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Eco-Friendly In Situ ZnO Synthesis on PET Fabric Using Oxygen Plasma and Plant Waste

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Abstract: This study presents an eco-friendly protocol for the hydrophilization of polyethylene terephthalate (PET) fabric and the in situ synthesis of ZnO particles. The alkaline medium and reducing agent for ZnO synthesis were prepared as aqueous extracts from wood ash and pomegranate peel, respectively. Due to the hydrophobic nature of the PET fabric, oxygen plasma treatment was included in the process. The influence of plasma treatment in different synthesis steps on the formation of ZnO and consequently on the morphological, colour and ultraviolet (UV) protective properties of the samples was discussed. The study showed that incorporating oxygen plasma treatment before immersing the samples in each solution for the ZnO in situ synthesis (natural alkaline medium of wood ash, zinc salt and natural reducing agent from pomegranate peel) produced PET fabric with the most uniform ZnO layer without visible cracks and the highest UV-blocking ability with a UV protection factor (UPF) of 300+. The colour measurements showed that increasing the number of plasma treatments leads to higher colour strength of the samples. Herein, a novel protocol for the production of protective PET fabrics is presented, which is also an example of a completely environmentally benign textile functionalization process.

Keywords: polyester; ZnO; zinc oxide; in situ synthesis; green synthesis; oxygen plasma

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1. Introduction

Polyethylene terephthalate (PET), which has excellent physical and chemical properties, is the most commonly used polymer for the production of synthetic fabrics [1]. However, due to the high hydrophobicity of the raw PET fibres [2,3], increasing wettability is crucial for successful functionalisation. Since conventional textile treatments (e.g., alkaline treatment for increasing hydrophilicity) produce a large amount of often harmful wastewater [4], the development of environmentally friendly functionalisation processes is needed. Zinc oxide (ZnO) has been intensively researched due to its multifunctional properties when applied to textiles and labelled as "generally recognised as a safe substance" by the US Food and drug administration [5]. Since the typical process of ZnO synthesis and application involves the use of reducing, stabilising, and binding agents, and the procedures are usually carried out at high temperatures, environmentally friendly protocols for in situ (direct) and ex situ syntheses of ZnO on textiles are developing rapidly. Many plant extracts have already been used for the in situ synthesis of ZnO nanoparticles, especially on cotton fabrics, either as reducing or stabilising agents or to impart new properties to the material, such as antimicrobial properties or colour. However, it was soon realised that fully green syntheses performed directly on a textile substrate are not easily achievable, and the use of classical reducing agents and solvents was often further pursued in addition to the natural extract. There are only a few published studies in which green in situ synthesis was performed directly (in situ) on a textile substrate using only natural aqueous extracts [6–8], without any chemicals acting as an alkaline medium or reducing agent. However, those

syntheses were performed on cotton fabrics. Generally, the authors concluded that for the green synthesis of ZnO on cotton, two criteria must be met, i.e., the alkaline conditions [9,10] and the presence of phenolic compounds in the natural extract is necessary for the synthesis to take place [6,7]. Moreover, it was discovered that the sequence of synthesis solutions is crucial to obtain small and uniformly distributed ZnO particles [7]. Based on the obtained results, this study presents the implementation of the suitable in situ ZnO synthesis protocol described in Verbič et al. 2022 [7] on a new textile substrate. The synthesis was performed by immersing samples in three synthesis solutions: natural alkaline medium, zinc precursor and natural reducing agent. The alkaline medium and reducing agent were prepared from plant waste that would normally be discarded. An aqueous wood ash extract was used as a natural alkaline medium and aqueous pomegranate peel extract as a natural reducing agent. Since this procedure was performed on a synthetic fabric (PET) for the first time, the properties of the material had to be taken into account and the procedure had to be modified accordingly. Due to the hydrophobic nature of PET, the protocol was modified by adding an oxygen plasma treatment before immersing the samples in the synthesis solutions. The samples were plasma treated before immersion in wood ash extract, before immersion in wood ash extract and zinc acetate, or before immersion in wood ash extract, zinc acetate and pomegranate peel extract. Plasma was selected because it is considered an eco-friendly technology that avoids waste production compared to wet-chemical functionalization processes [11–13]. Furthermore, with plasma technology, surface properties can be improved without affecting the bulk properties of the textile material [9]. In our research, the effect of the oxygen plasma treatment in each individual step of the synthesis was observed and discussed.

2. Materials and Methods

2.1. Materials

De-lustred polyethylene terephthalate (PET) (weight: 75 g/m^2, number of warp threads: 43 threads/cm, number of weft threads: 27 threads/cm) (Commerce, Ljubljana, Slovenia) and zinc acetate dihydrate (Honeywell, Charlotte, NC, USA) were used in this study.

2.2. Preparation of Natural Extracts

The natural extracts used in the study were prepared according to procedures described in Verbič et al. 2022 [7]. The aqueous extract of wood ash was prepared by adding the wood ash powder to the distilled water at a 10 g/L concentration. After 10 min at room temperature, the mixture was vacuum-filtered, and the obtained extract was used as an alkaline medium. The procedure is schematically depicted in Figure 1a. The aqueous extract of pomegranate peel was used as a natural reducing agent. Pomegranate fruit peels were washed with distilled water and air-dried. The dried peels were ground to a powder using a kitchen blender. The pomegranate peel powder was added to twice-distilled water at a concentration of 50 g/L, and the mixture was heated up to its boiling point. After 5 min of boiling, the mixture was left to cool to room temperature for 2 h and then centrifuged to separate the solid particles from the liquid extract. Lastly, the liquid extract was vacuum-filtered. The procedure is depicted in Figure 1b.

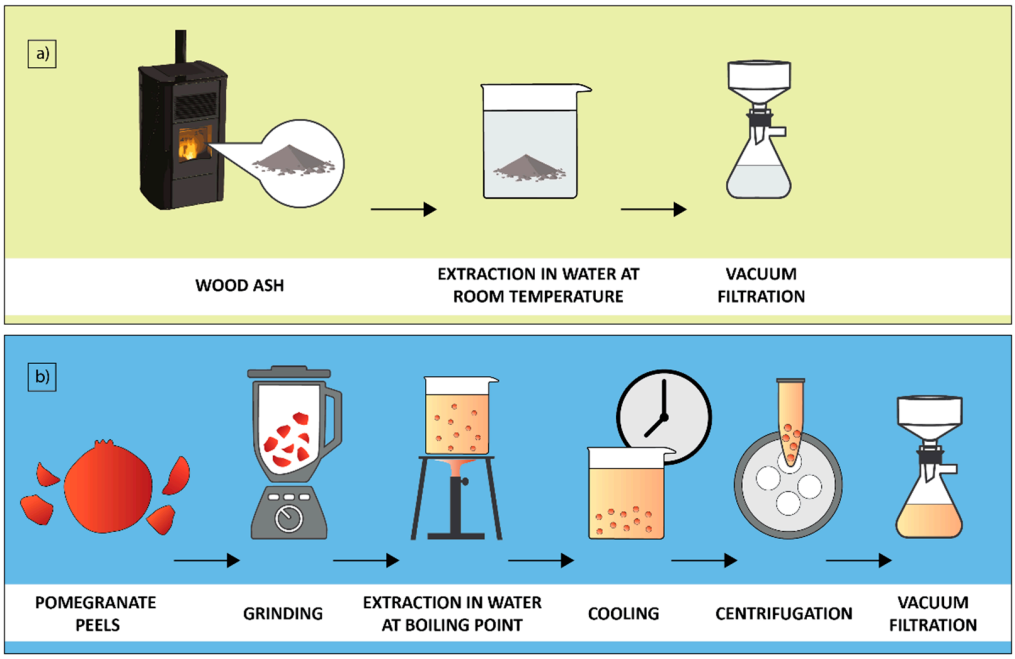


Figure 1. Schematic presentation of wood ash extract (**a**) and pomegranate peel extract (**b**) preparation.

2.3. Plasma Treatment of PET Fabric

To determine the importance of plasma surface activation in the in situ ZnO synthesis process, the PET samples were plasma treated before immersion in the synthesis solutions. The inductively coupled plasma system consisted of a 2 m long borosilicate tube with an outer diameter of 20 cm. The tube ends were terminated with aluminium flanges with movable closures. The system was pumped by a 2-stage rotary vane vacuum pump with an effective pumping speed of 65 m^3/h. After reaching the base pressure of 2 Pa, oxygen gas with a purity of 5.0 was introduced via a mass flow controller (FCU4, VACOM, Großlöbichau, Germany). The flow was 56 sccm, and the total pressure (residual atmosphere and oxygen) was 20 Pa. The reactor was cooled with forced air. A copper coil in a double-coil configuration (4 turns of each coil) was wound around the tube as schematically depicted in Figure 2. The coil was connected to a self-made matching network with adjustable vacuum capacitors (COMET, Flamatt, Switzerland). The matching network was further connected to a radiofrequency generator via a coaxial cable. The generator operates at a frequency of 27.12 MHz, and its nominal forward power is 10 kW. A fixed forward power of 1.8 kW was used in this set of experiments. PET samples were cut to 10 cm × 15 cm. Each sample was treated for 4 s in inductively coupled oxygen plasma. After each treatment, the system was flooded with filtered ambient air, fresh pieces were put into the tube, and the whole process of evacuation, gas leakage, and plasma treatment was repeated.

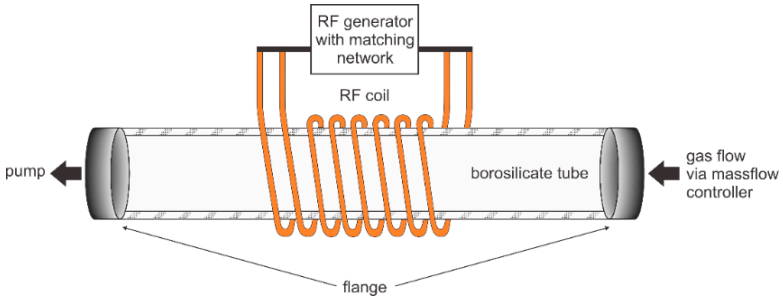
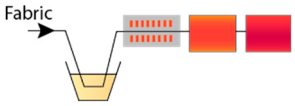
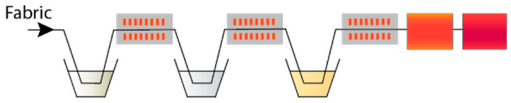
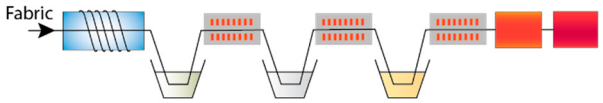
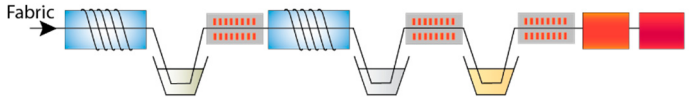
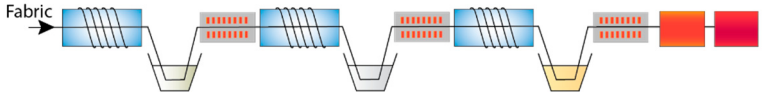


Figure 2. Schematic presentation of plasma system used.

2.4. In Situ Synthesis of ZnO on PET Fabric

For the in situ synthesis of ZnO, the procedure described in Verbič et al. [7] was used and applied for the first time on PET fabric. The synthesis was performed in three steps, the first consisting of immersion in aqueous wood ash extract, the second in 0.5 M zinc acetate dihydrate and the third in aqueous pomegranate peel extract. The samples remained immersed in each synthesis solution for 1 min and dried in a continuous flow dryer (Werner Mathis, Zurich, Switzerland). At the end of functionalization, the samples were dried in a laboratory oven at 100 °C for 30 min and cured at 150 °C for 5 min. Table 1 shows different functionalization combinations, as plasma was used at different points of various syntheses. Besides raw PET fabric, samples were functionalized with pomegranate peel extract only ("Extr") and without plasma functionalisation ("Ash-ZnAc-Extr"). Three different procedures of ZnO in situ synthesis including plasma functionalization were performed: using plasma treatment only before immersion in wood ash extract ("P-Ash-ZnAc-Extr"), using plasma treatment before immersion in wood ash extract and zinc acetate ("P-Ash-P-ZnAc-Extr") and using plasma treatment before immersion in wood ash extract, zinc acetate and pomegranate peel extract ("P-Ash-P-ZnAc-P-Extr").

Table 1. Description of functionalisation procedures and their abbreviations.

Sample Code	Description	
Extr	Immersion in pomegranate peel extract	
Ash-ZnAc-Extr	Immersion in wood ash, zinc acetate and pomegranate peel extract	
P-Ash-ZnAc-Extr	Plasma treatment, immersion in wood ash, zinc acetate and pomegranate peel extract	
P-Ash-P-ZnAc-Extr	Plasma treatment, immersion in wood ash extract, plasma treatment, immersion in zinc acetate and pomegranate peel extract	
P-Ash-P-ZnAc-P-Extr	Plasma treatment, immersion in wood ash extract, plasma treatment, immersion in zinc acetate, plasma treatment, immersion in pomegranate peel extract	

2.5. UV Protection Factor Measurements

The sample's ultraviolet protection factor (UPF) was determined according to the test method AATCC 183 [14]. The measurements were performed using Lambda 850+ UV/Vis spectrophotometer (Perkin Elmer, Waltham, MA, USA). The transmission of ultraviolet radiation through the samples was measured in the spectral range between 290 and 400 nm and the UPF rating and UVR protection categories were determined based on the measured UV transmission according to the Australian/New Zealand Standard: Sun Protective Clothing—Evaluation and Classification [15].

2.6. Colour Measurements

CIE L*a*b* values of the samples were measured using the Datacolor Spectro 1050 reflectance spectrophotometer (Datacolor, Luzern, Switzerland). The sample's colour strength (K/S values) was calculated from the reflectance measurements.

2.7. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

The morphology of the raw and functionalised PET samples was examined using a JSM-6060 LV (Jeol, Japan) scanning electron microscope. The samples were coated with a layer of gold before SEM analysis to ensure sufficient electrical conductivity. The samples were coated using a Jeol JFC-1300 auto fine coater for 60 s at 30 mA, and the thickness of the gold coating was approx. 19 nm.

EDS was performed with an environmental SEM Quanta 650 operated in low-vacuum mode at 70 Pa, therefore no coating was needed. It has a tungsten filament, excellent analytical current of up to 2000 nA, and the latest state of the art Oxford Live EDS Ultim max 40 mm^2 SDD detector.

3. Results and Discussion

Completely green synthesis of ZnO was performed directly on PET to accomplish excellent UV protective properties of the fabric. Due to the PET's hydrophobicity, the samples were pre-treated with inductively coupled oxygen plasma to achieve better adsorption of the synthesis solutions. Plasma activation causes the separation of hydrogen from the PET polymer backbone, generating free radicals that can interact with compounds present in the environment. Depending on the gas used, different new functional groups can be created. Oxygen is commonly used because it significantly improves hydrophilicity [1]. Besides the separation of hydrogen from polymer backbone, according to Ventzek's theory [16], oxygen atoms can also degrade aromatic rings. Vacuum ultraviolet (VUV) radiation arising from oxygen plasma (the main line is at 130 nm) definitely accelerates the ring's destruction [17], but not much systematic work has been published. The treatment of polymers by oxygen plasma is unlikely to cause the formation of larger volatile molecules since the oxidation is supposed to be complete (i.e., formation of CO_2 and H_2O molecules). To determine the importance of oxygen plasma treatment in each step of the synthesis, three different samples with plasma functionalisation were prepared. The first one included plasma treatment only before immersion in wood ash extract ("P-Ash-ZnAc-Extr"), while the next two included plasma treatment also before the immersion in zinc acetate ("P-Ash-P-ZnAc-Extr") and zinc acetate and pomegranate peel extract ("P-Ash-P-ZnAc-P-Extr"). The UV protective properties, CIE L*a*b* colour values, colour strength, SEM micrographs and EDS analysis results are presented below.

The UV protection ability, colour strength (K/S values) and colour coordinate (CIE L*a*b*) values of the samples are presented in Table 2. Since ZnO has excellent UV blocking ability, using UV protection measurements of our samples, we can determine whether the transition from the zinc salt to ZnO was achieved. The UPF value of the raw PET is 16.5, which is specified as minimal UV protection according to the AS/NZS: 4399:2017 standard. When the sample was treated with pomegranate peel extract only, the UPF value increased to 34.9, which corresponds to good UV protection. Comparing the UPF values of the samples where the in situ synthesis protocol was performed, it is evident that all samples exhibit high UV blocking ability, marked as excellent UV blocking ability (UPF 50+) according to the AS/NZS standard. Using the synthesis protocol without plasma treatment ("Ash-ZnAc-Extr"), a UPF value of 177.9 was achieved. This value further increased when plasma treatment was included in the synthesis protocol. The sample "P-Ash-ZnAc-Extr", where samples were treated by plasma only before the immersion in wood ash extract, reached a UPF value of 218.6 and the value increased even further when the plasma treatment was performed between the immersions in synthesis solutions. The protocol containing plasma treatment also before immersion in the zinc precursor solution ("P-Ash-P-ZnAc-Extr") gave a UPF value of 295.2. At the same time, the protocol that

included plasma treatment, not only before immersion in the zinc precursor, but also before the immersion in the pomegranate peel extract ("P-Ash-P-ZnAc-P-Extr"), exhibited a UPF value of 303.7.

Table 2. Ultraviolet protection factor (UPF), colour strength (K/S value), CIE L*a*b* colour coordinates and images of scanned raw and functionalised PET samples.

Sample	UPF	K/S	L*	a*	b*	Scanned Image
Raw PET	16.5	0.03	93.1	−0.4	0.0	
Extr	34.9	2.21	76.2	5.1	22.5	
Ash-ZnAc-Extr	177.9	7.48	72.2	1.6	44.7	
P-Ash-ZnAc-Extr	218.6	8.32	76.2	−2.5	50.5	
P-Ash-P-ZnAc-Extr	295.2	11.46	74.9	0.2	53.4	
P-Ash-P-ZnAc-P-Extr	303.7	12.14	73.7	1.0	54.6	

Since the UV blocking ability can be significantly affected by the sample's colour [18], the colour measurements were performed. The CIE L*a*b* results are further presented to determine if there is a correlation between the colour of the samples and UV protection. Based on the results of the CIE L*a*b* colour measurements and the sample's scanned images, it can be observed that there are no significant colour differences between the samples where in situ ZnO synthesis was performed. Nonetheless, as mentioned earlier, there are significant differences in these sample's UPF values. While the lightness values of the samples without plasma treatment ("Ash-ZnAc-Extr") were 72.2, these values were slightly higher for the samples where plasma treatment was included in the protocol. The values ranged from 73.7 for the sample "P-Ash-P-ZnAc-P-Extr" and 76.2 for the sample "P-Ash-ZnAc-Extr". This means that the plasma-treated samples had a slightly lighter colour. The values of the green–red colour coordinates are on the red side of the colour coordinate for the samples "Ash-ZnAc-Extr" (CIE a* = 1.6), "P-Ash-P-ZnAc-Extr" (CIE a* = 0.2) and "P-Ash-P-ZnAc-P-Extr" (CIE a* = 1.00), while for the sample where the plasma treatment was performed only before immersion in the wood ash extract ("P-Ash-ZnAc-Extr") the value is shifted to the green side of the coordinate (CIE a* = −2.5). The values of the blue–yellow coordinate range from 44.7 to 54.6. Again, the lowest CIE b* value is observed for the sample where the synthesis was performed without plasma treatment, meaning that the sample is the most blueish. For the plasma-treated samples, it is evident that the CIE b* colour coordinate values increased with increasing the number of plasma treatments (from 50.5 to 54.6) meaning that the samples become more yellow. The same is not observed with the red–green coordinate, where the values do not increase with increasing the number of plasma treatments. While the highest value (CIE a* = 1.6) was measured for the sample without plasma pre-treatment, the lowest value (CIE a* = −2.5) was obtained with only plasma treatment before immersion in wood ash extract ("P-Ash-ZnAc-Extr"). All the above suggests that the samples without plasma functionalization were more reddish, and contrary, the value decreased when plasma functionalization was included, thus the samples were less red ("P-Ash-P-ZnAc-Extr" and "P-Ash-P-ZnAc-P-Extr") or the value was

even shifted to the green side of the colour coordinate ("P-Ash-ZnAc-Extr"). Besides colour, also the colour strength values (K/S) were analysed. The higher K/S value means that the sample contains more colourant [19]. The raw PET fabric had a K/S value of 0.03. The value increased to 2.21 when the sample was treated with pomegranate peel extract only. The sample where in situ ZnO synthesis was performed without the plasma treatment exhibited a value of 7.48. The value further increased when the plasma treatment was included in the functionalisation process. Inductively coupled oxygen plasma treatment, among other effects, increases the number of oxygen functional groups on the treated material's surface. The oxygen plasma oxidizes the PET's C−H groups to COOH or C−OH groups, which improves surface hydrophilicity [20]. Consequently, more compounds from the wood ash extract, zinc salt, or pomegranate peel extract can be adsorbed onto the fabric's surface. The sample where the surface was treated with plasma only before the immersion in wood ash extract ("P-Ash-ZnAc-Extr") had a K/S value of 8.32. When the plasma treatment was also performed before the immersion in zinc salt ("P-Ash-P-ZnAc-Extr"), the value increased to 11.46. Since plasma increases the number of binding sites on PET, more of the solution's constituents can be adsorbed on the fabric's surface. The highest amount of extract can be absorbed on the surface of the sample when the plasma treatment was performed also before immersion in pomegranate peel extract ("P-Ash-P-ZnAc-P-Extr") resulting in the highest colour strength (K/S value = 12.14). This is in accordance with the results of other authors, who reported significantly increased adsorption of natural dyes after the plasma functionalisation [21,22]. The described differences are visible on the sample's scanned images below (Table 2).

The PET samples where in situ ZnO synthesis was performed were additionally analysed with a scanning electron microscope (SEM) and compared with the raw PET sample. The SEM micrographs are presented in Figure 3. These micrographs show that when the synthesis protocol was performed without plasma treatment ("Ash + ZnAc + Extr"), the entire fabric surface was coated, but the coating did not adhere well to the fibres. The coating had large cracks and in certain areas, it had already begun to detach from the fabric. This is in agreement with the UPF values discussed previously, as this sample had the lowest UPF value of the in situ ZnO functionalised samples. All of the oxygen plasma-treated PET samples had a much thicker ZnO coating. While the morphology of the synthesised particles was similar for the "P-Ash-ZnAc-Extr", "P-Ash-P-ZnAc-Extr", and "P-Ash-P-ZnAc-P-Extr" samples, there was a big difference in the coating adhesion and surface homogeneity. When plasma treatment was performed only before the immersion in wood ash extract ("P-Ash-ZnAc-Extr"), cracking of the ZnO layer is visible between all individual fibres. The cracking of the ZnO layer is not present when the sample was plasma treated prior to immersions in every synthesis solution ("P-Ash-P-ZnAc-P-Extr"). From the surface morphology analyses, we can conclude that oxygen plasma functionalization, which creates numerous new binding sites on PET fabric, consequently increases the uniformity of the synthesised ZnO layer. The protocol including plasma treatment before immersion in every synthesis solution gave uniformly ZnO-coated PET with homogeneous and stable coating, without any cracking. Consequently, the UPF value of this sample was the highest.

To analyse how plasma functionalisation in the different synthesis steps affects the ZnO formation, the elemental composition of the samples was performed. The quantity of carbon, oxygen, and zinc was determined, and the results are presented in Figure 3 and Table 3. The raw PET sample is composed of 65.8 wt.% carbon and 33.4 wt.% oxygen, and no zinc is present in the sample. The samples where the synthesis procedure was performed without the plasma pre-treatment had a lower value of carbon (54.0 wt.%) but a higher amount of oxygen on the surface (39.0 wt.%). This can be explained by the presence of polyphenols from the natural extract in which the sample was immersed in the last step of the synthesis ("Ash-ZnAc-Extr"). The measured zinc content was 6.9 wt.%, which is fairly high. However, from the SEM micrographs, it appears that the ZnO layer without the plasma pre-treatment is not adequately adhered to PET fibres. Activation of the

PET's surface by oxygen plasma before the immersion in wood ash extract ("P-Ash-ZnAc-Extr") increased the hydrophilicity of the sample and consequently the amount of zinc and oxygen on the surface also increased (7.1 and 42.3 wt.%, respectively). Consequently, the carbon content decreased to 46.9 wt.%. When the oxygen plasma treatment was performed also before immersion in the zinc acetate ("P-Ash-P-ZnAc-Extr") and zinc acetate and pomegranate peel extract ("P-Ash-P-ZnAc-P-Extr"), the zinc content increased even further to 8.1 and 11.0 wt.%. This means that the inclusion of oxygen plasma in the functionalization process hydrophilizes the PET sample and supports the formation of ZnO, which is consequently uniformly distributed, as already confirmed by the UPF and SEM micrograph results discussed previously.

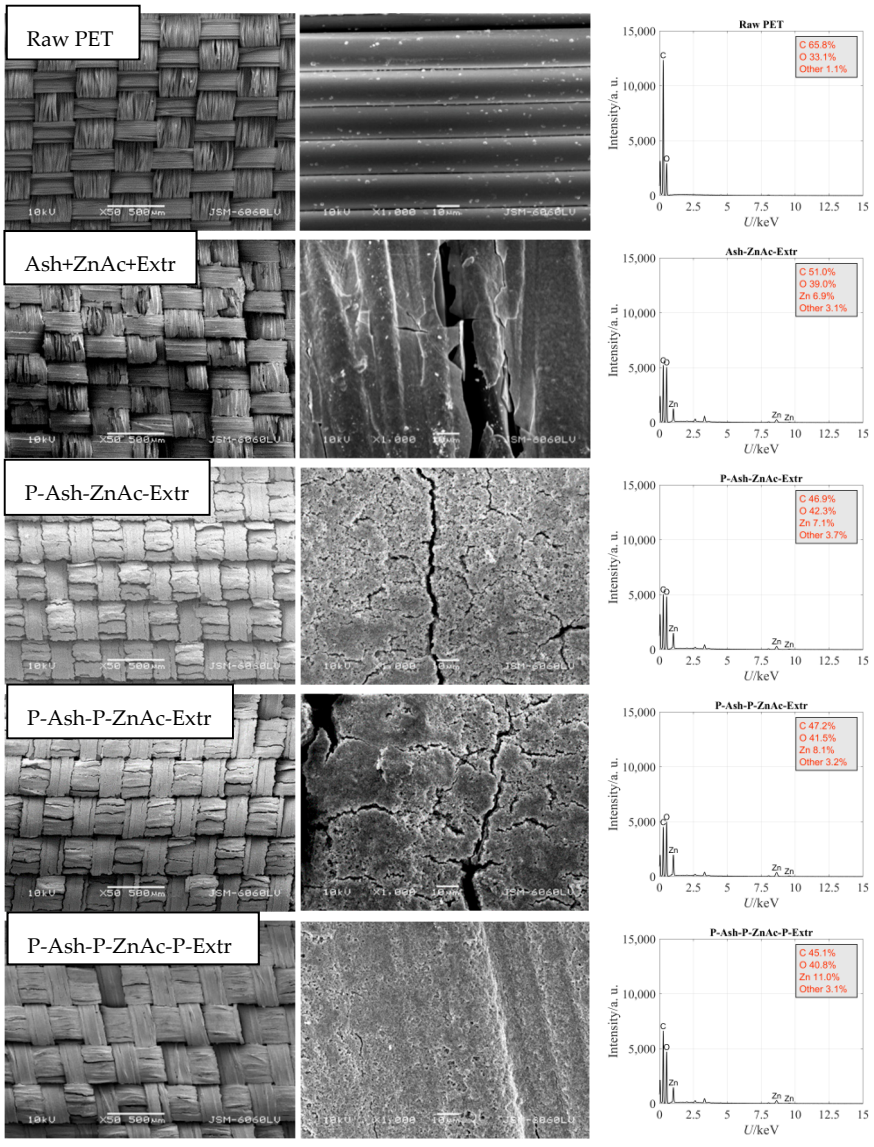


Figure 3. SEM micrographs and EDS analysis of raw PET and samples "Ash+ZnAc+Extr", "P-Ash-ZnAc-Extr", "P-Ash-P-ZnAc-Extr", and "P-Ash-P-ZnAc-P-Extr".

Table 3. Quantity of carbon, oxygen, and zinc (wt.%) of the raw and functionalised PET samples determined by EDS analysis.

Sample	C (wt.%)	O (wt.%)	Zn (wt.%)	Other (wt.%)
Raw PET	65.8	33.1	0.0	1.1
Ash-ZnAc-Extr	51.0	39.0	6.9	3.1
P-Ash-ZnAc-Extr	46.9	42.3	7.1	3.7
P-Ash-P-ZnAc-Extr	47.2	41.5	8.1	3.2
P-Ash-P-ZnAc-P-Extr	45.1	40.8	11.0	3.1

4. Conclusions

In this study, ZnO was synthesised directly on PET fabric using zinc acetate as a precursor and natural aqueous plant waste extracts as the alkaline medium and reducing agent. Since PET fabric is naturally hydrophobic, oxygen plasma treatment was incorporated into the functionalization process to achieve hydrophilization. Three different plasma treated samples were prepared: (i) a sample with plasma treatment before immersion in wood ash extract, (ii) a sample with plasma treatment before immersion in wood ash extract and zinc acetate, and (iii) a sample with plasma treatment before immersion in wood ash extract, zinc acetate, and pomegranate peel extract. For comparison, a raw PET sample, a sample functionalized with pomegranate peel extract only, and a sample where in situ synthesis was performed without plasma pre-treatment were prepared and analysed. The synthesis protocol, which includes oxygen plasma treatment prior to the immersion in every synthesis solution (alkaline medium from wood ash, zinc precursor and reducing agent from pomegranate peel) enabled the highest UV protective properties of PET sample with a UPF value 300+. In addition, plasma treatment before immersion in every synthesis solution resulted in the most uniformly distributed ZnO layer, with no visible cracking between fibres. While all functionalised PET samples in which in situ ZnO synthesis was performed exhibited excellent UV blocking ability, a significant difference in the adhesion of the ZnO layer to the fibres was observed, which increased with increasing the number of oxygen plasma pre-treatments. This study presents a completely eco-friendly in situ synthesis process using plant waste extracts and oxygen plasma to achieve new functional properties of PET fabric that could be used in clothing or technical textiles industry, e.g., as awnings, parasols, hats, textiles for architecture (canopies).

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

EDS	Energy dispersive spectroscopy
PET	Polyethylene terephthalate
SEM	Scanning electron microscopy
UPF	Ultraviolet protection factor
UV	Ultraviolet
VUV	Vacuum ultraviolet
ZnO	Zinc oxide

References

1. Štular, D.; Primc, G.; Mozetič, M.; Jerman, I.; Mihelčič, M.; Ruiz-Zepeda, F.; Tomšič, B.; Simončič, B.; Gorjanc, M. Influence of non-thermal plasma treatement on the adsorption of a stimuli-responsive nanogel onto polyethylene terephthalate fabric. *Prog. Org. Coat.* **2018**, *120*, 198–207. [CrossRef]
2. Gorenšek, M.; Gorjanc, M.; Bukošek, V.; Kovač, J.; Jovančić, P.; Mihailović, D. Functionalization of PET fabrics by corona and nano silver. *Text. Res. J.* **2010**, *80*, 253–262. [CrossRef]
3. Azeem, M.; Javed, A.; Morikawa, H.; Noman, M.T.; Khan, M.Q.; Shahid, M.; Wiener, J. Hydrophilization of Polyester Textiles by Nonthermal Plasma. *Autex Res. J.* **2021**, *21*, 142–149. [CrossRef]
4. Weerasinghe, D.U.; Perera, S.; Dissanayake, D.G.K. Application of biomimicry for sustainable functionalization of textiles: Review of current status and prospectus. *Text. Res. J.* **2019**, *89*, 4282–4294. [CrossRef]
5. Jiang, J.; Pi, J.; Cai, J. The advancing of zinc oxide nanoparticles for biomedical applications. *Bioinorg. Chem. Appl.* **2018**, *2018*, 18. [CrossRef]
6. Verbič, A.; Šala, M.; Jerman, I.; Gorjanc, M. Novel green in situ synthesis of ZnO nanoparticles on cotton using pomegranate peel extract. *Materials* **2021**, *14*, 4472. [CrossRef] [PubMed]
7. Verbič, A.; Brenčič, K.; Primc, G.; Gorjanc, M. Importance of protocol design for suitable green in situ synthesis of ZnO on cotton using aqueous extract of japanese knotweed leaves as reducing agent. *Forests* **2022**, *13*, 143. [CrossRef]
8. Aladpoosh, R.; Montazer, M. The role of cellulosic chains of cotton in biosynthesis of ZnO nanorods producing multifunctional properties: Mechanism, characterizations and features. *Carbohydr. Polym.* **2015**, *126*, 122–129. [CrossRef] [PubMed]
9. Irfan, M.; Naz, M.Y.; Saleem, M.; Tanawush, M.; Głowacz, A.; Glowacz, W.; Rahman, S.; Mahnashi, M.H.; Alqahtani, Y.S.; Alyami, B.A.; et al. Statistical study of nonthermal plasma-assisted ZnO coating of cotton fabric through ultrasonic-assisted green synthesis for improved self-cleaning and antimicrobial properties. *Materials* **2021**, *14*, 6998. [CrossRef] [PubMed]
10. Xu, J.; Huang, Y.; Zhu, S.; Abbes, N.; Jing, X.; Zhang, L. A review of the green synthesis of ZnO nanoparticles using plant extracts and their prospects for application in antibacterial textiles. *J. Eng. Fibers Fabr.* **2021**, *16*, 15589250211046242. [CrossRef]
11. Raslan, W.M.; El-Halwagy, A.A.; Elsayad, H. Recent advances in plasma/nanoparticles treatments of textile fibers. *J. Text. Coloration Polym. Sci.* **2020**, *17*, 87–105. [CrossRef]
12. Gorjanc, M.; Gorenšek, M.; Jovančić, P.; Mozetič, M. Multifunctional textiles—Modification by plasma, dyeing and nanoparticles. In *Eco-Friendly Textile Dyeing and Finishing*; Gunay, M., Ed.; Intech: Rijeka, Croatia, 2013; Volume 1, pp. 3–31.
13. Kan, C.W. *A Novel Green Treatment for Textiles: Plasma Treatment as a Sustainable Technology*; CRC Press: Boca Raton, FL, USA, 2014.
14. AATCC Test Method: 183. In *Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation Through Fabrics*; American Association of Textile Chemists and Colorists: Durham, NC, USA, 2020.
15. *AS/NZS 4399*; Sun Protective Clothing—Evaluation and Classification. Standards Australia/Standards New Zealand: Wellington, New Zealand, 2017.
16. Longo, R.C.; Ranjan, A.; Ventzek, P.L. Density functional theory study of oxygen adsorption on polymer surfaces for atomic-layer etching: Implications for semiconductor device fabrication. *ACS Appl. Nano Mater.* **2020**, *3*, 5189–5202. [CrossRef]
17. Zhang, Y.; Ishikawa, K.; Mozetič, M.; Tsutsumi, T.; Kondo, H.; Sekine, M.; Hori, M. Polyethylene terephthalate (PET) surface modification by VUV and neutral active species in remote oxygen or hydrogen plasmas. *Plasma Process. Polym.* **2019**, *16*, 1800175. [CrossRef]
18. Urbas, R.; Kostanjšek, K.; Dimitrovski, K. Impact of structure and yarn colour on UV properties and air permeability of multilayer cotton woven fabrics. *Text. Res. J.* **2011**, *81*, 1916–1925. [CrossRef]
19. Gorjanc, M.; Mozetič, M.; Primc, G.; Vesel, A.; Spasić, K.; Puač, N.; Petrović, Z.; Kert, M. Plasma treated polyethylene terephthalate for increased embedment of UV-responsive microcapsules. *Appl. Surf. Sci.* **2017**, *419*, 224–234. [CrossRef]
20. Elabid, A.E.; Zhang, J.; Shi, J.; Guo, Y.; Ding, K.; Zhang, J. Improving the low temperature dyeability of polyethylene terephthalate fabric with dispersive dyes by atmospheric pressure plasma discharge. *Appl. Surf. Sci.* **2016**, *375*, 26–34. [CrossRef]
21. Haji, A.; Ashraf, S.; Nasiriboroumand, M.; Lievens, C. Environmentally friendly surface treatment of wool fiber with plasma and chitosan for improved coloration with cochineal and safflower natural dyes. *Fibers Polym.* **2020**, *21*, 743–750. [CrossRef]
22. Dave, H.; Ledwani, L.; Chandwani, N.; Kikani, P.; Desai, B.; Nema, S.K. Surface modification of polyester fabric by non-thermal plasma treatment and its effect on coloration using natural dye. *J. Polym. Mater* **2013**, *30*, 14.