RESEARCH ARTICLE OPEN ACCESS

Titanium Dioxide Nanoparticles Finishing Of Atmospheric Pressure Plasma Treated Polyester Fabric for Inkjet Printing

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ABSTRACT
In the present study the application of the atmospheric pressure plasma (APP) to the polyester fabric has been investigated in order to enhance the printing properties of inkjet printed fabric instead of the traditional pretreatment process. Also plasma increase the fixation of titanium dioxide nanoparticles (TiO_2 NPs) inside the fiber.Different gases were investigated viz. oxygen (O_2), air, argon (Ar), nitrogen (N_2), O_2/Ar, air/Ar, and N_2/Ar, The effect of exposure time of plasma treatment at different discharge currents on the colour strength of treated polyester fabric printed with disperse ink was studied.Factors that affecting TiO_2 NPs treatment have been studied viz. TiO_2 conc., sodium alginate conc., sodium hypophosphite conc. (SHP), citric acid conc. Curing temperature and curing time. Different measurements to evaluate the treatment process have been investigated, i.e. color strength, UV protection, Anti-bleeding performance, self cleaning, antimicrobial properties, durability to wash, SEM and fastness properties. The results indicate that the increase in the K/S of modified polyester fabrics is depends profoundly on the plasma exposure time and the intensity of the current used irrespective of gas type. Also plasma improved anti bleeding performance more than sodium alginate treatment.Treating polyester samples with TiO_2- NPs improve their ultraviolet protection and colour strength values. The optimum condition for the treatment is TiO_2 NP.con.: 0.75% (o.w.f), 4 g/l SHP, 20 g/l Citric acid, curing temp. is 200, for 5 min.The result of durability to wash indicates to the strong bond formed between TiO_2NPs and the fiber.

Key words: Titanuim dioxide nanoparticles, Atmospheric pressure plasma, polyester, inkjet, antibleeding.

Date of Submission: 20-07-2018 Date of acceptance: 04-08-2018

I. INTRODUCTION

Inkjet printing is becoming increasingly important and popular for the printing of textiles (1) because of excellent pattern quality, considerably little pollution, and especially rapid response to the frequently shift of clothing fashion (2) . Inkjet printing furthermore allows visual effects such as tonal gradients and infinite pattern to repeat sizes that cannot be practically achieved with a screen printing process (3,4).polyester fabric is often used as inkjet printing substrate due to its special characteristics such as superior strength and resilience, Nevertheless, patterns which are directly printed on polyester fabrics with inks have poor color yields and bleed easily. Therefore, pretreatment of fabric must be done before printing to obtain better inkjet printing effects.(1)

Traditional preprocessing was sizing process with thickener, such as sodium alginate to modify the surface of fabrics. This process is very long and complicated, with huge energy and water consumption.(2)In recent years, researchers have paid great attention to plasma treatments on textiles (5-9). It has been reported that plasma treatments can enhance the wettability of the fiber surface mainly by oxidation and etching.The plasma technique one of the environmental friendly processes, plasma treatment has the following advantages: it only modifies the outermost thin layer of the surface, while the bulk properties will be kept untouched; lower chemical consumption and higher security; no waste water produced , less burden on environment and totally fit to the definition of ecological textile manufacturing(10).Nanotechnology and nanomaterials development have been flourishing. nanomaterials refer to materials with special properties, whose geometric dimension reaches nanoscale. Among nanomaterials, great importance has been attached to nano-oxide owing to its promising application prospect in textiles due to its outstanding characteristics. A typical example is that the photocatalysis and ultraviolet absorption properties of nano-TiO2. It can be utilized for antibacterial finishing and anti-ultraviolet finishing of textiles to meet the demand of multi-functional finishing of textiles (11). The application of nanomaterials has been widely reported (12-16).In the present study, titanium dioxide nanoparticles

(TiO2NP) treatment was carried out before inkjet printing to insert desirable properties to polyester fabric.

Also the application of the atmospheric pressure plasma (APP) to the polyester fabric has been investigated in order to improve titanium dioxide nanoparticles treatment and enhance the printing properties of inkjet printed fabric.

II. EXPERIMENTAL

1. Materials and Chemicals:

a. Fabric:

100% polyester fabric with warp yarn number 132, weft yarn number 58, weight of square meter 190/m^2 and width 120 cm was used throughout this work. The fabric was supplied by Misr Company for spinning and weaving, Mehalla El Kobra. Polyester fabric was washed with a solution containing 2.0 gm/l anionic detergent at 60ºC for 30 min. Then it was air dried at room temperature.

1.1. Ink:

In this work disperse ink jet (CYAN/BLUE) with trade cod (INK-1702 CYAN) was used and supplied by dye star company.

1.3 Chemicals and Auxiliaries:

- Titanium dioxide, nanopowder, 21 nm particle size (TEM), 99.5 % trace metals basis supplied by SIGMA- ALDRICH. CO. Germany.
- Commercial sodium alginate of low viscosity was supplied by Fluk Biochemika company.
- Sodium hypophosphite NaH_2PO_2 supplied by Merck Chemical Co., Germany.
- Citric acid, supplied by Al- Nasr Company, Egypt.
- Non -ionic detergent (Tanaterge SD) was supplied by Tanatex Sybron Co.

2. Technical procedures:

2.1. Plasma pretreatment

Polyester samples were subjected to atmospheric pressure glow discharge plasma (APGD) before inkjet printing process at different currents and periods of time with different gasses i.e. oxygen, nitrogen, and air.

Exposing time variables were 1, 3 and 5 min, while discharge current variables were 2, 4, 6, 8 and 10 mA.

2.1.1 Plasma reactor :

Atmospheric pressure dielectric-barrier discharge (DBD) resembles the electrical discharge between two metal electrodes separated by an insulating dielectric material with high dielectric strength Schematic diagram of the DBD reactor is shown in Figure 1. The discharge cell consists of two rectangular parallel, separated by Pyrex glass sheet through an O ring leaving a gap space of about 2mm. The upper electrode was a rectangular Al- sheet of 15.0 cm width & 20 cm length pasted on a rectangular (20X 25 cm^2) glass sheet of thickness 1.0 mm. While, the lower electrode was a bare rectangular stainless steel plate (20X 25 cm^2). The ground electrode is fixed on Perspex sheet through fixing nails which connected to the ground through 100 Ohm resistance. The life electrode is connected to a high voltage setup transformer generates sinusoidal voltage (50 Hz, 0-12Kv, 30 mA) to drive the discharge. The working gas is injected to the discharge zone through holes in the ground electrode. A limiting resistor connected between the power supply and life electrode R_L is used to limit the discharge current, stabilize the discharge and preventing formation of spark discharge. The polyester fabric samples were inserted in the discharge gap between two electrodes. The current and voltage waveforms are recorded with 100 MHz two channel digital storage oscilloscope (Type HM1508), one channel is connected to a high voltage potential divider (1:1000) to measure the applied voltage on the discharge cell, while other channel was connected to a 100 Ohm resistance inserted between the inner electrode and the ground to measure the discharge current. The consumed power is measured by replacing the 100 Ohm resistance with 10 nF capacitor to measure the charge accumulated in the discharge cell. The discharge power was calculated using the Q-V Lissajous figure.

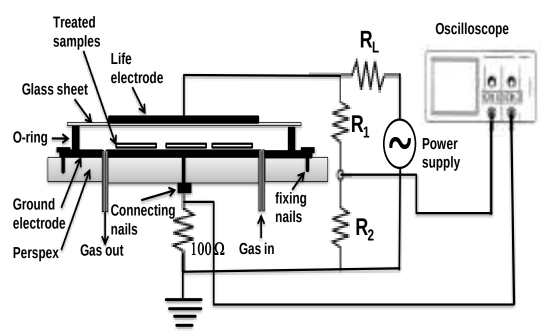


Fig.(1): Schematic diagram for planar DBD

2.2. TiO_2 nanoparticles treatment:

The prepared solution containing TiO2, sodium hypophosphite, citric acid and sodium alginate was first stirred with a high round mixer for 5 min. then put it in the ultrasonic bath for 30 min. at 70°C to obtain a uniform suspension of nano TiO2 particles. Then the samples were impregnated with the finishing solution using the 2-dip 2-nip technique, liquor ratio 1:20 with 80% pickup, followed by drying at 70 °C for 2 min. After that ink jet printing was carried out followed by curing at 200 °C for 5 min. Finally treated samples rinsed and washed with 2g/l non- ionic detergent at 60oc for 10 min.

2.3. Printing process:

In the first part of the thesis plasma treated polyester samples were subjected to ink jet printing process by using Cyan blue disperse ink in HP inkjet printer (model 1280, China). While in the second part the printing process was carried out after plasma and TiO_2 NPs treatment. After that the samples were fixed by hot air at 200°C for 5 min. Finally rinsing and washing process was performed.

III. MEASUREMENTS

3.1. Color Strength and whiteness:

The colour strength (K/S) of the printed samples and The whiteness of the area around the printed regions were evaluated by Ultra scan pro-spectrophotometer, Hunter Lap, by light reflectance technique, the K/S values of the printed samples were automatically calculated according to Kobelka-Munk equation. [17]

3.2. Determination of UV:

Ultraviolet protection factor (UPF) values were calculated according to the Australian/ New Zealand (As/ NZS 4366- 1996). According to this standard, fabric can rated as providing good protection, very good protection and excellent protection if their UPF values range from 15 to 24, 25 to 39 and above 40 respectively.

3.3. Self- cleaning:

The self-cleaning property of treated fabric with titanium dioxidnano particles was studied, treated fabric be able to transforming the absorbed light into the self- cleaning power to decompose its coffee stain on fabrics after 24 hour irradiation.

3.4. Antimicrobial properties:

The antimicrobial activity of polyester fabrics was carried out using Gram-Positive bacteria Staphylococcus aureus G^+, Gram- negative bacteria Pseudomonas aeruginosa G^- and the fungus Asperigillusniger at concentration of 7-11x 10^7CFU/ml of tested bacteria and 24x10^4 CFU /ml of tested fungus according to the antimicrobial standard AATCC Test Method 100-2012[18], which is a quantitative method for the assessment of antimicrobial finished textile materials.

3.4. Durability to wash:

Polyester fabric was subjected to repeated washing cycles according to AATCC Test Method 124-1996 [18].

3.5. Fastness properties:

The colour fastness to washing, crocking, perspiration and light were determined according to the AATCC test method 61-1996, AATCC test 8-1996, AATCC test method 15-1997 [18] and BS (test no: 1006-1978) respectively.

3.6. Scanning electron microscope (SEM):

The SEM photomicrographs were recorded using JEOL, JXA- 840 an Electron probe micro analyzer, to study the changes in the surface morphology of plasma treated and nano coated fabrics.

IV. RESULTS AND DISCUSSION

4.1 Plasma treatment

In the present work, different gases were investigated viz. oxygen (O_2), air, argon (Ar), nitrogen (N_2), O_2/Ar, air/Ar, and N_2/Ar to enhance the inkjet printing properties such as the colour yield and sharpness. Also plasma treatment activate the surface of polyester fabric to improve the titanium dioxide nanoparticles treatment.

The effect of exposure time of plasma treatment at different discharge currents on the colour strength of treated polyester fabric printed with disperse ink was studied.

The results of the colour strength of printed fabric were illustrated in figure 2.

It can be concluded that generally there are a significant increase in the color strength of modified polyester fabric with all types of gases used under the investigation.

Plasma can change the chemistry of treated fabric, introducing a new polar groups on the surface of polyester fabric due to the chain scission and etching effect, activate the surface of the fabric.

This changes depending on the plasma conditions even if one uses the same gas plasma, due to different degrees of etching occurring [19]. So the increase in the K/S of modified polyester fabrics is depends profoundly on the plasma exposure time and the intensity of the current used irrespective of gas type.

For example, increasing the current of oxygen plasma from 2mA to 6 mA is accompanied with increase in the colour intensity irrespective to time exposure. For example, treating samples for 2 min. causes a percentage increasein the K/S for (15 %, 20.94%, 28.44%,) with 2,4, and 6 mA. respectively, compared to the untreated sample.

These increase in the colour strength may be attributed to the bombardment effect of exited and energetic plasma species (ions, radicals, electrons, and metastable) onto the textile or polymer surface, which results in surface etching and activation.

By using a higher discharge current, a relatively decreased colour yield would be obtained. For example, the percentage increasein the K/S for 8 and 10 mA. was 18.44% and 1.25% respectively.

This decrease in the colour strength may be due to the decrease in the amorphous regions of the fabric and increase its crystalline regions whereas plasma etching preferentially occurs in the non-crystalline phase. Also, cross-linking between the fiber molecules may have occurred [20].

From figure (2) in the case of air plasma, one can notice that the K/S values increase with increasing time exposure by using low discharge current (2 mA). By using higher currents, increase the time exposure over 3 min. is accompanied with a relatively decrease in the K/S of printed samples.

This result can be observed with high period of plasma exposure, because in the beginning of treatment, plasma cause the breaking of the chain molecules of polyester, resulting in opening of the structure for the fabric and more voids ended achieving more diffusion of disperse dye to penetrate inside the fiber. after period of time the new polar groups formed on the polymer chain tend to react each other in different places and form cross linkage which prevent the penetration of the dye molecules causing a decrease in the K/S values. So selecting a suitable time and current is very important to gain plasma benefits.

It may be concluded from the results that the maximum K/S was obtained by treating polyester samples with air plasma with 4 mA. for 3 min.The percentageincrease in the colour strength of printed fabric is 62.5% related to the untreated sample.

4.2 Titanium dioxide nanoparticles finishing :

Since plasma causes etching of the fibers and leads to an increase of the surface roughness, higher adhesion properties towards metal particles onto substrates can be achieved [21]. Furthermore, introducing extra hydroxyl and carboxyl groups using plasma treatment increase the binding of TiO_2 nanoparticles.

So polyester samples were subjected to air plasma at 4 mA for 3 min., then titanium dioxide NPs treatment was carried out, after that treated PET samples were subjected to inkjet printing with disperse inks. The colour strength for printed samples was measured as well as UPF factor to estimate the UV protection for treated PET samples. To optimize the conditions of TiO_2 NPs treatment, different factors have been studied.

4.2.1. Effect of TiO_2 NPs concentration:

The results that presented in figure 3a indicate that treating polyester samples with TiO_2- NPs improve their ultraviolet protection. The UPF are increase with rising TiO_2- NPs concentration in the treatment bath. The higher value of the UPF was 65.46 compared to 45.01 for untreated fabric. The increase in the UPF values with increase the concentration of TiO_2 is attributed to its high refractive index and its effect on reflecting and / or scattering most of the UV- rays [22,23] also some investigations refer to its characteristics as a semi conductive properties and its effect on the absorption of the UV radiation [24,25].

Also it can be abstracted from the results that the K/S values are increase gradually with increase the concentration of TiO_2- NPs in the treatment bath. The best results are given by using 0.75% (o.w.f) TiO_2, the percentage increase in the K/S is about 108% compared to the untreated sample. After this concentration a decrease in the K/S is observed. This decrease is about 26.7% related to the highest value. Even though is still higher than untreated sample. The increase in the colour strength for treated samples with TiO_2 particles may be due to increase the roughness of polyester surface.

4.2.2 Effect of sodium alginate concentration:

It is very important to study the effect of sodium alginate treatment on the printing properties of inkjet printed fabric. So different concentrations of sodium alginate inserted in the TiO_2 NPs treatment bath, viz. (25,50,75,100, and 150 g/l). The results of the UPF and K/S of pretreated and printed polyested fabric were presented in the figure 3b.

It can be observed from the results that sample which treated without sodium alginate exhibit the highest K/S and UPF values. Adding sodium alginate in the treatment bath has a negative effect on the ultraviolet protection of printed samples. Increasing the amount of sodium alginate in the pad liquor leads to a proportional decrease in the UPF values, the possible explanation for this phenomenon that the migration of TiO_2 NPs into the fabric would be slowed by the thicker films formed at higher concentrations of sodium alginate.

The K/S values show a similar trend, that increase the concentration of the sodium alginate in the pad- liquor cause a decrease in the K/S values until it reaches the lowest by using 75g/l sodium alginate after this concentration an obvious increase in the K/S was demonstrated.

4.2.3. Effect of SHP concentration:

To investigate the effect of sodium hypophosphite on the crosslinking reaction efficiency, different concentrations of sodium hypophosphiteviz.(2, 4, 6, and 8 g/l) at a constant citric acid concentration were studied.

The results presented in figure (3c) indicate to a significant increase in the color strength values with increasing sodium hypophosphite concentration. The maximum color strength was observed using a SHP concentration of 4g/l after which a decrease in the color strength can be achieved.

Also we can easily notice from the results that the UPF values are increase with increasing the concentration of SHP due to increasing the extent of anhydride production by catalyst action, increasing the rate of esterification, and producing carboxylic active sites which increase the absorption and fixation of TiO_2- NPs within the modified substrate, resulting in improving the ultraviolet protection of the polyester fabric [(26)]. By using 4g/l SHP maximum catalytic action and anhydride formation could occur.

On the other side, increase the concentration of SHP beyond 4 g/l leading to decrease the UPF factor for treated fabric. This is attributed to the neutralization of free carboxyl groups, thereby inhibiting the action of citric acid crosslinker in binding the TiO_2- NPs resulting in decreasing the UPF values [(27)].

4.2.4. Effect of citric acid concentration:

Polycarboxylic acid crosslinking agents, such as citric acid, are commonly used to strongly fix the TiO_2 NPs to the fibers. As it is evident from the previous studies [(28-30)] that air plasma treatment introduce hydroxyl groups on the surface of polyester fibres.

In the presence of the crosslinker, the hydroxyl groups that presented to the polyester fibers by air plasma treatment can bond covalently with the carboxyl groups of the citric acid via esterification reaction, resulting in the formation of crosslinks between the TiO_2 and polyester fibers. Crosslinking significantly enhances the durability and washing fastness of treated fabrics. In the present study, sodium hypophosphite was used to catalyze the crosslinking reactions.

It can be concluded from the results plotted in figure 3d that adding citric acid to the TiO_2 treatment bath had an effective impact on the UV protection properties of polyester fabric, this is attributed to that hydroxyl groups of citric acid attract the TiO_2 NPs through cation-anion interaction resulting in increase the UV protection property of treated fabrics[(31)].

Also The results presented in figure 3c indicate that maximum K/S is obtained by using 20 g/l citric acid after which a slight decrease in the K/S is observed, because increase the cross-linking inside the fiber may be decrease the diffusion of disperse dye in to the fiber and this reflected on the K/S values for printed fabric.

4.2.5 Effect of curing temperature

The results of the UPF and the K/S were shown in figure (3e).It is clear from the results that both of the ultraviolet protection and the colour strength of printed samples were improved with increasing the temperature of curing. This is attributed to increase the rate of anhydride formation which enhance the esterification reaction and create new active sites within the fabric lead to increase the TiO_2 NPs fixation and improve the ultraviolet protection.

Also the high temperature is needed to increase the fixation of disperse ink inside the polyester fabric. The maximum K/S of printed samples was obtained by using $200^{o}C$ for 5 min.

4.2.6 Effect of curing time

To study the effect of curing time on the UPF and the K/S of printed polyester fabric, different durations of time under constant temperature $200^{o}C$ were investigated. The results were illustrated in figure (3f).

It can concluded from the results that increase curing time from 1 to 5 min cause a significant increase to about 37.67% in the UPF of printed fabric. Also increase the curing time to 5 min. cause a great increase in the K/S value (15.87) compared with (8.47) obtained by using 3 min.

Anti-bleeding performance

Without any pretreatments, polyester fabric has lower ability to hold on water due to the smooth surface and chemistry characteristics of polyester fibers. Therefore, designs directly printed with pigment inks have poor color yields and easily bleed [(32)]. In this study atmospheric pressure plasma was used successfully to pre-treat polyester fabric in order to provide an active surface for the inkjet printing.

To investigate the effect of plasma treatment on the anti bleeding performance for printed fabric, samples of polyester fabric were subjected to whiteness measurements on a white area around the printed one. The results are shown in table (1).

As can be seen from table (1), the whiteness of the sample increase after plasma treatment to about 32.26% related to the untreated and printed sample compared to only 8% by using sodium alginate, that indicate to the improvement in anti bleeding performance. This improvement is due to the hydrophilic increase of the fabric, consequently expediting the absorption speed and increasing the holding ability of inks [(32)].

The etching action of plasma increases the surface roughness as well as induces the active polar groups on the polyester surface, which increased the amount of ink colorant stayed on per area of the fabric.

It also contributed to the increase of K/S value of inkjet printed sample by decreasing the fraction of light reflected from treated rough surface compared with untreated smooth surface [32].

On the other hand, untreated samples exhibit lower value of whiteness and the K/S because the ink particles were difficult to be fixated on the smooth surface of polyester fiber and spread freely even into the gaps between two fibers.

It is interesting that the sample treated by plasma has better anti bleeding and colour performance than the sample treated by sodium alginate.

Introduce both of plasma and alginate treatments on the polyester fabric caused a dramatically improved the anti-bleeding and colour performance. The increase in whiteness of area around the printing is about 67.74%.

Table (1): The effect of different treatments on the bleeding and colour performance of inkjet printed fabric.

Polyester Fabric	**Whiteness of area around the printing**	**K/S of printed area**
Untreated and printed	62	3.5
Alginate treatment	67	4.20
Plasma treatment	82	5.05
Alginate and plasma treatment	104	5.9

Plasma treatment condition: air (4 mA for 3 min.).
Alginate treatment: L.R 1:50, 100 g/l sodium alginate.

Self cleaning

During the recent years, the semiconductors have been used to functionalize different textiles to impart photocatalytic self-cleaning properties. These functionalized fabrics have the ability to oxidize the coloring substances in the form of solutions and stains [33].

Mostly, the nanoparticles of TiO_2 prepared by sol-gel and hydrothermal methods have been used to generate self-cleaning textiles [34,35].

In the present study, self-cleaning properties of TiO_2 NPs treated polyester fabrics were assessed by staining the fabric with 0.02 % methyl red. After drying the stained samples were subjected to UV radiation for different periods of time.

The results of self- cleaning behavior of treated fabric with plasma and/or TiO_2-NPs are given in table (2).

Table (2): Stain reduction of untreated and treated polyester fabric with plasma and /or TiO_2-NPs.

Polyester fabric	**Percent reduction of stain (%)**			
	UV radiation Period (h)			
	6	**12**	**18**	**24**
Plasma treated sample	60	60	65	70
TiO_2 treated sample	80	85	85	90
Plasma+ TiO_2	90	93	95	95

Plasma treatment condition: air (4 mA for 3 min.).
finishing condition: L.R 1:50, TiO_2 NP.con.: 0.75% (o.w.f),4 g/l NaH_2PO_2, 20 g/l Citric acid, curing temp: 200^oC, curing time: 5min.

The results illustrated in table (2) present self cleaning properties expressed as a percentage reduction of methyl red stain for polyester fabric samples treated with plasma and TiO_2 nanoparticles. The results indicate that titanium dioxide nanoparticles have photo catalytic properties [36] that explain the reduction of stain to about 90% with the sample subject to 24 hours UV radiation, this rate increase with plasma treatment to reach to 95%.

Antimicrobial activity:

To investigate antimicrobial activity of polyester fabric treated with TiO_2 NPs, the antimicrobial test was carried out using Gram-Positive bacteria Staphylococcus aureus G^+, Gram-negative bacteria Pseudomonas aeruginosa G^- and the fungus Asperigillusniger.

The antimicrobial activity is expressed as the % reduction of the surviving organisms. The percentage reduction was calculated using the following formula: % reduction colony-forming units (CFU/mL) = A − B/A × 100, where A is the surviving colony-forming units (CFU/mL) for the untreated fabrics and B is that for the treated fabrics. The results are presented in table (3).

As it can be seen from the table, polyester samples treated with TiO_2NPs exhibit limited inhibition of all microorganism used under the study. For example, 32.8%, 26.4% and 19.1% for S. aureus, P.aeruginosa and A.niger respectively.

Plasma treatment prior to TiO_2 NP increases the polyester resistance against Gram-positive, Gram-negative bacteria and fungus more effectively than treatment with TiO_2 NPs alone. For example, 48.6%, 36.4%, and 26.8% for S. aureus, P.aeruginosa and A.niger respectively.

In general, the activity against Gram-positive S. aureus is higher than that against Gram-negative P.aeruginosa and fungus A.niger.

Table (3): Antimicrobial activity of treated polyester fabric**.**

Polyester fabric	Staphylococcus aureus G^+		Pseudomonas aeruginosa G^-		fungus Asperigillusniger	
	CFUx10^7	R%	CFUx10^7	R%	CFUx10^4	R%
Untreated	5.0x10^7	27.8	8.7x10^7	20.9	20.2x10^4	15.8
Treated with TiO^2NPs	4.7x10^7	32.8	8.1x10^7	26.4	19.4x10^4	19.1
Plasma+ TiO^2 NPs	3.6x10^7	48.6	7.0x10^7	36.4	30.4x10^4	26.8

Plasma treatment condition: air (4 mA for 3 min.).
finishing condition: L.R 1:50, TiO_2 NP.con.: 0.75% (o.w.f),4 g/l NaH_2PO_2, 20 g/l Citric acid, curing temp: 200^{o}C, curing time: 5min

Durability to wash:

In order to study the efficiency of TiO_2NPs treatment on the ultraviolet protection of polyester fabric and the extent of fixation of TiO_2NPs inside the fabric, printed and un printed polyester fabric were subjected to repeated laundering cycles.

The data of the UPF values after 5, 10, and 15 laundering cycles are presented in table (4). It can be seen from the results that repeating washing cycles cause a slightly reduced in the UPF values.

For example, the percentage decrease in the UPF is about 5.33%, 5.88% with increase the washing cycles from 5 to 15 for the printed samples treated with TiO_2 and TiO_2/plasma respectively.

This result indicates to the strong bond formed between TiO_2NPs and the fiber.

The decrease in the UPF values is attributed to the release of the unfixed and physically attached TiO_2- NPs molecules.

Table (4): Effect of repeated washing on the UPF values for TiO_2NPs treated polyester fabric

Washing cycles	UPF			
	Printed		Un printed	
	TiO^2	TiO^2+plasma	TiO^2	TiO^2+plasma
5	48.8	54.4	30.7	33.1
10	47.5	52.2	30.5	31.5
15	46.2	51.2	29.7	30.1

Plasma treatment condition: air (4 mA for 3 min.).
finishing condition: L.R 1:50, TiO_2 NP.con.: 0.75% (o.w.f),4 g/l NaH_2PO_2, 20 g/l Citric acid, curing temp: 200^{o}C, curing time: 5min.

Colour Fastness Properties:

Untreated and treated polyester samples were subjected to colour fastness measurements, the data are presented in table (5).

The results show that all samples exhibit excellent grades of washing and perspiration fastness, untreated and treated samples ranges between (4-5), very good to excellent.

Rubbing fastness show a slightly decrease by plasma/TiO_2- NPs treatment which range between (2-3), (1-2) for wet and dry rubbing compared with (4-5), (3-4) for untreated sample respectively.

It is interesting that the sample treated with TiO_2- NPs or plasma/TiO_2- NPs has a better light fastness.

Table (5): Colour fastness properties of printed polyester fabric with disperse ink.

Treatment condition	UPF	K/S	Washing fastness			Rubbing fastness		Perspiration fastness Acidic			light
			SI*	SI**	Alt.	Dry	wet	ST*	ST**	Alt.	
Untreated		6.70	4-5	4-5	4-5	3-4	4-5	4-5	4-5	4-5	5
plasma treated sample Air (4mA, 3min)	45.01	7.06	4-5	4-5	4	3-4	4-5	4-5	4-5	4-5	5
Tio_2- NPstreated sample		17.74	4-5	4-5	3-4	1-2	2-3	4-5	4-5	4	6
Air plasma Tio_2- NPs treatment	67.78	20.74	4-5	4- 5	3-4	1-2	2	5	5	4-5	6

-St* = staining on cotton fabric
-St** = staining on polyester fabric
-Alt. = Alteration
-Plasma treatment condition: air (4 mA for 3 min.).
-finishing condition: L.R 1:50, TiO_2 NP.con.: 0.75% (o.w.f),4 g/l NaH_2PO_2, 20 g/l Citric acid, curing temp: 200^{o}C, curing time: 5min.

Scanning electron microscopy (SEM)

The surface images of modified polyester fiber were taken and presented in figure (4). The images illustrate the effect of plasma etching and the distribution of TiO_2 NPs on the surface of polyester fiber. This indicated that the rough surface of plasma treated fibers could provide more capacities for the fabric to captureTiO_2 NPs.

V. CONCLUSION

Polyester fabric was treated with atmospheric pressure plasma to enhance the inkjet printing properties such as the colour yield and sharpness. Also plasma treatment activate the surface of polyester fabric to improve the titanium dioxide nanoparticles treatment.

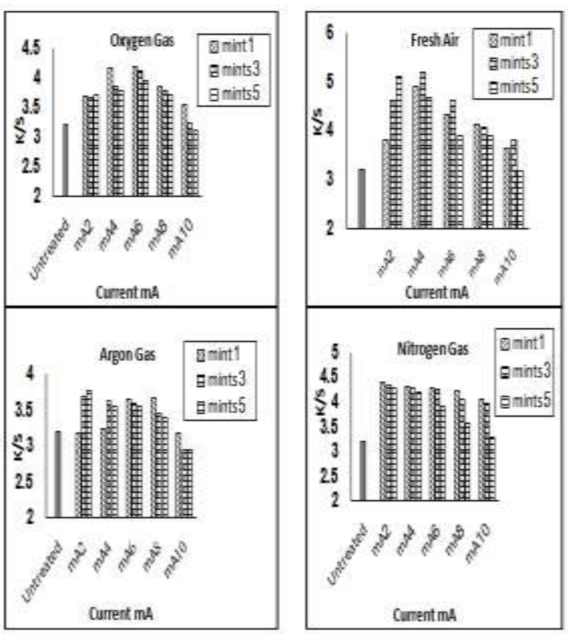
The results indicate that plasma treatment enhance bleeding properties and introduce both of plasma and alginate treatments on the polyester fabric caused a dramatically improved the anti-bleeding and colour performance.

To study the effect of plasma, different gases was investigated viz. oxygen (O_2), air, argon (Ar), nitrogen (N_2), O_2/Ar, air/Ar, and N_2/Ar. The investigation was carried out under different currents and time of exposure.

The results indicate that plasma improve the colour yield of disperse ink on the polyester fabric efficiently. This improvement is depends on the gas type, time exposure and discharge current used.

The effect of TiO_2 NPs treatment on the inkjet printing properties was also investigated. Titanium dioxide treatment was carried out to impart polyester fabric desirable characteristics such as self cleaning, ultraviolet protection, and antibacterial activity.

The results indicate that treating polyester samples with TiO_2- NPs improve their ultraviolet protection and colour strength values. The results are affected with type and concentration of ingredients in the treatment bath.viz, sodium alginate, citric acid, and sodium hypophosphite. Also, the results depended on the curing temperature and time.



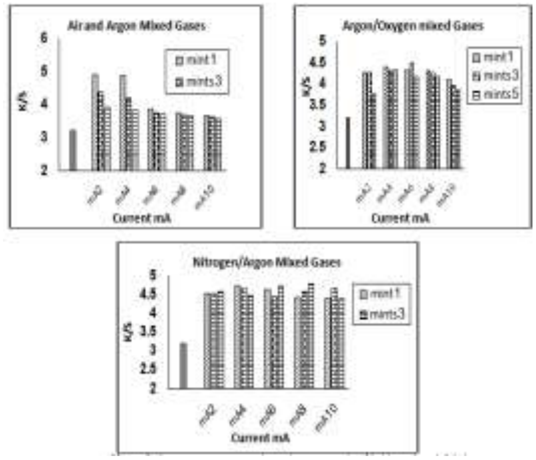


Fig (2): Effect of plasma treatment on the colour strength of inkjet printed fabric.

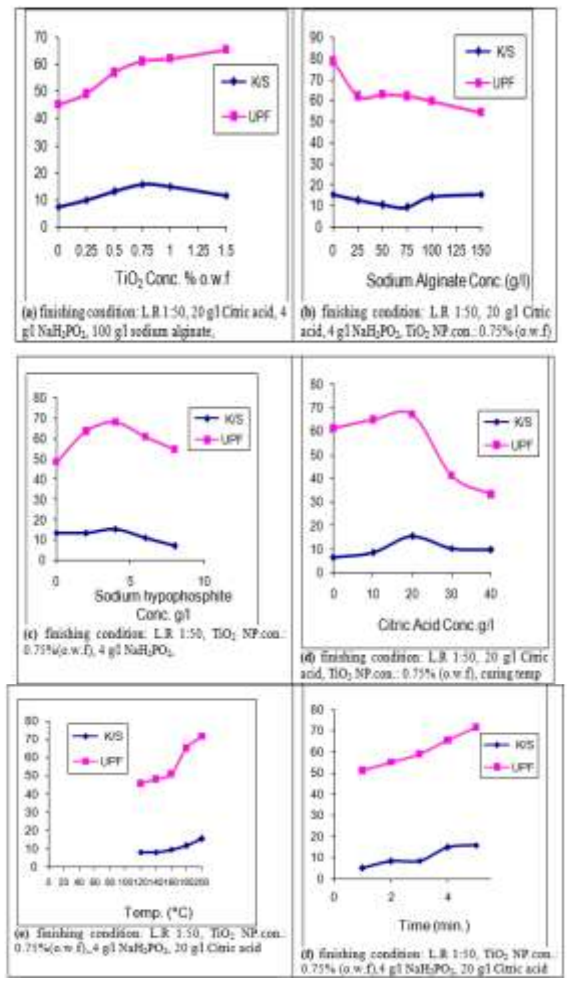


Fig (3): Effects of different treatment factors on colour strength (K/S) and ultraviolet protection factor. The samples in (a), (b), (c) and (d) were dried 5 min at 70°C and cured 5 min at 200°C. The effects of curing time and temperature are graphed in (e) and (f).

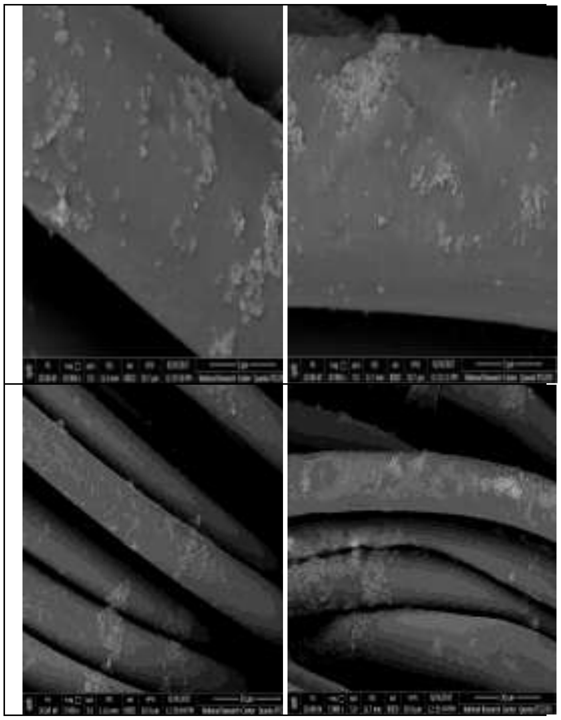


Fig. (4): SEM images of plasma modified polyester fiber treated with TiO2-NPs.

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Asmaa.A Salem " Titanium Dioxide Nanoparticles Finishing Of Atmospheric Pressure Plasma Treated Polyester Fabric for Inkjet Printing"International Journal of Engineering Research and Applications (IJERA) , vol. 8, no.7, 2018, pp. 74-83