods

Functional groups of pristine polyester fabric (C0) and the treated fabrics (C1-C2) were measured from the attenuated total reflection - Fourier transform Infrared (ATR-FTIR) technique, INVENIO-S FT-IR spectrometer, PerkinElmer in the range of 4000 cm⁻¹ to 400 cm⁻¹. Phase characterization and crystallographic structure of the synthesized Zn(OH)2/ZnO coated on polyester fabric samples were carried out by using Raman scattering characterization was performed by a confocal Raman spectrometer, Jobin Yvon horiba LabRAM HR, with an excitation wavelength of 532 nm at room temperature. Plus, powder X-ray diffraction (XRD), Rigaku MiniFlex 600, with X-ray sources from Cu Kα irradiation ($\lambda = 1.5406$ Å) and operated at 40 kV, 15 mA, 2 range scan of 10° to 80°, step scanned of 0.02°, speed scanned of 20°C·min⁻¹. After that, phase identification was done by comparing with the diffraction patterns (JCPDS and ICSD card) database. Moreover, the morphology of the untreated and treated fabric samples was analyzed by field emission scanning electron microscope (FE-SEM), JSM 6335 F, operating at 15.0 kV as accelerating voltage, equipped with EDX. Finally, the hydrophobicity of treated fabrics was determined by water contact angle. Water contact angles measuring and contour analysis on the sample fabric surfaces were analyzed by Dataphysics, OCA40, operating the volume of DI water of 10 μL dropping at 23°C and humidity of 63% for 3 s.

3. Results and discussion

3.1 ATR-FTIR and Raman spectroscopic results

The functional groups of pristine polyester fabric (C0) were measured by ATR-FTIR and Raman techniques. For the ATR-FTIR spectra are illustrated in Figure 2(a) that present two weak vibrational bands at 2967 cm⁻¹ and 2907 cm⁻¹ for C–H stretching, the strong peak at 1715 cm⁻¹ corresponded to C=O stretching and also in the region bands of 1620 cm⁻¹ and 1400 cm⁻¹ to 1000 cm⁻¹ assigned of C=C and C–O stretching of the aromatic ester functional groups as reported in [22] and excellent confirmed from Raman spectrum of pristine polyester fabric (C0) as given in Figure 2(b), the characteristic bands appear at 275 cm⁻¹ of skeletal C–C deformation, at 658 cm⁻¹ and 699 cm⁻¹ of ring C–C stretching, at 791 cm⁻¹ and 856 cm⁻¹ of C–C and C–O–C bending, at 994 cm⁻¹, 1093 cm⁻¹ and 1113 cm⁻¹ of C–O and C–C stretching, at 1178 cm⁻¹ of C–C ring stretching, at 1289 cm⁻¹ of COO stretching, and at 1371 cm⁻¹, 1412 cm⁻¹, and 1460 cm⁻¹ of CH₂ bending [28].

Surprisingly, ATR-FTIR spectra of treated fabrics shows also a new sharp peak at 1538 cm⁻¹ corresponded for the COO⁻ stretching [29,30] due to surface of polyester fabric (PET) was may not only

scoured but also its surface at ester-bonded carbonyl carbon was possible hydrolyzed and formed of ammonium terephthalate salt with the use of hot aqueous ammonia or NH₄OH as similar found in [20,31]. Moreover, its carboxylate and hydroxyl groups of terephthalate and ethylene glycol were bonded with Zn²⁺ ion after treated with two different Zn solutions, with/without starch addition, and following dried at 100°C for 1 h for dehydration formed of ZnO-(PET-terephthalate)₂ ((HO–ethane)-PET)₂ and ZnO-(HO–C-starch)(PET-terephthalate)₂ ((HO–ethane)-PET) (as shown in Equation (3-5)) that ATR-FTIR result shows two more sharp bands of C–H stretching shifted lower wavenumber of 2917 cm⁻¹ and 2848 cm⁻¹ and also observed two very weak peaks at 1620 cm⁻¹ and 580 cm⁻¹ represented OH bending and Zn–O bonding, respectively, as compared to C0. The propose alkaline hydrolysis reaction and formation of Zn(OH)₂/ZnO is represented in Scheme 1. Figure 2(c) and Table 2 present all Raman vibrational modes are ascribed of Zn(OH)₂, ZnO, ZnO-starch, and polyester fibers. Bands at 340, 369, 396, 432, 509, 548, 551, and 579 cm⁻¹ are assigned to the wurtzite structure of ZnO belongs to the C_{6v}^{4} point group symmetry with each Zn ion is surrounded by a tetrahedron of oxygen ions and vice versa. This arrangement gives rise to polar symmetry along the hexagonal vertical axis (*c* axis). Bands at 369 cm⁻¹ and 396 cm⁻¹ are assigned to the two polar phonons which can split into transverse optical (TO), A₁-TO and E₁-TO vibrational modes, another peak at 432 cm⁻¹ is corresponded the non-polar mode E₂^high that associated with the vibration of oxygen atoms, and the polar phonon of longitudinal optical (LO), and last peak at 579 cm⁻¹ is ascribed the A₁-LO mode, respectively, as reported in [32]. Other two bands at 672 cm⁻¹ and 685 cm⁻¹ are related the B₁^high and TA, and E₂^high as observed in [34].
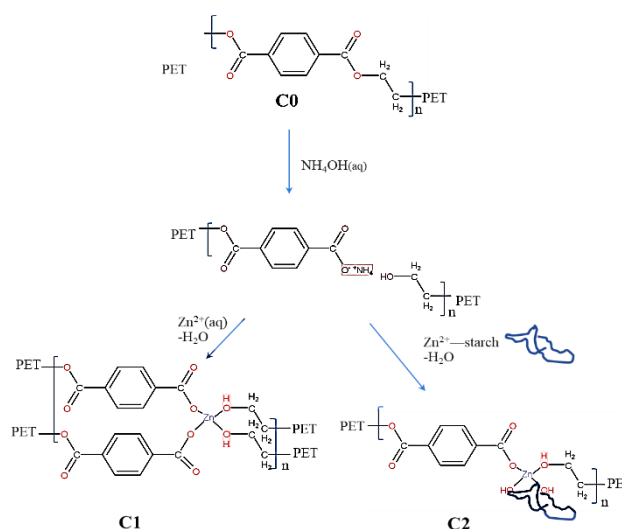
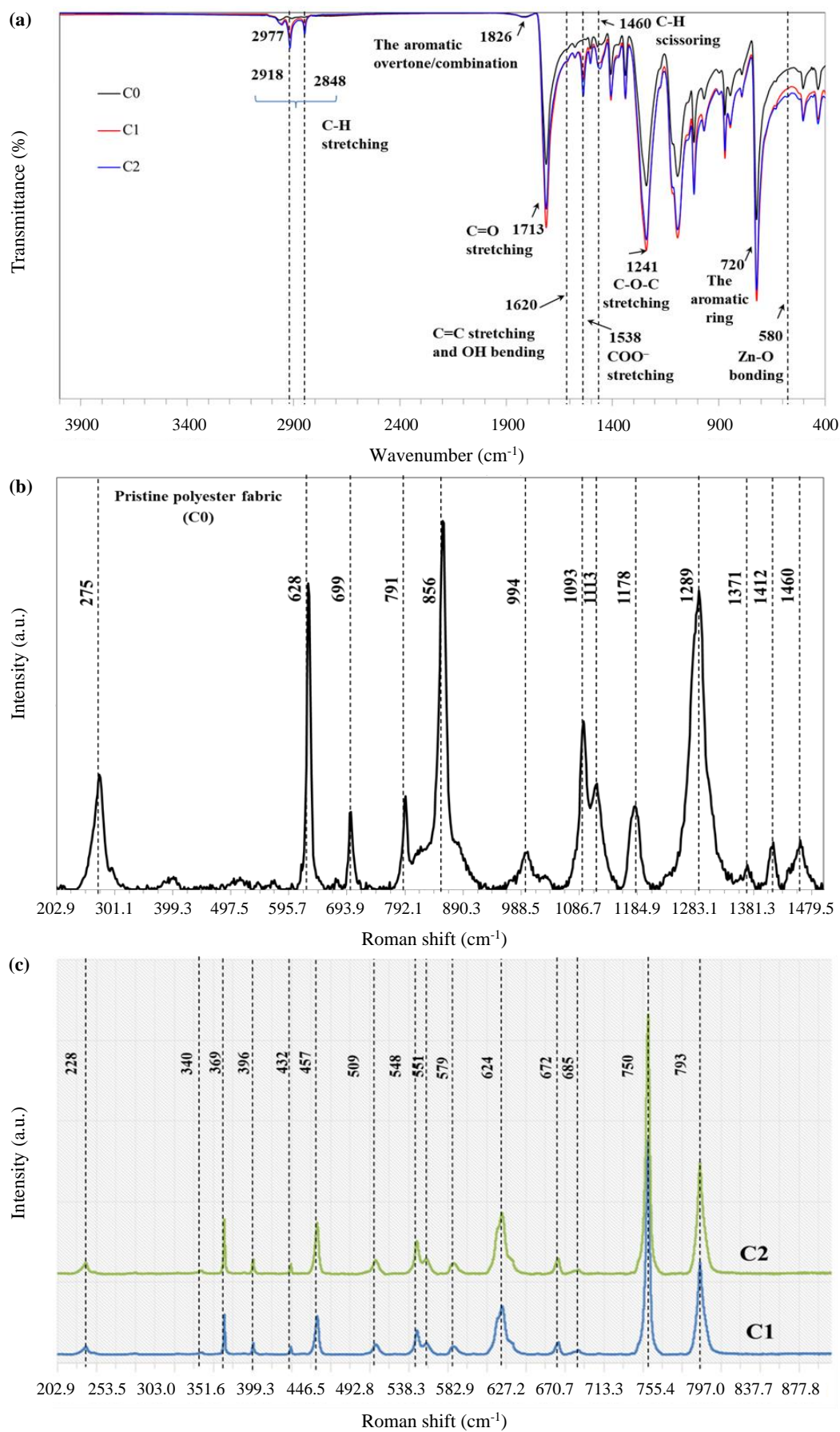**Scheme 1.** The alkaline hydrolyzed PET and formation of ZnO/Zn(OH)₂.

Figure 2. (a) ATR-FTIR of C0, C1, and C2, (b) Raman spectrum of C0, and (c) Raman spectra of as-prepared coated polyester fabrics.

Table 2. Raman spectra of as-prepared hydrophobic polyester fabrics.

Band (cm⁻¹)	Vibrational mode	Assignment
228	Zn-OH [32]	Zn(OH)$_2$
340	E_2^{high}- E_2^{low} [35]	ZnO
369	A_1-TO [27], Zn-OH [34]	ZnO, Zn(OH)$_2$
396	E_1-TO [27]	ZnO
432	E_2^{high} [33]	ZnO
457	δ(CCO), δ(CCC), ring deformation, skeletal bending [32]	starch
509	B_1	ZnO
548, 551	A_1-LO [32]	ZnO
579	A_1-LO [27]	ZnO
624	δ(COC), ring deformation [28]	Polyester
672	B_1^{high}+TA [33]	ZnO
685	E_2^{high} [33]	ZnO
750	Zn-OH [33]	Zn(OH)$_2$
793	Ring deformation [28]	Polyester

In addition, the bands at 228 cm⁻¹ and 369 cm⁻¹ are also attributed to the symmetric Zn–O stretching modes of the ZnO$_4$ tetrahedron in Zn(OH)$_2$ [32,35], while a strong band at 750 cm⁻¹ are assigned to the translational modes and the OH librations, respectively, as found in [34]. In addition to bands at 624 cm⁻¹ and 793 cm⁻¹ are corresponded δ(COC) and ring deformation of polyester as reported from [36]. Raman peak at 457 cm⁻¹ is also assigned of δ(CCO), δ(CCC), ring deformation and skeletal bending of glucose unit in starch that observed in [37]. Moreover, the intensity of vibration modes of 369 cm⁻¹, 457 cm⁻¹ and 750 cm⁻¹ with relation of Zn(OH)$_2$ are increased as followed the wet chemical conditions of C2 > C1 due to the starch and NH₄OH addition.

3.2   X-ray diffraction studies

From the XRD results of the finished polyester fabrics as shown in Figure 3, revealed a diffraction peak at 2θ about 31.58° corresponded of (100) plane of ZnO that crystallized in hexagonal wurtzite structure with space group $P6_3mc$, a = 3.24 Å and c = 5.19 Å, as referred of JCPDS card no.1451-36 . The broad diffraction peak is assigned of ZnO as referred of ZnO-starch as well [27]. Another the diffraction peaks at 2θ about 25.15° and 32.12° are accorded the wulfingite ε-Zn(OH)$_2$ structure that crystallized in orthorhombic structure (space group $P2_12_12_1$, a = 5.17, b = 8.55, c = 4.93 Å), as referred of ICSD #50447 and JCPDS card No. 38-0385 as good agreement with those reported of [35,38,39], although the low crystalline XRD diffraction peak in this work.

Crystalline sizes of Zn(OH)$_2$ and ZnO were calculated by using XRD result and Debye-sherrer's equation, Dhkl = Kλ/βhklcosθ, where λ is the wavelength of incident X–rays for Cu Kα (λ = 1.5406 Å), βhkl is the full width at half maximum (FWHM) of the orthorhombic ε-Zn(OH)$_2$ and the hexagonal wurtzite ZnO peak at (211) and (100) planes (in radians), θ corresponded the ε-Zn(OH)2 and ZnO peaks at 2θ = 32.12° and 31.58°, and K is a constant, which has been assumed to be 0.9, in this results which the particle sizes of all crystalline products showed the range about ~9 nm and ~8 nm, respectively, that were as referred to the earlier studies of S.V. Nistor *et al.* [39] and AbdElhady M. M. [40]. Moreover, the diffraction peak at 2θ about 17.37°, 22.18° and 25.40° assigned to (110), (002) and (101) planes of polyester as reported in [41].
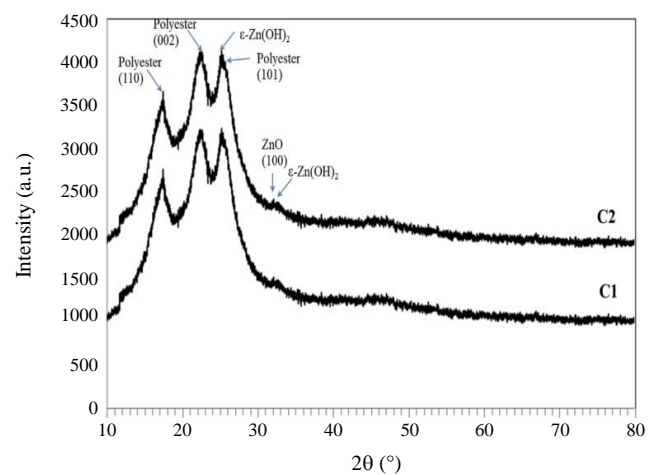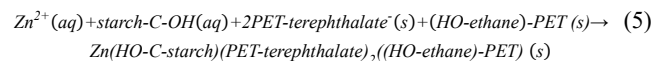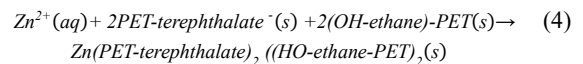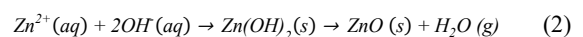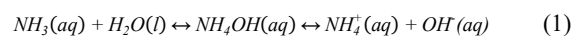

Figure 3. XRD patterns of as-prepared polyester fabrics coating as referred in JCPDS card no.1451-36 , ICSD card no.50447 and JCPDS card No. 38-0385.

$$NH_3(aq) + H_2O(l) \leftrightarrow NH_4OH(aq) \leftrightarrow NH_4^+(aq) + OH\,(aq) \qquad (1)$$

$$Zn^{2+}(aq) + 2OH\,(aq) \rightarrow Zn(OH)_2(s) \rightarrow ZnO\,(s) + H_2O\,(g) \qquad (2)$$

$$PET(s) + NH_4OH\,(aq) \rightarrow PET\text{-}terephthalate\,^-NH_4^+(s) + (OH\text{-}ethane)\text{-}PET \quad (3)$$

$$Zn^{2+}(aq) + 2PET\text{-}terephthalate\,^-(s) + 2(OH\text{-}ethane)\text{-}PET(s) \rightarrow \quad (4)$$
$$Zn(PET\text{-}terephthalate)_2\,((HO\text{-}ethane\text{-}PET)_2(s)$$

$$Zn^{2+}(aq) + starch\text{-}C\text{-}OH(aq) + 2PET\text{-}terephthalate\,^-(s) + (HO\text{-}ethane)\text{-}PET\,(s) \rightarrow \quad (5)$$
$$Zn(HO\text{-}C\text{-}starch)(PET\text{-}terephthalate)_2((HO\text{-}ethane)\text{-}PET)\,(s)$$

For after washing of 5 cycles and 10 cycles, EDX spectra show the amount of Zn element (C2 condition) is remained higher than other preparation routes due to more OH group in starch as a good biopolymer binder agent between surfaces of polyester material and those nanoparticles as Equation of (4), but also, reduced agglomeration of Zn(OH)$_2$ and ZnO [27]. The other peaks at 1.739 keV, 2.120 keV, 2.419 keV, 2.621 keV, and 8.040 keV related of silicon (Si), gold (Au), chlorine (Cl), bismuth (Bi), and copper (Cu) elements from the metal supporter and conducted coating of SEM/EDX sample preparation.
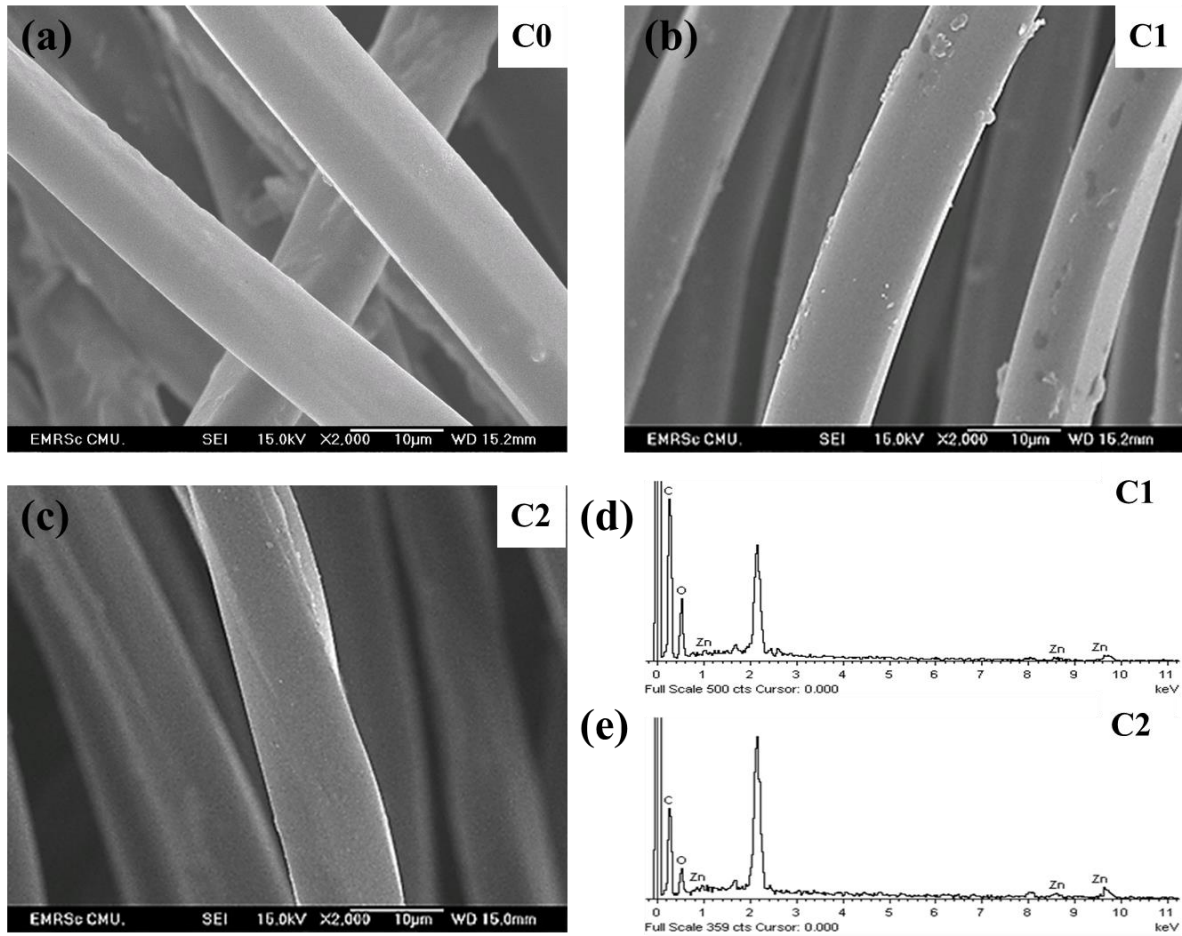
Figure 4. SEM images of as-prepared polyester fabrics coating (a) pristine (C0), (b) C1, and (c) C2, and EDX analysis of (d) C1 and (e) C2.

Table 3. Elemental analyses of as-prepared hydrophobic fabrics and after 5, 10 and 20 washing cycles (WC).

Samples	%Weight		
	C	O	Zn
C1	58.31	22.80	18.89
C1-5WC	58.96	39.80	1.23
C1-10WC	59.38	39.42	1.20
C1-20WC	57.01	42.96	0.03
C2	60.02	30.45	9.53
C2-5WC	57.96	36.96	5.08
C2-10WC	58.81	39.14	2.05
C2-20WC	60.73	39.05	0.22

3.3 Hydrophobic property studies

The fabric surfaces herein were treated by fabrication of the roughness $Zn(OH)_2$/ZnO nanoparticles for C1 and include ZnO-starch nanocomposite for C2 for artificial natural surface as similar of lotus leaf surface. The hydrophobicity of untreated and treated fabrics was determined by WCA as shown in Figure 5. From the C1 condition, using hot NH_4OH pretreatment prior followed by dipping in an aqueous solution of zinc exclude starch. Before washing, the maximum water contact angle of 138° of treated fabric sample was observed as compared with the original polyester fabric (C0, WCA = 76°) as similar to [22]. In addition to, the water contact angles of 136° after 5 washing cycles.

While other conditions, the water contact angles have lowered than C1. It is clearly due to pre-alkaline treatment of the softened basic aqueous ammonia solution (NH_4OH) at 90°C, which had improved the accessibility of the surface of polyester fibers in such of still remains unique by occurred in only at ester-bonded carbonyl carbon of the terephthalate and ethylene regions that observed in ATR-FTIR spectra result in this work, in addition, increased COO^-/OH groups at the surface of polyester resulted to ~9 nm $Zn(OH)_2$ and ~8 nm ZnO NPs were more deposited on the treated fabric which can be improved hydrophobic behavior although 5 washing cycles (C1, WCA = 136°) as compared to C2 (WCA = 117°) and the original polyester fabric (C0, WCA = 0°). As the mention that, the advantages

of starch which acts as both binder and hydrophilic agents, resulted to decrease the hydrophobic properties of the treated fabric.

As compared with the previous studied of S. Nourbakhsh *et al.* (2016) [20] reported the time of disappearing water drop was longer on ZnO roughness treated PET surface with pre-alkaline hydrolysis of NaOH as compare to the original polyester fabric. In addition, M. S. Han and coworkers [43] achieved to prepare superhydrophobic polyester fabrics using alkaline hydrolysis (NaOH) and coating with fluorinated polymers. Last, M. Wang and their groups [22] that reported

the hybrid organic-inorganic fabrication of polysiloxane-ZnO coated polyester fabrics at 200℃ in ambient air resulted of highly durable the coated fabric (WCA of 152°) still retains its superhydrophobicity after 40 laundering cycles test and even stored for a few weeks. Although, the WCA of the modified polyester fabric in this work (about 138°) and durable after 5 washing cycles test that obtained lower than previous work, but advantages of this work are easy route and environmentally friendly of softened basicity of NH₄OH for suitable modified polyester fabric application in large scale.
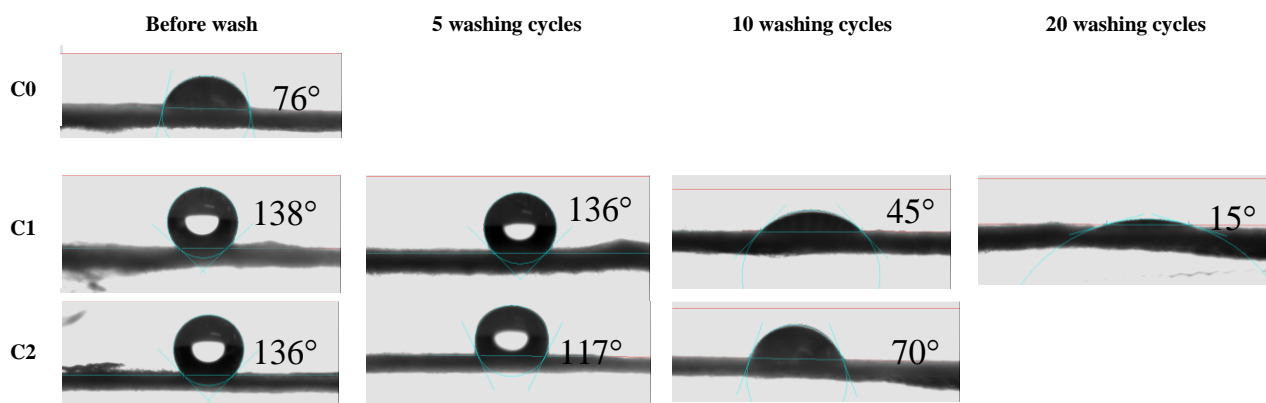

Figure 5. WCA of the untreated sample (C0) and some as-prepared polyester fabrics coated with mixed Zn(OH)₂/ZnO NPs for C1, and Zn(OH)₂/ZnO NPs and ZnO-starch nanocomposite for C2. The WCA of 5, 10 and 20 washing cycles of C0, and 20 washing cycles of C2 were observed approximate WCA = 0° and not shown here.

4. Conclusion

The functionalized hydrophobic polyester fabric was successfully by using hot NH₄OH pretreatment prior for scoured polyester fiber and also offered carboxylate/hydroxide sources with enhanced zinc precursor adsorbing for more deposited hydrophobic Zn(OH)₂/ZnO NPs agents on fabric with improvement of WCA of 138° and laundering durability is about 5 washing cycles.

Acknowledgement

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