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A Cleaner Affordable Method for Production of Bactericidal Textile Substrates by in situ Deposition of ZnO/Ag Nanoparticles

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Abstract: This contribution renders an affordable clean method for deposition of Ag, ZnO and ZnO/Ag nanoparticles on polyester (PET) substrates by in situ wet chemical approach utilizing available *Seidlitzia rosmarinuser* ashes. Replacement of using hazardous chemicals such as toxic reductants and solvents as well as simplification of the process for industry through one-step process instead of separate synthesis/buying nanoparticles are the advantages of this route from the both human health/environmental and economic observations. Successful formation of silver, zinc oxide and silver/zinc oxide nanoparticles on PET fabrics was evidenced by field-emission scanning electron microscope, mapping images and energy-dispersive x-ray spectroscopy. The nano-treated samples including PET/ZnO, PET/Ag and PET/Ag/ZnO have proper bactericidal performances of 71, 94, 99 % toward *Staphylococcus aureus* and 63, 91 and 93 % against *Escherichia coli* bacteria, respectively. Also, the color difference among the prepared samples and the raw PET fabric is very slight which is preferred for textile and garment industry. Moreover, tensile strength of the modified fabrics was slightly promoted compared to the raw PET sample owing to nanoparticles formation over the fabric surface and the modified fabrics indicated softer handle and greater flexibility. In addition, wettability behavior for all the modified samples together with resistance to ignition in the case of ZnO deposition on the fabric was promoted. Overall, the introduced technique in this research can contribute to textile industry for producing antibacterial textiles with good textile performance using a clean way through formation of nanoparticles.

Keywords: Cleaner synthesis, PET fabrics, Antibacterial poperties, Silver nanoparticles, Zinc oxide nanoparticles

Introduction

With respect to current attention to human health and emerge of new diseases resulted by different microbes, antibacterial materials have aroused great consideration all around the world [1-3]. They have an ability to avoid growing photogenic bacteria as well as killing them, therefore they are known as effective substances to diminish the risk of infection [4,5]. Textile fabric as one of the most utilized goods by human is a place for landing different bacteria that can play a role for transferring them from one place to other casing to propagate such harmful microorganisms [6]. In this regard, many researchers have attempted to manufacture antibacterial textiles via applying diverse antibacterial materials such as metal/metal oxide coating, nanoparticles, *N*-halamine and quarternary amunium compounds [7-9]. Nanoparticles can be applied on textiles through three principle procedures of fabric coating with colloidal solution via padding, drying and curing processes, embedding of nanoparticles into fiber by spinning as well as nanoparticles formation by in situ wet processing in presence of textile substrate [10-12]. Among these approaches, the in situ wet processing for synthesis of nanoparticles on the textile surface has been achieved higher priority than the other ones in recent research works [13]. Unrequired high energy consumption including high temperature and pressure, simplicity, being affordable and proper uniformity over the textile surface can be listed as some advantages of this method [14,15]. In addition, surface modification of textiles is possible at the same time of formation of nanoparticles on the fabric surface [16]. Furthermore, a variety of nanoparticles such as silver [17], copper [18], copper oxide [19], zinc oxide [20], titanium dioxide [21] and much more are utilized widely for fabricating antibacterial textiles. It is well-known that silver nanoparticles exhibit strong antibacterial efficiency against pathogenic bacteria nonetheless they are expensive [17]. In this regard, an effective solution for reducing the cost of the silver nanoparticles is combining with other low-cost nanoparticles that have mostly same function namely copper nanoparticles [22,23]. However, lower usage of toxic chemicals should be considered in nano-functionalization of textiles with nanoparticles. It is highly preferred from the view point of both human health safety and environmental issues [24]. On this basis, green synthesis of varied nano-particles on diverse textiles has been performed recently [25,26]. In addition, ashes of *Seidlitzia rosmarinus* were

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employed widely in recent years as green alkaline source for both nanoparticles formation and surface modification of polyester (PET) fibers [27-29]. However, they have not been reported for coinciding formation and assembling of silver, zinc oxide and silver/zinc oxide nanoparticles and alkaline modification of PET nanoparticles in the literatures.

Nanoparticles possess other influences such as changing wettability and mechanical performances of the modified textile or acting as flame-retardants on the textile surface [30]. Forming nano-roughness on the fabric surface, producing surface oxygen vacancies for photocatalyst nanoparticles or generating hydrophilic/hydrophobic groups through the modification can alter the wettability of the fabric surface [30,31]. Moreover, mechanical properties of the resultant modified fabrics can be increased or decreased depending on the type of nanoparticles synthesis approach [31]. In addition, presence of nanoparticles with low thermal conductivity can contribute to avoid propagating fire over the modified fabric [32,33].

On the other hand, PET fabric is used broadly in textile industry because of its availability, popper textile features and outstanding physical and chemical performances [34, 35]. However, some disadvantages encompassing hydrophobicity, accumulation of static electric charge and soil release owing to lack of functional hydrophilic groups in their surface can be listed [34]. Hydrolysis of the PET fabrics under alkaline condition to reach more hydrophilicity is common in textile industry [36]. Similar to the other chemical treatments, clean materials are preferred in the case of such alkaline hydrolysis of PET fabric.

With the above background in mind, this study at hand tries to propound an affordable clean method for deposition of Ag, ZnO and ZnO/Ag nanoparticles on PET by in situ wet chemical approach utilizing available *Seidlitzia rosmarinuser* ashes. Elimination of hazardous chemicals such as toxic reductants and solvents as well as simplifying the process for industry via in situ formation of nanoparticles on the textile surface instead of separate synthesis/buying nanoparticles considering both human health/environmental and economic observations are the advantages of this route. Successful formation of silver, zinc oxide and silver/zinc oxide nanoparticles on the PET fabrics was evidenced by field-emission scanning electron microscope, mapping images and energy-dispersive X-ray spectroscopy. An excellent bactericidal performance against both pathogenic bacteria of *Escherichia coli* and *Staphylococcus aureus* was achieved for the treated samples with nanoparticles. Furthermore, tensile strength of the modified fabrics was slightly promoted compared to the raw PET sample owing to nanoparticles formation over the fabric surface and the modified fabrics indicated softer handle and greater flexibility. They also displayed an enhancement in wettability for all the modified samples together with a promoted resistance to ignition in the case of ZnO deposition on the fabric.

Experimental

Materials and Methods

Zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O$ and silver nitrate ($AgNO_3$) were purchased from Merck Company, Germany and Cetyltrimethylammonium Bromide (CTAB) was also provided from Darmstadt company, Germany. A PET fabric with weight of 88 g/m^2 was supplied from Hejab Shahrkord Company. *Seidlitzia Rosmarinus* ashes were bought from a local market in Kashan, Iran.

Pre-treatment and Alkaline Hydrolysis of PET Fabrics

To remove any impurities from the fabric surface, a 20-min treatment was applied for the PET fabrics at 60 ^{o}C using a bath with a liquor to good ratio of (L:G)=40:1 containing 1 g/*l* nonionic detergent. After that, distilled water was used to wash the fabrics and they were dried at room ambient. In addition, 10 g *Seidlitzia Rosmarinus* ash was dissolved in distilled water, properly stirred and maintained overnight to precipitate and form a clear alkaline solution. This prepared solution was utilized as alkaline source for both alkaline hydrolysis of PET fabric and in situ formation of nanoparticles. Furthermore, a bath with L:G=50:1 comprising 10 m*l* prepared alkaline solution and 2 g CTAB was applied in order to surface modification of the washed PET fabrics. The surface modified fabrics were then rinsed well with distilled water and hung up in room temperature to be dried.

Functionalization of PET Fabric by in situ Formation of Zinc Oxide Nanoparticles

In order to formation of zinc oxide nanoparticle on the PET surface, zinc acetate (0.8 w/v %) along with the hydrolyzed PET fabric was added to a bath with L:G=50:1 under stirring for 30 min. Afterwards, the prepared alkaline solution (25 m*l*) was dropwise inserted to the synthesis bath. The treatment was kept at boil for 1 h to form zinc oxide nanoparticle on the fabric surface. The nano-treated fabric was subsequently placed in an oven with 80 ^{o}C for 30 min and cured at 150 ^{o}C for 3 min. It was then washed with distilled water, dried at room conditions and labeled as PET/ZnO sample.

Functionalization of PET Fabric by in situ Formation of Silver Nanoparticles

At first a solution of sliver nitrate (0.1 w/v %) was prepared and used for formation of silver nanoparticle on the PET surface. The hydrolyzed PET fabric was put into a bath with L:G=40:1 and silver nitrate was added to the solution. After 5 min stirring, the provided alkaline solution (5 w/v %) was poured dropwise into the synthesis bath and the treatment was continued at boil for 1 h. The modified sample was rinsed with distilled water, dried at room temperature and labeled as PET/Ag sample.

Functionalization of PET Fabric by in situ Formation of Silver/Zinc Oxide Nanoparticles

In order to formation of silver/zinc oxide nanoparticle on the PET surface, zinc acetate (0.8 w/v %) along with the hydrolyzed PET fabric was firstly added to a bath with L:G=50:1 under stirring for 25 min. subsequently, sliver nitrate solution (0.1 w/v %) was poured into the synthesis solution. After 10 min, the prepared alkaline solution (10 w/v %, 25 m*l*) was dropwise introduced to the synthesis bath. The modification was completed after 1 h at boiling point. The functionalized fabric by silver/zinc oxide nanoparticles was subsequently placed in an oven with 80 °C for 30 min and cured at 150 °C for 3 min. At final step it was rinsed with distilled water, dried at room conditions and labeled as PET/Ag/ZnO sample.

Test Method

Field-emission scanning electron microscope (FESEM) (Mira 3-XMU, Czech Republic), energy-dispersive spectroscopy (EDX) and mapping analysis were employed to specify surface morphology, elemental analysis and distribution of diverse elements on the surface through the alkaline hydrolysis and nano-functionalization of the PET fabric, respectively.

Weight change of different prepared samples was evaluated as absorption efficiency of the modification according to equation (1) with considering W_1 and W_2 as the weight of the fabric before and after the treatment, respectively:

$$\Delta W\,\% = [(W_2 - W_1)/W_1] \times 100 \tag{1}$$

The wettability behavior of the hydrolyzed and nano-functionalized PET fabrics was investigated in comparison to the raw PET fabric based on water spreading time (AATCC Test Method 79-2000). Ten repeats were considered for each sample and the average was recorded.

L^*, a^* and b^* fabrics as three color coordinates expressing lightness, redness-greenness and yellowness-blueness of the raw and modified PET were considered via utilizing a Color eye XTH spectrophotometer (Standard illuminant D65/ 10 °). Furthermore, the total color difference for the nano-functionalized samples was determined in comparison with the raw fabric using equation (2) [37]:

$$\Delta E = [(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2]^{0.5} \tag{2}$$

In addition, an Instron (USA) with extension rate of 100 mm min^{-1} and 10 cm gauge length was applied to measure the tensile strength of the raw and nano-functionalized PET fabrics according to BS2576. Three measurements were carried out and the average was reported. A Shirley fabric stiffness tester was further applied to study the bending length of the raw and different modified samples in warp direction with considering three repeats for each sample and the average value was noted.

Also, bactericidal activities of the raw and diverse nano-functionalized fabrics were examined against two pathogenic bacteria encompassing *Staphylococcus aureus* and *Escherichia coli* bacteria according to AATCC-100 as a quantitative test route. In short, the fabricated or pristine fabrics were cut in circular form with a diameter of 4.8 cm^{-1} and placed in a 250-m*l* glass jar with a screw cap. The sample was further immerged with 1 m*l* inoculum and left in the jar. A sterile petri dish was used to place each sample and then the sample was transferred to the jar. After that, a 100-m*l* neutralizing solution was added to each jar. The jars were then vigorously shaken and water was also used to prepare serial dilutions plated on nutrient agar. Incubation of all plates was performed for 48 h at 37 °C. The percentage of reducing bacteria was also specified based on equation (3) in which R, A and B are defined as bacteria reduction percentage and number of bacterial colonies from the raw and prepared samples, respectively [38]:

$$R\% = [(A - B)/A] \times 100 \tag{3}$$

Besides, vertical flammability test was applied for the raw and varied modified samples according to BS3119 standard and the char length of the samples was determined accordingly for three measurements and the average was finally reported. In addition, the weight of each sample before (W_1) and after (W_2) heating in an oven with a temperature of 600 °C for 3 h was used for calculating char yield using equation (4) [39]:

$$\text{Char yield} = \left[\frac{W_2}{W_1}\right] \times 100 \tag{4}$$

Results and Discussion

Study of Surface Morphology

In this research work, the PET substrate was functionalized through in situ wet chemical technique for synthesis of ZnO, Ag and Ag/ZnO nanoparticles by means of using available *Seidlitzia rosmarinuser* ashes. Additionally, the surface of the PET was activated via surface hydrolysis process utilizing the same ashes of *Seidlitzia rosmarinuser* prior to the nano-treatment. On this basis, FESEM analysis was implemented on the raw PET, hydrolyzed PET and varied samples with different nanoparticles to figure out morphological properties after the treatment and the results are exhibited in Figure 1. As observed, the raw PET displays completely smooth surface as expected whereas the alkaline treatment of the PET leads to generate some fine roughness on the fiber surface for the hydrolyzed PET. It was stated in literature that hydrolysis of PET fiber caused to separation of some oligomers from the polymeric backbone to create roughness on the fiber surface [34,36].

In addition, for the nano-treated samples Ag, ZnO and combination of Ag/ZnO nanoparticles can be observed on the fiber surface with different shapes of spherical, rod and spherical/rod shapes, respectively, confirming prosperous functionalization of PET substrate via in situ green nano-

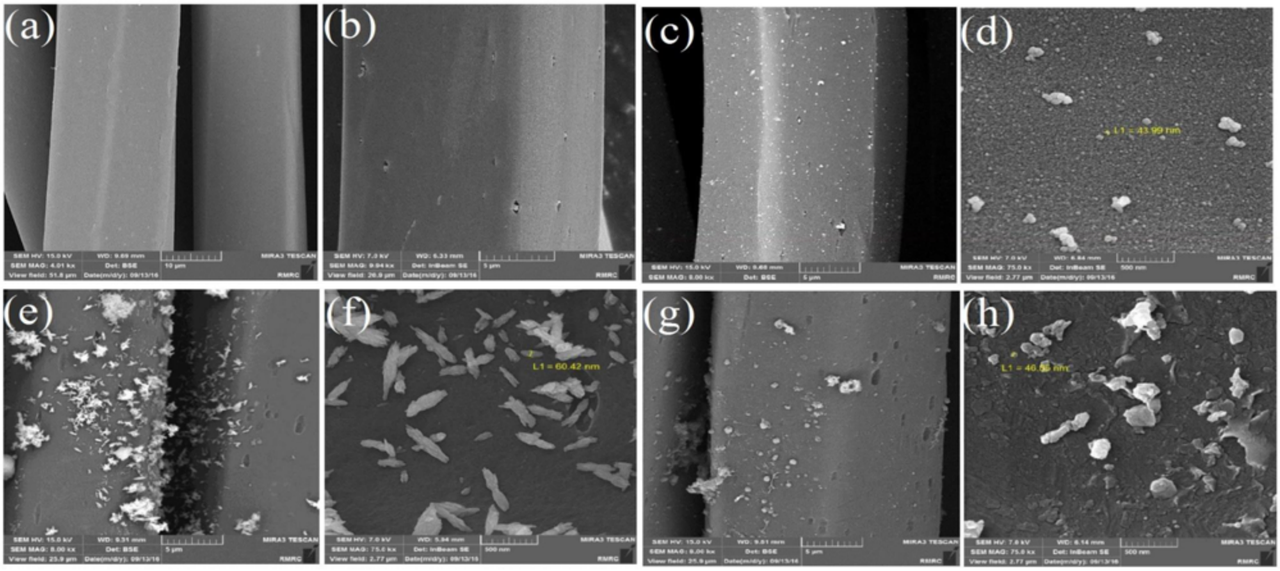

Figure 1. Images of FESEM analysis related to (a) raw PET, (b) hydrolyzed PET, (c, d) PET/Ag, (e, f) PET/ZnO, and (g, h) PET/Ag/ZnO.

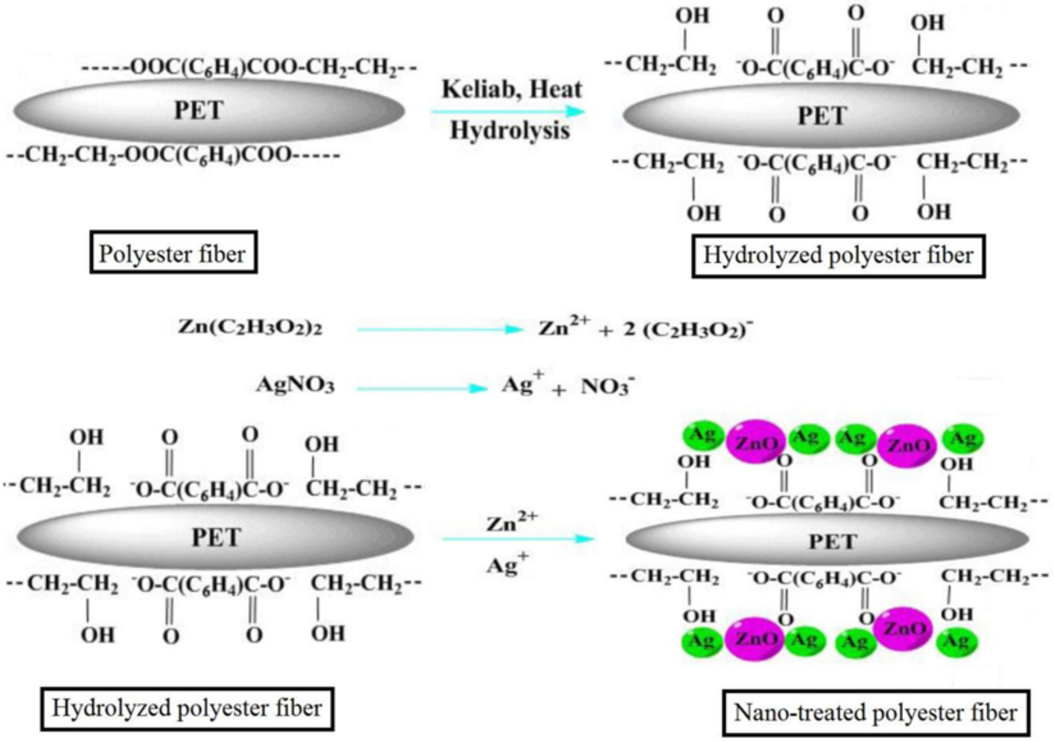

Figure 2. Schematic illustration of nano-treatment of the surface modified PET fabrics (PET/Ag/ZnO) through using a clean wet chemical approach.

treatment. In fact, dissolving *Seidlitzia rosmarinuser* ashes in water creates hydroxyl ions because of the alkaline trait of such natural powder which has sodium and potassium carbonates [27]. In this condition, polymeric chains of the PET fiber hydrolyze to form some oligomers and low molecular fragments on the fiber surface containing functional groups of carboxyl ($-COO^-$) hydroxyl (-OH) [28]. These mentioned active groups generated on the PET surface have an ability of playing a rule for nucleation of diverse nanoparticles [27,28]. Also, it is well-known that

PET fabric has an isoelectric point of ~pH=2.6 with negative surface charge above this point owing to the carboxyl groups as well as formation of hydroxyl groups on the surface through hydrolysis [40]. On other hand, silver and zinc ions with positive charge can be formed through dissolving the corresponded salts in water and subsequently can absorb on negative sites on the surface modified PET fibers with electrostatic interactions [31]. The electrostatic interaction was remarked in literature as possible mechanism for absorbing nanoparticles on the surface of modified PET [27, 29]. At final stage, the hydroxyl ions produced by addition of *Seidlitzia rosmarinuser* ashes cause to reduce the silver and zinc ions to form nanoparticles on the fiber surface [31, 41]. Hydrogen bonding between formed zinc oxide and hydroxyl groups of PET chains is also possible as such bonding was stated in literature between the materials with hydroxyl groups and polymeric composites containing oxygen or hydroxyl groups [42,43]. Physical embedment of the synthesized nanoparticles on the fiber surface can be considered as well. The silver and zinc oxide nanoparticles, hence, are generated well on the PET fibers with applying green nanoparticles formation route. Figure 2 demonstrates schematic illustration of nano-treatment of the surface modified PET fabrics via green wet chemical technique.

EDX and Mapping Analysis

EDX analysis was conducted to specify elemental composition of the different samples. Figure 3 points out the results of the EDX tests for the raw PET, PET/ZnO, PET/Ag and PET/Ag/ZnO samples. As can be seen, the raw PET fabrics consist of carbon and oxygen elements as expected, however zinc element with a considerable extent of 7.51 wt% is observed for the sample of PET/ZnO apart from the oxygen and carbon elements. Likewise, samples PET/Ag and PET/Ag/ZnO indicate silver and zinc/silver elements with amounts of 1.26 and 1.26/0.52 wt%, respectively. It is obvious that the carbon and oxygen elements are relevant to the polymeric backbone of the PET fibers and the silver and zinc elements are resulted from formation and incorporation of nanoparticles on the PET surface. Thus, this clearly implies successful green synthesis of both silver and zinc oxide nanoparticles and loading them on the fabric surface.

In addition to the EDX test, distribution of the detected elements was examined by using mapping analysis. Figure 4 shows mapping data for the different samples comprising the raw PET, PET/ZnO, PET/Ag and PET/Ag/ZnO samples. According to the obtained results, a uniform distribution is observed for the both silver and zinc oxide nanoparticles on the PET surface. This expresses that the synthesized nanoparticles are existed properly throughout the PET surface. Hence, mapping analysis further proves clean functionalization of PET samples via the both zinc and silver nanoparticles.

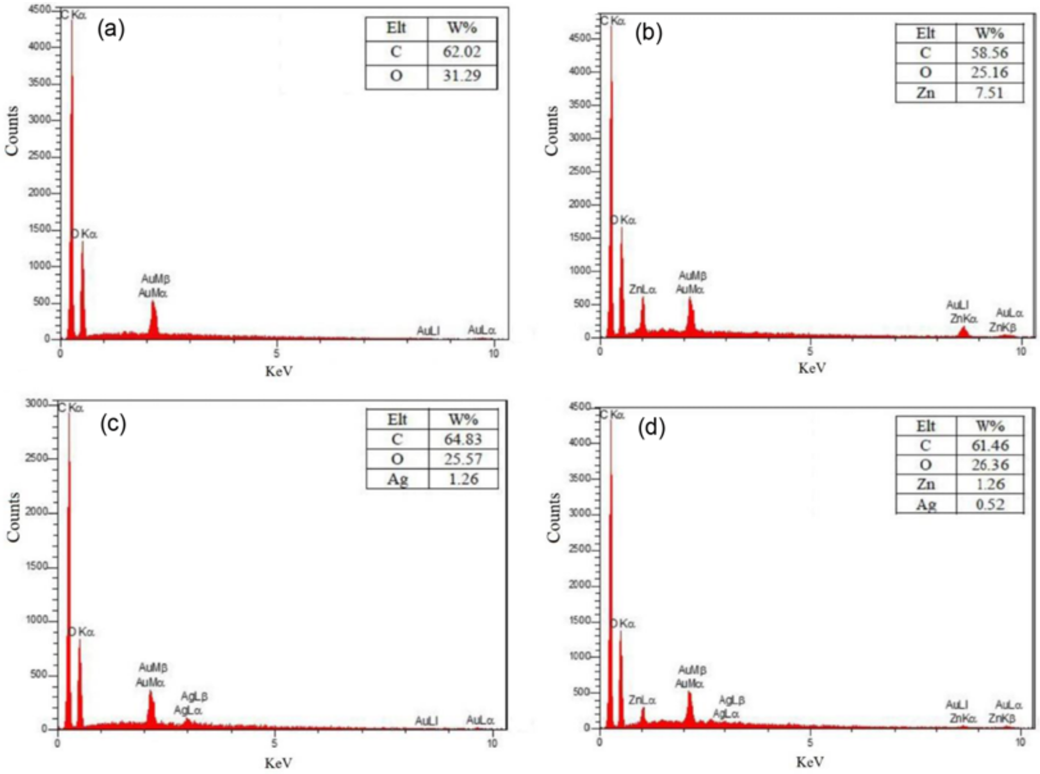

Figure 3. EDX analysis of various samples; (a) raw PET, (b) PET/ZnO, (c) PET/Ag, and (d) PET/Ag/ZnO.

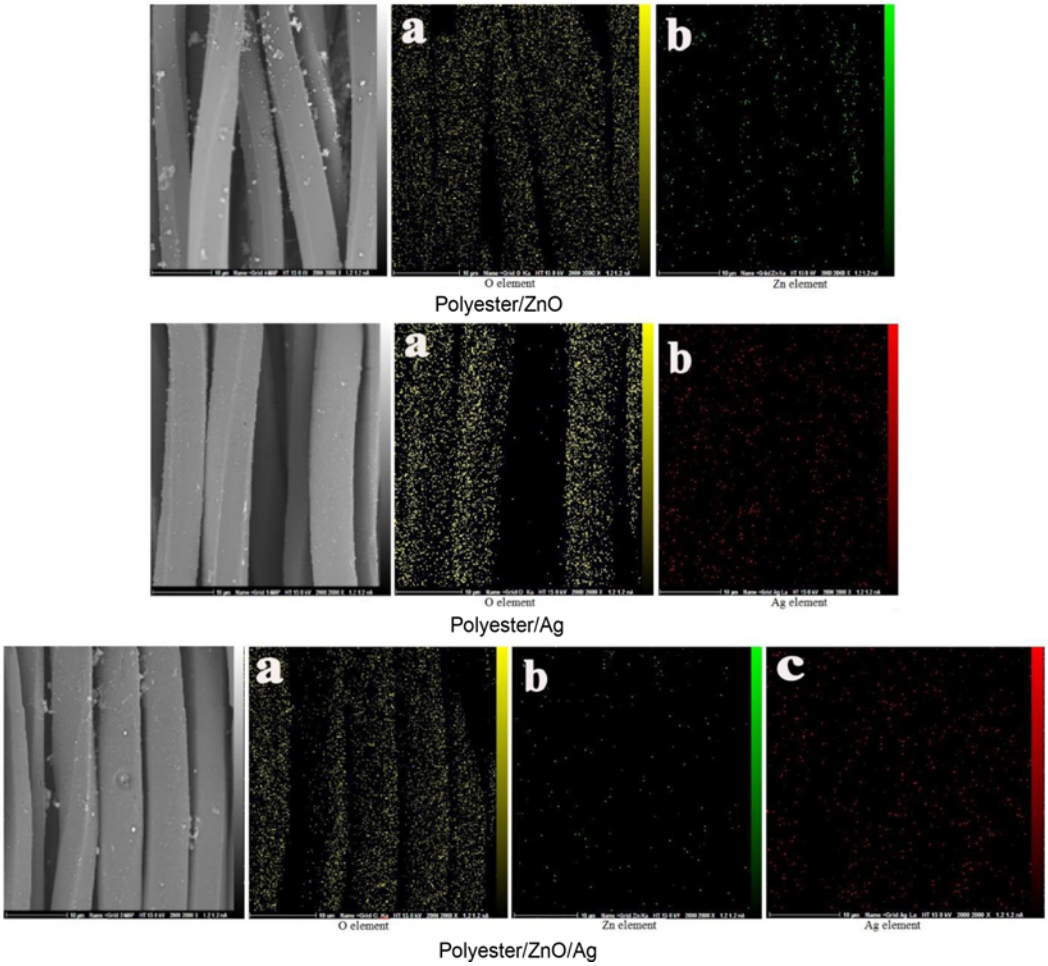

Figure 4. Distribution of different elements of diverse samples detected by mapping analysis.

Weight Change, Wettability Performance and Color Alterations

Any type of textile and polymer surface modification can trigger to weight gain or weight loss as an effect of addition or separation of some chemicals on the surface of such polymeric substrates [38]. On this basis, weight change is considered commonly as one important parameter in order to specify quality of a modification. Here, weight changes of the prepared samples through the PET hydrolysis and nano-functionalization compared to the raw PET are given in Table 1. Based on the obtained results, the hydrolyzed PET sample displays a weight loss of 4.5 % which is owing to dissever some parts of the PET polymeric backbone as a result of alkaline hydrolysis of ester bond under alkaline condition provided by *Seidlitzia rosmarinuser* ashes [34, 36]. In contrast, no weight loss can be seen for the nano-functionalization of the PET substrate. The weight change becomes zero for both PET/ZnO and PET/Ag samples, and 1.2 % for PET/Ag/ZnO sample. It confirms effective in situ formation and deposition of silver, zinc oxide and combination of silver/zinc oxide nanoparticles on the fiber surface. The reason behind this is that we have two opposite modification processes in the synthesis bath. The first phenomenon is hydrolysis of the PET surface in presence of hydroxyl ions under alkaline condition. The second case is synthesis and formation of the nanoparticles with addition of alkaline source and absorption of them on the PET surface. Depending on which process becomes dominant, the weight alteration goes ahead. Obviously, loading of as-formed Ag/ZnO nanoparticles was greater than the hydrolysis process, thus in this case we have weight gain. Such phenomenon was remarked for in situ fabrication of a variety of nanoparticles in literature [6,19,34].

Besides, wettability behavior of the modified PET samples is a significant factor in the view of textile industry applications. Achievement to more hydrophilic PET fabrics is usually preferred by researchers in order to exploit full advantages of PET goods in textile industry [34,39]. Wettability performance of the diverse fabricated samples was determined based on the time of spreading a water

Table 1. Weight change, water spreading time and color coordinates of the diverse prepared samples

Sample	ΔW (%)	Water spreading time (s)	L^*	a^*	b^*	ΔE
Raw PET	-	8.43	80.40	-0.27	-1.33	-
Hydrolyzed PET	-4.5	0	-	-	-	-
PET/ZnO	0	0	85.10	-0.39	-1.16	4.70
PET/Ag	0	3.00	60.13	-0.92	17.17	17.87
PET/Ag/ZnO	1.2	0	79.51	-0.19	3.29	0.54

droplet on the fabric surface in comparison with the raw PET and the results are rendered in Table 1. The raw fabric illustrates a hydrophobic trait with water spreading time of 8.43 s which reduces to instantaneous absorption (0 s) for the hydrolyzed PET, PET/ZnO and PET/Ag/ZnO and 3.00 s for PET/Ag. This reveals that all the fabricated samples have better wettability behavior than the raw PET fabric. It is well-known that PET hydrolysis in alkaline condition generates some hydroxyl and carboxyl functional groups on the PET fiber surface increasing the hydrophilicity of the modified PET fabric [34,36,44]. In addition, in situ formation of silver and zinc oxide nanoparticles is happened simultaneously along with the PET alkaline hydrolysis. It was mentioned in literature that surface modification of PET fabric with in situ synthesis of nano ZnO utilizing sodium hydroxide led to lessen water spreading time compared to the pristine fabric [44]. Production of surface oxygen vacancies as a result of light absorption of ZnO nanoparticles with photocatalyst feature can also contribute to adsorption of water molecules on the surface [31]. Although water spreading time for PET/Ag is lower than the raw PET sample, presence of silver nanoparticles causes to formation of surface roughness and physical barrier action compared to the other modified samples [34].

In addition, raise of fabric wettability can enhance attraction of moisture on fabric surface resulting in lowering surface electrical charge [19,38]. Therefore, the introduced approach in the paper at hand would be potentially helpful for improving electrostatic dissipation on the surface of the modified fabrics.

Furthermore, color of a textile can vary through nano-treatment [12]. Three color coordinates of the prepared samples were obtained to study the influence of in situ formation and deposition of silver, zinc oxide and combination of silver/zinc oxide nanoparticles on the PET surface using clean *Seidlitzia rosmarinuser* ashes in comparison with the raw fabric. Table 1 represents overall color difference (ΔE), L^*, a^* and b^* of the raw PET and different modified fabrics. Overall color difference varies from 0.54 for PET/Ag/ZnO to 17.87 for PET/Ag which implies successful formation and loading of nanoparticles led to make color difference for the modified fabrics compared to the raw one. Lightness value of the modified fabrics, L^* becomes greater for PET/ZnO owing to the white color of the ZnO nanoparticles formed on the fabric surface. It further changes to 60.13 for PET/Ag because of silver nanoparticles synthesis on the surface of the modified sample nonetheless it alters to 79.51 for PET/Ag/ZnO which is roughly the same value of the raw PET lightness (80.40). The greenness-redness value (a^*) remains approximately unchanged for all the treated samples compared to the raw PET fabric. Moreover, b^* value is -1.33 for the raw fabric that turns to -1.16, 17.17 and 3.29 for PET/ZnO, PET/Ag and PET/Ag/ZnO samples, respectively. It demonstrates that the color of the modified fabrics becomes a little bit blueish for PET/ZnO sample and more yellowish for PET/Ag and PET/Ag/ZnO samples.

All in all, the color difference among the prepared samples and the raw PET fabric is acceptable as the lower value is more preferred for textile and garment industry.

Antibacterial Efficiency

Bactericidal activities can be imparted to textile goods via in situ formation and deposition of a variety of metal oxide and metal nanoparticles on the textile surface as an affordable effective route [38,39]. In this regard, producing antibacterial textiles in various forms of fiber, fabric and polymeric membrane for medical usages is widely followed up by many research groups in the world [38,45,46]. Here, the raw PET fabric and diverse modified samples were evaluated from bactericidal point of view with considering Gram-negative bacteria (*Escherichia coli*) and as Gram-positive bacteria (*Staphylococcus aureus*). The results of antibacterial performances of the samples are given in Table 2 with regard to bacteria reduction percentage. Based on Figure 5, colonies of both photogenic bacteria can be seen

Table 2. Bactericidal activities of the raw PET fabric and different nano-treated samples

Sample	R (%)	
	S. aureus	*E. coli*
Raw PET	-	-
PET/ZnO	71	63
PET/Ag	94	91
PET/Ag/ZnO	99	93

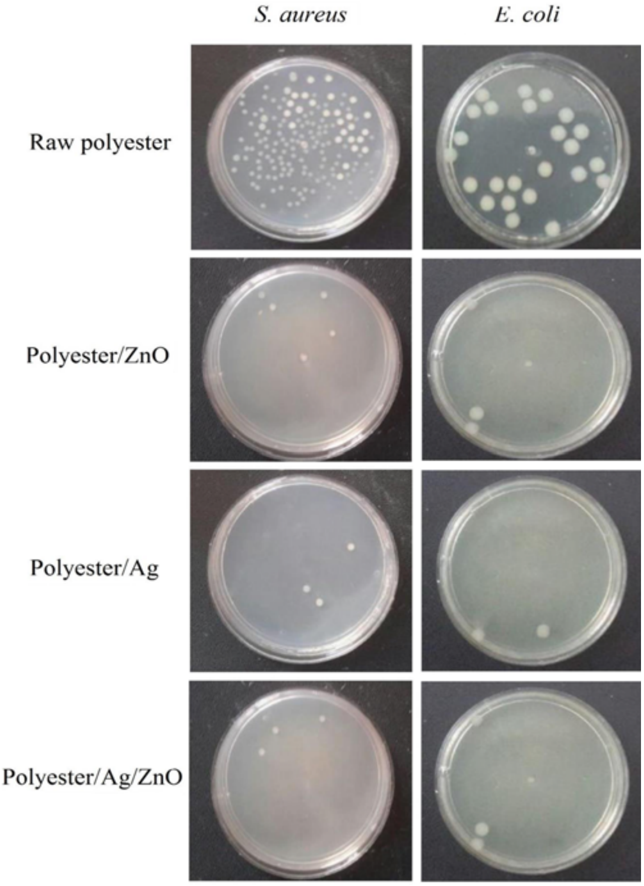

Figure 5. Antibacterial efficiency of raw PET and diverse prepared samples.

for the raw PET fabric representing no antibacterial activities of the raw sample. The raw fabric, therefore, is a good place for photogenic bacteria landing, growing and transferring which is unpleasant matter.

The nano-treated samples including PET/ZnO, PET/Ag and PET/Ag/ZnO have proper bactericidal performances of 71, 94, 99 % toward *Staphylococcus aureus* and 63, 91 and 93 % against *Escherichia coli* bacteria, respectively. According to the obtained results, formation and loading of different nanoparticles of silver, zinc oxide and combination of them on the fabric surface can impart appropriate antibacterial activates to the ultimate fabricated fabrics. The feasible proposed mechanisms for bactericidal effectiveness of silver and zinc oxide nanoparticles reported in literature are listed below [31,41,44]:

a) Bacterial cell membrane destruction through creating reactive oxygen species (ROS) by nanoparticles
b) Forming oxidative stress by nanoparticles together with physical interaction of them in contact of bacteria cell with abrasive surface texture of the nanoparticles
c) Releasing silver and zinc ions through water absorption which can react with microorganisms upon surface oxidation
d) Damaging the lipids, DNA and proteins of the bacteria cell and inhibiting biochemical processes of them, finally leading to rupture and death of the bacteria.
e) Higher surface area obtained from nano-size of the nanoparticles can also highly contribute to be more efficient for contacting with the photogenic bacteria in comparison with the bulk or mico-size particles.

In addition, as can be observed combination of Ag and ZnO nanoparticles triggers to have a synergistic impact on bactericidal effectiveness of the modified sample and enhance its performance against both photogenic bacteria compared to the sample treated by only zinc oxide nanoparticles. In fact, presence of silver nanoparticles known with excellent antibacterial activity among the metal and metal oxide nanoparticles can help to promote bactericidal performance of PET/Ag/ZnO sample [31].

Altogether, the paper at hand presents an affordable clean method to impart antibacterial effectiveness to PET substrates by wet chemical formation of silver, zinc oxide and silver/zinc oxide nanoparticles on the fabric surface utilizing *Seidlitzia rosmarinuser* ashes.

Mechanical Performance

Mechanical properties of a textile can be varied through any type of textile finishing and modification [6,30]. On this basis, it is valuable to assess influence of nano-functionalization of PET fabric on mechanical properties of the prepared samples. Table 3 indicates the mechanical performances of the raw PET, hydrolyzed PET, PET/ZnO, PET/Ag and PET/Ag/ZnO including tensile strength and bending length of the samples.

The raw PET fabric points out a bending length of 2.20 cm which experiences a noticeable decline for the hydrolyzed and nano-treated samples. Bending length value of the hydrolyzed PET, PET/ZnO, PET/Ag and PET/Ag/ZnO samples is 1.07, 1.25, 1.17 and 1.29, respectively, expressing softer handle and greater flexibility for all the modified samples. Indeed, alkaline hydrolysis of PET fibers in presence of *Seidlitzia rosmarinuser* ashes is the reason for this phenomenon. This is in consent of mentioned works in literature explained such effect of alkaline hydrolysis of PET even along with formation of nanoparticles on the fiber

Table 3. Mechanical features of the varied prepared samples

Sample	Bending length (cm)	Maximum load (N)	CV (%)
Raw PET	2.20	357.8	0.70
Hydrolyzed PET	1.07	320.1	0.14
PET/ZnO	1.25	365.2	0.80
PET/Ag	1.17	369.8	0.80
PET/Ag/ZnO	1.29	373.9	0.90

surface producing PET fabrics with silk like hand feel [44].

Moreover, tensile strength extent is 357.8 N for the raw PET fabric which diminishes to 320.1 N for the hydrolyzed PET sample. It is clear that this reduction of tensile strength is relevant to weight loss, formation of some oligomers and separation of PET backbone in some parts through hydrolysis in alkaline condition. In contrast, tensile strength of all the modified fabrics by nanoparticles augments owing to formation and deposition of nanoparticles on the fabric surface. The nanoparticles, in fact, play a role as fillers inhibiting stress concentration over the fabric and also they can form nano cross-linking among the PET chains leading to enhancement of the tensile strength of the modified fabrics [6,30]. Nonetheless, since alkaline hydrolysis of the PET is taken place at the same time of nanoparticles synthesis the value of tensile strength improvement is slight. Similar function of nanoparticles formation on tensile strength of different fabrics was detected in literature [6,30]. On the whole, an improvement in tensile strength together with a softening influence on hand feel of the fabric is achieved through modification of the PET fabric via silver, zinc oxide and silver/zinc oxide nanoparticles.

Resistance Against Ignition

Application of different nanoparticles on diverse textile fabrics may change the behavior of the modified fabrics against ignition which can be considered as a parameter of textile finishing [32,33,39]. On this basis, char yield of the different treated fabrics was determined by considering the weight of the fabric before and after heating at 600 °C for 3 h. The raw PET fabric exhibits a char residue of 2 % which is probably due to some impurities on the fabric surface. Furthermore, the char residue is 2 % for the hydrolyzed PET sample, while improves to 37.34, 30.98 and 28.57 % for PET/ZnO, PET/Ag and PET/Ag/ZnO samples, respectively. The reason for increase of the char residue is presence of nanoparticles as non-flammable char residues on the fabric surface [33,39].

In addition, photograph of vertical flammability test for the raw and diverse modified fabrics is illustrated in Figure 6. The char length is further considered for different samples to specify how the fabric resists against ignition. The raw fabric indicates a char length of 50 mm, whereas it alters to 31, 53 and 50 mm for PET/ZnO, PET/Ag and PET/Ag/ZnO samples, respectively. In other words, the resistance of the fabric against ignition increases for PET/ZnO sample, decreases slightly for PET/Ag sample and remains unchanged for PET/Ag/ZnO sample. The promotion of flame-resistant property of the modified fabric is due to the action of ZnO nanoparticles on the fabric surface as physical barriers forming non-flammable char in condensed phase and possibly trapping active radicals in vapor phase [33]. Also, the observed decrease is related to formation and loading of silver nanoparticles with high thermal conductivity on the fabric surface which can simplify heat transfer over the fabric leading to greater char length. For PET/Ag/ZnO sample, the char length has no change possibly owing to have a combination of aforementioned phenomenon. All in all, the results suggest that formation of nanoparticles with low thermal conductivity such as ZnO nanoparticles on textile fabric can impart a flame-resistance effect on the modified fabrics, while deposition of high thermally conductive nanoparticles namely Ag nanoparticles on the fabrics may lead to diminish resistance against ignition for the resultant samples.

Conclusion

This contribution presents deposition of Ag, ZnO and ZnO/Ag nanoparticles on PET substrates via in situ wet chemical technique utilizing available *Seidlitzia rosmarinuser* ashes as an affordable clean method. Replacement of hazardous chemicals such as toxic reductants and solvents as well as simplification of the processing for industry through one-step processing instead of separate synthesis and buying nanoparticles are the advantages of this route from the both human health/environmental and economic observations. The nano-treated samples including PET/ZnO, PET/Ag and PET/Ag/ZnO have proper bactericidal performances of 71, 94, 99 % toward *Staphylococcus aureus* and 63, 91 and 93 % against *Escherichia coli* bacteria, respectively. This is due to formation of nanoparticles with bactericidal activity trait on

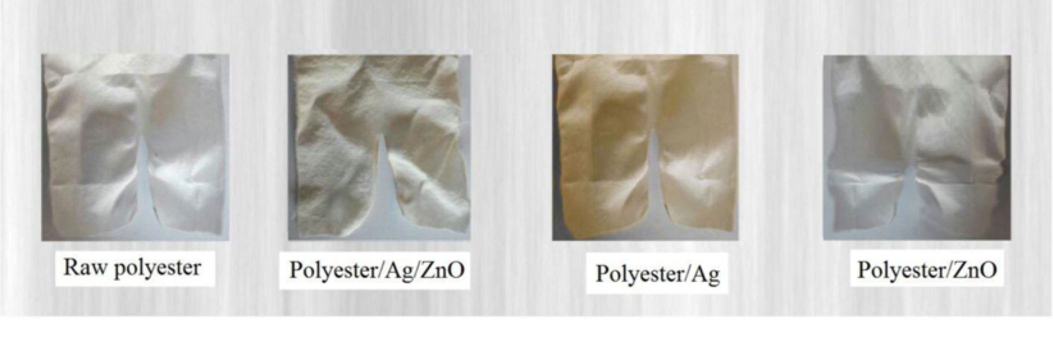

Figure 6. Photograph of vertical flammability test for raw and modified PET fabrics.

the surface of the modified fabrics. Also, the color difference among the prepared samples and the raw PET fabric is relatively low which is preferred for textile and garment industry. Tensile strength of the modified fabrics, further, was slightly enhanced in comparison with the raw sample due to nanoparticles formation over the fabric surface. Also the modified fabrics had softer handle and better flexibility. In addition, wettability of all the modified samples together with resistance to ignition in the case of ZnO deposition on the fabric was promoted. These are associated to surface modification of PET fabrics under alkaline condition and presence of ZnO nanoparticles with low thermal conductivity feature on the surface acting as physical barriers against propagating fire. All in all, the rendered technique in this research can contribute to textile industry for producing antibacterial textiles with proper properties using a clean way through formation of nanoparticles.

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