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Rendering of Some Properties of Cellulose Acetate Fabric through Treatment with Laser/TiO2 Nanoparticles in Alcoholic Media

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Abstract

Due to their capacity to impart certain qualities, such as increased strength and functionality, nanoparticles are being used as a treatment agent for cellulose acetate fibres. It was attempted to provide cellulose acetate (CA) fabric special qualities by treating it with titanium dioxide nanoparticles (TiO_2 NPs) in various alcoholic solutions with or without pretreatment by excimer laser irradiation. We evaluated weight loss, area shrinkage, tensile strength, wettability, whiteness index, antibacterial activity, and UV protection factor (UPF) to determine the impact of various treatments on the characteristics of acetate fabric. Scanning electron microscopy (SEM) is used to study surface morphology. FT-IR and EDX are also provided. The outcomes show that nano TiO_2 treatment in an alcoholic medium with or without laser pretreatments greatly improves wettability, UPF, and antibacterial activity. Additionally enhanced are the fiber's tensile strength and whiteness.

Keywords: cellulose acetate, nanoparticles, laser irradiation, antibacterial activity, UV protection factor

1. Introduction

Cellulose acetate (CA) fibers are usually dyed and printed with dispersed dyes. The effects of plasticization and swelling with some organic compounds on the coloration of CA fibers are related to the easy diffusion of the dye molecules into pre-swelled fibers. [1] The dye affinity of CA fibers increases with the increase of the swell-ability. Ethanol is a polar solvent that can swell CA fibers. [2, 3] It was found that crystallinity decreased and fiber flexibility increased. [4] An increase in surface roughness was attained. [4-6] Also, the solubility parameters and molar volume of the used solvent and their effect on fiber swelling are reported. [6]

Treatment of CA fabric with ethylene glycol could improve its water resistance. Some improvement in textile properties was recorded such as a decrease in the thermal stability and the crystallinity of the fibers. [7, 8] The influence of the plasticizing effect of polyethylene glycol on the properties of cellulose acetate was investigated. It can affect the fiber morphology and its crystallinity. [9-12] Treating CA with glycerol increases fiber flexibility because of its plasticizing effect. The treatment reduces the fabric flammability, crease, and wrinkle while the thermal stability is found to be improved. [13-15]

Laser treatment is a non-thermal process and can modify the surface properties of textiles. This treatment causes changes in the surface and morphology and improves fiber wettability. Excimer laser treatment is considered a promising methodology to improve the coloring properties of textiles and enhances the nanoparticle uptake by the fiber. The induced changes in physical and chemical properties due to laser treatment of CA fibers were studied. It was found that the dyeability improved and the wettability behavior changed. [16] Nanoparticles (NPs) can be applied to acetate fibers by different methods to give functionality to the fiber. The modification of CA gives a great chance for new applications. It is reported that TiO_2 is a semiconductor and can be applied in solar cells. [17, 18]

In the present investigation, the interest is focused to study the effect of NPs such as TiO_2 in alcoholic media on some characteristics of cellulose acetate. The applied media in this treatment are mono-, di- and trihydric alcohols such as ethanol, ethylene glycol, and glycerol. Efforts are performed to characterize the induced changes in cellulose acetate properties such as shrinkage, loss in weight, mechanical properties, whiteness, wettability, ultraviolet protection factor (UPF), self-cleaning,

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surface morphology, functionality, antibacterial activity and printability with both disperse and natural dyes as well as fastness properties.

2. Methodology and Measurements

2.1. Materials

White secondary cellulose acetate fabric (CA), satin weave, of density 1.32 g/ml and 38.5% acetyl content was used. The fabric was cleaned in an aqueous solution containing 2 g/1 of nonionic detergent (Hostapal CV, Clariant), at 60°C for 20 min., followed by warm and cold rinses. The fabric was dried at ambient conditions.

Chemicals and reagents of pure grade such as Ethanol, Ethylene Glycol, Glycerol, and Titanium dioxide (TiO_2) NPs were used in this study. Commercial C. I. Disperse Red 167 from Bayer Co of the known chemical structure was used in this study. Commercial natural dye yellow, turmeric tincture, was bought from the local market.

2.2. Treatments

The treatment was carried out by padding technique upon applying different proportions of alcohols/water solutions of 10-50 % (v/v), containing TiO_2 NPs of different concentrations of 0.3- 1 (g/100g fiber). Then the solution is subjected to sonication for 60s using an ultrasonic processor (UP 100H, Hielscher Ultra-Sound Technology, Germany). Other samples were exposed to laser before treatment using (Excimer Laser, power: 500 mw, λ 1064 nm, pulse) for 60-120s. The samples are padded for 30 min in the previous solutions at room temperature, squeezed to pick up 100%, and then placed to cure in an oven (DPTA 79/08, Carbolite) at 110°C for 5 min. Other samples are cured in a microwave (model KOR-1316 Olympic Electric, Korea) for 60s. The samples are then dried at ambient conditions.

2.3. Measurements

2.3.1. Shrinkage

The length and breadth of the samples were determined before and after treatment. The percentage shrinkage of the samples was calculated according to the following equation:

$$\% \text{ shrinkage} = \frac{Ao-A}{Ao} \times 100$$

Where A_o: original area (cm^2) of acetate sample before treatment. A: area (cm^2) of the sample after treatment. [19]

2.3.2. Change in Weight

The weight of the acetate sample was determined accurately before and after the chemical treatment. The percentage change in weight was calculated according to the following equation taking into consideration the acquired relative humidity of samples:

$$\% \text{ Weight loss} = \frac{Wo-W}{Wo} \times 100$$

Where W_o: original dry weight (g) of acetate sample before treatment. W: dry weight (g) of acetate sample after treatment. [19]

2.3.3. Tensile Strength

The tensile strength and elongation at break were reported by the ASTM examination method (D5034) using (the Grab test). All reported values were the average of three readings. [20]

2.3.4. Whiteness and Yellowness

Changes in fabric whiteness after treatment were measured using an Ultra Scan PRO-Hunter Lab spectrophotometer according to the AATCC test method 153-2004. [21]

2.3.5. Wettability

The wettability was evaluated by measuring the wetting time according to the AATCC-39 method. [22] A drop of water is allowed to fall from a fixed height onto the surface of the fabric under examination. The time needed for the drop of water to disappear was measured and taken as wetting time, and the results were the average value of five readings.

2.3.6. Antimicrobial Activity

Two bacterial strains were E-coli ATCC I 1229 (Gram -ve) and S. aureus ATCC 6538 (Gram +ve). In addition, two fungal strains were Aspergillus Niger and Candida albicans. These bacterial strains were selected as test cells because they are the most frequent bacteria in the wound infection. Fresh inoculants for antibacterial assessment were prepared on nutrient broth at 37°C for 24 hours. The agar colony counting method was applied. [23-28]A liquid culture was prepared by mixing 0.5 g peptone and 0.3 g beef extract in 100 ml water. 1 cm diameter of the fabrics was cut and put into 10 ml of liquid culture, to which 10 ml of microbe culture was inoculated. All samples were incubated for 24 h at 37°C. From each incubated sample, 100 ml of solution was taken, diluted, and distributed onto an agar plate. All plates were incubated for 24 hours and the colonies formed were counted. The percentage of bacterial reduction was determined as follows:

$$\text{Reduction in CFU (colony forming units) \%} = \frac{C-A}{C} \times 100$$

Where A is CFU/ml after contact (end test), and C is CFU/ml at zero contact time.

2.3.7. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded on the JASCO FTIR spectrometer (ATR). [29] It was used to analyze the spectrum of the untreated and treated samples. The tester examined the transmittance of the infrared in the film between the values of 400-4000 cm^{-1}.

2.3.8. Scanning Electron Microscopy (SEM)

The surface morphology of untreated and laser-treated fabric was investigated by using SEM, JSMT-20, and JEOL-Japan.

2.3.9. Measurement of Ultraviolet Protection Factor (UPF)

Australian/New Zealand standard method AS/NZ S4399:1996 by using JASCO U-750 spectrophotometer as described in AATCC. Test method 183:2010 was used for UPF measurements of the dyed fabric. The final results are the average values of three measurements for each fabric sample. [24, 28, 30-38]

3. Results and discussions

3.1. Change in Weight

The weight changes were recorded for cellulose acetate samples treated with the TiO_2 NPs in alcoholic media under various conditions. Examination of the obtained data indicated that the loss in weight appeared to be dependent on the treatment conditions such as the ratio of alcohol/water mixture, the used alcohol as well as the curing methods either thermally in an electric oven or by irradiation via microwave.

The effect of ratios of ethanol/water mixture on the change in weight of treated cellulose acetate fabric is given in Table (1). It was shown that there is a slight decrease in the weight of treated cellulose acetate samples compared with untreated ones. It also seemed that there is a gradual increase in loss in weight of treated samples with increasing the ratio of ethanol in the treatment bath. The maximum loss in weight is of value 1.5% upon treatment of CA with 0.5 g TiO_2 NPs (o.w.f) in ethanol/water mixture of ratio 50 % (v/v). This observed slight decrease in weight may be due to the decrease in the degree of crystallinity and the increase in the amorphous regions. Also, ethanol could partially dissolve cellulose acetate fibers because of forming hydrogen bonds with acetyl groups in CA. Also, it is reported that the solubility parameter of ethanol is 26.3 $(cal/cm^3)^{1/2}$ and that of cellulose acetate polymer is about 12-13 $(cal/cm^3)^{1/2}$ resulting in a few partial dissolving of the fiber. [19]

Table 1: Loss in weight and area shrinkage of treated CA fabric with TiO_2 NPs concerning the concentration of ethanolic medium

Type of Sample	Loss in Weight %	Shrinkage %
-Untreated CA	0	0
-Treated CA with TiO_2 in ethanol/water (v/v%)		
10:90		
20:80	0.34	0
30:70	0.79	1.6
40:60	0.98	2.0
50:50	1.4	2.4
	1.5	3.0

Treatment: padding, pick up100%, 25°C, 0.5 g (o.w.f) TiO_2, Curing: 110°C, 5 min.

Table 2 shows the loss in weight % of treated cellulose acetate fibers with TiO_2 NPs in different alcoholic media as well as the sample pretreated with laser irradiation then with TiO_2 NPs in ethanol/water (50 % v/v). It is observed that ethanol/water medium is found to be the most effective one in resulting in a loss in weight of CA, followed by ethylene glycol/water followed by glycerol/water. Pretreatment with an excimer laser for 60 seconds could produce cracking on the cellulose acetate surface and consequently increase the loss in weight. [16]

Table 2: Loss in weight of treated CA fibers with TiO_2 NPs in different alcoholic media and different curing methods

Type of Sample	Loss in Weight %	
	Thermal curing	Microwave Curing
-Untreated CA	0	0
Treated CA with TiO_2 NPs:		
-Ethanol /water	1.5	2.3
-Ethylene glycol/water	1.08	2.1
-Glycerol/water	0.97	1.9
Treated with laser/TiO_2 in ethanol/water	2.1	1.9

Treatment: padding, pick up 100%, 25°C, TiO_2 0.5% (o.w.f), alcohol/water 50 % (v/v), Curing: Oven 110 °C, 5 min - Microwave: 60s - Excimer laser: 60 s

3.2. Area Shrinkage

Cellulose acetate samples were treated with TiO_2 NPs in different alcoholic media and then cured thermally in an oven or microwave. Variations in the fabric dimensions were recorded and calculated as area shrinkage percentages. The % area shrinkage of treated cellulose acetate fabric with TiO_2 NPs in different concentrations of ethanol/water mixture is shown in Table (1). The area shrinkage is increased with increasing the ratio of alcohol in the treatment bath. It was observed from Table (3) that ethanol/water medium was the most effective one in producing area shrinkage either upon applying thermal curing or exposure to microwave irradiation. The order of media reactively is ethanol > ethylene glycol > glycerol solutions. It was reported that the alkaline treatment causes some shrinkage and increases the tensile strength of acetate fabric. Ethanol solution is slightly basic because the oxygen in ethanol has lone electron pairs capable of accepting protons. So, ethanol can act as a weak base**.** The pka values for ethanol, ethylene glycol, and glycerol are 16.0, 15.1, and 14.4 respectively [18]. It is noticed that ethanol has lower acidity (higher pka) and consequently higher basicity. So, the resulting shrinkage may be due to the slight hydrolysis effect on cellulose acetate fabric. It could be also referred to the swelling effect of ethanol on acetate samples and its easy penetration into the fiber.

Table 3: Area shrinkage of treated CA fibers with TiO_2 NPs in different alcoholic media and different curing methods

Type of Sample	Area Shrinkage %	
	Thermal curing	Microwave curing
-Untreated CA	0	0
-Treated CA with TiO_2 NPs in:		
- Ethanol /water		
- Ethylene glycol/water	3	2.5
- Glycerol/water	2.5	2.5
Treated with laser/TiO_2 in ethanolic medium	0	0
	0	0

Treatment: padding, pick up 100%, 25°C, TiO_2 0.5% (o.w.f), alcohol/water 50:50 (v/v). Curing: Oven 110°C, 5 min Microwave: 60 s Excimer laser: 60 seconds

The molar volumes of ethanol and ethylene glycol are 58.4 and 56 cm^3/mol respectively while that of glycerol is 73.1 cm^3/mol. So, the results of % area shrinkage of treated cellulose acetate samples with ethanol and ethylene glycol are nearly the same while that treated with glycerol gives zero shrinkage due to the relatively higher value of its molar volume (73 cm^3/ mol). It is also observed from Table (3) that the treated cellulose acetate sample with laser/TiO_2 NPs in ethanolic medium records zero shrinkage. It is reported that laser treatment is applied for reducing the felting and shrinkage of textiles. [39, 40]

3.3. Whitness and Yellowness

The whiteness index (W.I) and the yellowness index (Y.I) are measured for untreated and treated cellulose acetate with TiO_2 NPs in alcoholic media. The changes induced in both whiteness and yellowness indexes of cellulose acetate treated with different concentrations of TiO_2 NPs in the ethanolic medium are illustrated in Table (4). It could be seen that the whiteness index of treated cellulose acetate samples increases concerning untreated ones. It is also observed the increase in (W.I) is dependent on the applied concentration of TiO_2 NPs. When the concentration of TiO_2 NPs increases from 0.3. to 0.5% (o.wf), the W. I slightly increases and further increase of concentration (up to 1%) leads to a slight decrease in W. I but it is still higher than the untreated one. It is also observed that using microwave irradiation for curing the treated CA samples is found to be slightly better than thermal curing. These results could be referred to the increase in the surface roughness.

Table (5) represents the values of whiteness and yellowness indexes of cellulose acetate fabric treated with TiO_2 NPs in different alcoholic media. It is seen from the table that the order of alcoholic media for enhancing the whiteness of cellulose acetate fabric is ethanol > ethylene glycol> glyceral. This result may be referred to as the amount of absorbed TiO_2 and the nature of the medium.

Table 4: Effect of concentration of TiO_2 NPs on whiteness and yellowness of CA fabric

Type of Sample	Whiteness index (W.I)		Yellowness index (Y.I)	
	Oven	Microwave	Oven	Microwave
-Untreated CA	87.32	87.32	-12.16	-12.16
-Treated CA with TiO_2 NPs of (g/100g fiber):				

0.3	97.8	100.2	-14.9	-15.6
0.5	98.2	101.1	-15.2	-15.8
1.0	93.5	96.4	-14.2	-13.1

Treatment: padding, pick up 100%, 25ºC, ethanol/water 50:50 (v/v). Curing: Oven 110 ºC, 5 min - Microwave: power 100%, 60 seconds

Table 5: Whiteness and yellowness of treated CA with TiO_2 NPs in different alcoholic media

Type of Sample	Whiteness index (W.I)		Yellowness index (Y.I)	
	Oven	Microwave	Oven	Microwave
-Untreated CA	87.32	87.32	-12.16	-12.16
-Treated CA with TiO_2 NPs in:				
• Ethanol /water	97.8	100.2	-14.9	-15.6
• Ethylene glycol/water	93.2	94	-13.4	-15.4
• Glycerol/water	93.0	92.0	-15	-17.0

Treatment : padding, pick up 100%, 25ºC, alcohol/water 50:50 (v/v), TiO_2 0.3% (o.w.f). Curing: Oven 110 ºC, 5 min - Microwave: power 100%, 60 seconds

3.4. Wettability

The wettability was estimated by evaluating the wetting time. The relation between the concentration of alcohols (v/v %) and the wetting time as an inverse function of the wettability of CA samples is shown in Figs (1, 2). Fig 1 represents this relation for cellulose acetate cured thermally after treatment while Fig 2 represents the same relation for samples cured via microwave irradiation. It is shown that as the concentration of alcohols increased from 10 to 50 (v/v %), the wetting time decreases and the CA fabric became more hydrophilic. Consequently, cellulose acetate fabrics become able to absorb water more than untreated ones after treatment with TiO_2 NPs in ethanol, ethylene glycol, and glycerol media. Using ethanol solution as a treatment medium was found to be the most effective one in enhancing the wettability of CA.

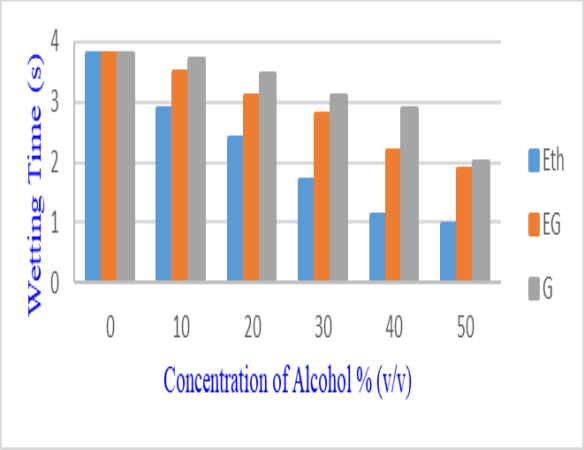

Fig 1: Effect of concentration of different alcohols on the wettability of treated CA cured thermally
Treatment: padding, pick up100%, 25ºC, $TiO_2$1.0 % (o.w.f), Curing : 110˚C, 5 min.

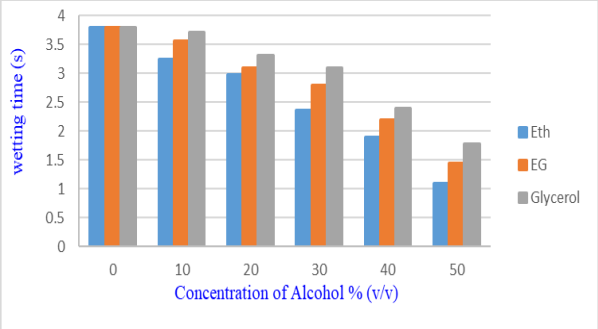

Fig 2: Effect of concentration of different alcohols on the wettability of treated CA cured via microwave
Treatment: padding, pick up100%, 25ºC, $TiO_2$1.0 % (o.w.f), Curing : 60 s

Figure (3) shows the dependence of the wetting time (s) on the concentration of TiO_2 NPs (g/100g fiber). The wetting time decreases gradually with increasing the concentration of NPs from 0.3 to 1.0 % (o. w. f). It is also seen that the treated sample in ethanol medium is more hydrophilic than that treated with ethylene glycol and glycerol.

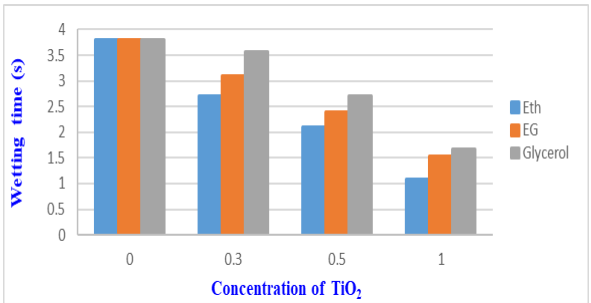

Fig 3: Effect of concentration of TiO_2 NPs on the wettability of CA cured thermally
Treatment: padding, pick up100%, 25ºC, alcohols (50% v/v), Curing : 110˚C, 5 min

Figure 4 shows the relationship between the exposure time of excimer laser irradiation and the wetting time of treated cellulose acetate with laser/0.5 % (o.w.f) TiO_2 NPs in ethanol medium (50% v/v). It

is clear that when the time of laser exposure increases, the wetting time increases gradually. So, the treated cellulose acetate sample becomes more hydrophobic. This may be due to the increasing surface roughness as shown later in images of scan electron microscopy.

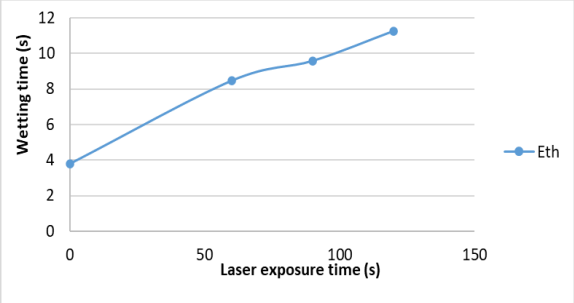

Fig 4: Effect of laser exposure time on the wettability of CA cured via microwave
Treatment: padding, pick up100%, 25°C, 0.5 % (o.w.f) TiO_2, ethanol (50 % v/v), Curing : 60 s

3.5 Tensile Properties

The tensile strength, elongation, and dimension stability are important mechanical properties of cellulose acetate fabric. Table (6) represents the tensile strength values for untreated and treated cellulose acetate with TiO_2 NPs of concentration 0.5% (o.w.f) in different alcohols/water mixtures and (50% v/v) by padding technique and pick up 100%. The tensile strength and elongation % at break of cellulose acetate (CA) treated samples are slightly increased. It was reported that the treatment of cellulose acetate with NPs enhances the tensile properties and crease recovery angle with no damage. [13]

The cellulose acetate samples treated with TiO_2 NPs in glycerol/water mixture (50% v/v) have the highest tensile strength followed by the sample treated in ethylene glycol followed by ethanol medium. These values are 26.83, 26.63, and 23.21 kg/mm^2 respectively compared to 21.89 kg/mm^2 for untreated one. It was reported elsewhere [13] that glycerol causes an increase in the tensile strength of cellulose acetate because the presence of glycerol as a plasticizer gives more flexibility and consequently higher tensile strength.

Table 6: Tensile strength and elongation at break of untreated and treated CA fabric

Type of sample	Tensile Strength (Kg_f/mm^2)	Elongation (%)
-Untreated CA	21.89	9.33
Treated CA with TiO_2NPs:		
- Ethanol/water	23.21	21.3
- Ethylene glycol/ water	26.63	24.67
- Glycerol/water	26.83	14.67

Treatment: padding, pickup 100%, 25°C, 0.5 % TiO_2 (o.w.f), 50% (vlv) alcohol/water. Curing: microwave, 60 s

3.6. Morphology Analysis

The morphology of the cellulose acetate surface has been observed by scan electron microscopy [SEM]. The images of SEM for untreated and treated acetate fabric are shown in Figs (5-9). Figure (5) represents the graph of untreated cellulose acetate while Figs (6-8) represents graphs for treated cellulose acetate with TiO_2 NPs in different alcoholic media; ethanol/water, ethylene glycol/water, and glycerol/ water, respectively. Figure (9) represents the image of pretreated cellulose acetate with laser irradiation and then treated with TiO_2 NPs in ethanolic solution (50% v/v).

The graphs show the changes which are formed on cellulose acetate fabric and surface morphology. Figure 5 shows that the surface of the untreated sample is smooth. Figures (6-8) show the presence of TiO_2 NPs on the cellulose acetate surface. It can be observed that the surface of CA-treated samples is not as smooth as untreated ones (Fig 5). It could be seen that TiO_2 NPs may agglomerate in spherical shapes with almost uniform distribution on the surface. A large number of NPs were evenly coated on the fiber surface. A film containing NPs is formed.

Figure (9) shows that the treatment of cellulose acetate with excimer lazar developed a ripple-like structure on the surface. So, this structure may allow more adsorption of TiO_2 NPs as shown later in EDX analysis in Figs (10-14). The laser treatment also reflects on improving the printability of cellulose acetate fabric. [13] Overall all images of treated CA samples exhibit rough surfaces of different size nanoparticles. It is reported [41] that when the content of TiO_2 was large, an agglomeration of particles formed on the surface and this holds with the image (Fig 9). Also, the change in the CA surface and the surface rougher led to an increase in fiber friction and a slight increase in mechanical properties (Table 6).

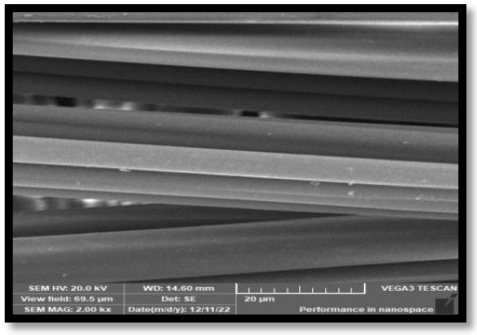

Fig 5: SEM image of untreated CA

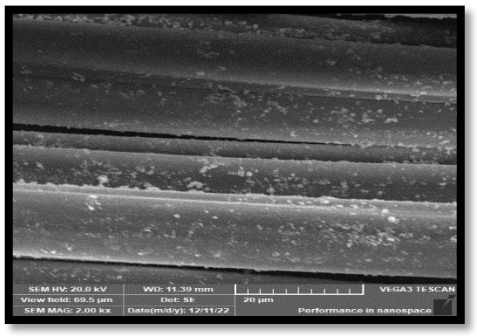

Fig 6: SEM image of treated CA with TiO_2 in ethanol /water medium

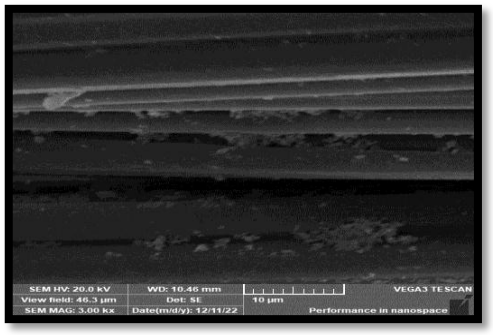

Fig 7: SEM image of treated CA with TiO_2 in ethylene glycol /water medium

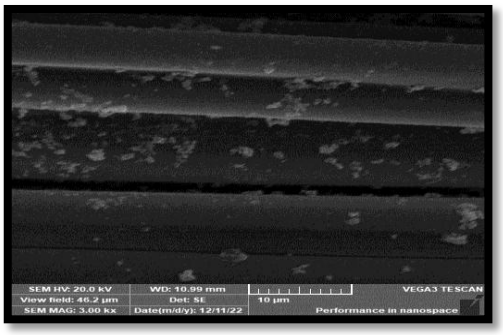

Fig 8: SEM image of treated CA with TiO_2 in glycerol/water medium

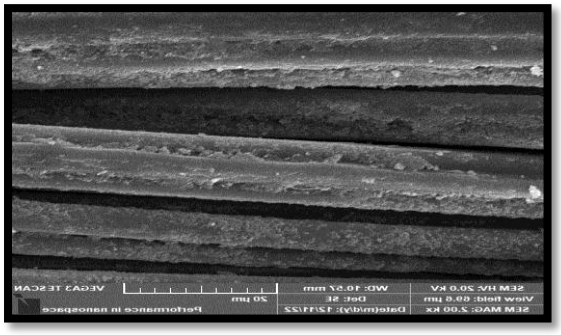

Fig 9: SEM image of treated CA with laser/ TiO_2 in ethanol /water medium

3.7. EDX of Treated Cellulose Acetate

Energy dispersive X-ray spectroscopy (EDX) could detect the elements that exist in the fibers. Figures (10-14) show the EDX of untreated and treated CA fabric. As shown in Fig. 10 the untreated CA elements are carbon (C) and oxygen (O) while titanium element (Ti) appears in EDX of treated samples with TiO_2 NPs in alcoholic media (Figs 11-14). It is clear that the % Ti element in treated CA has the highest value for treated CA with laser/TiO_2 in ethanol solution (Fig 14) followed by that treated in ethanol, then in ethylene glycol, then in glycerol solutions as shown in Figs (11-13) respectively. It is also clear that the induced change in fiber surface after laser treatment enhanced the adsorption of TiO_2 NPs (Fig 14).

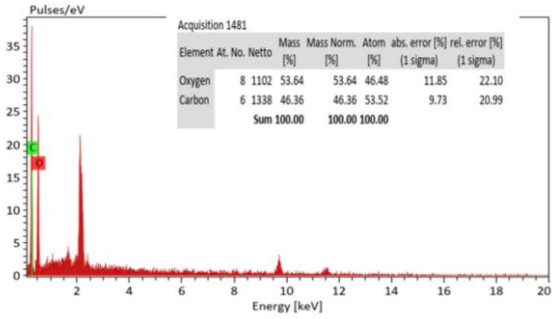

Fig 10: EDX of untreated CA fabrics

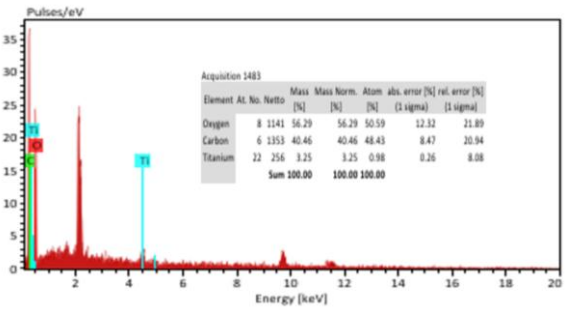

Fig 13: EDX of treated CA with TiO_2 NPs in glycerol medium

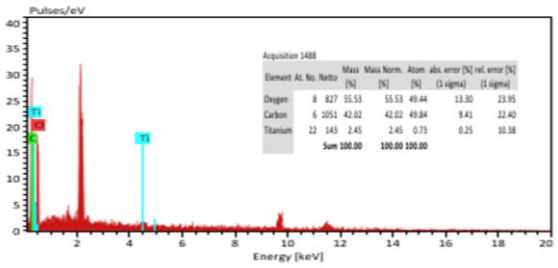

Fig 12: EDX of treated CA with TiO_2 NPs in ethylene glycol medium

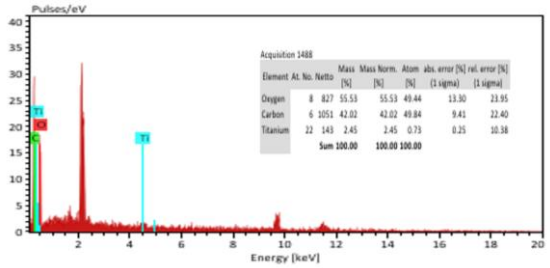

Fig 11: EDX of treated CA with TiO_2 NPs in ethanolic medium

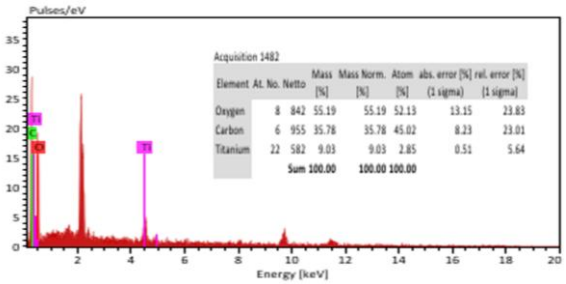

Fig 14: EDX of treated CA fabrics with laser / TiO_2 in ethanolic medium

3.8. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of untreated and treated cellulose acetate with TiO_2 NPs are shown in Figs (15-19). The FTIR of untreated cellulose acetate is shown in Fig (15). The absorption band at 3391.21 cm^{-1} is attributed to OH vibration. [42] The absorption band around 1646.91 cm^{-1} represents a strong bond between H_2O and cellulose acetate and a strong bond -OH group in the molecule. Peaks were also observed at 1731.76 and 2903.35 cm^{-1} corresponding to a carbonyl group (C=O) and C-H vibrations respectively [42] The FTIR spectra of cellulose acetate also show a peak at 1430 cm^{-1} which was attributed to CH_2 vibration. The sharp absorption peak at 1030 cm^{-1} was assigned to C-O stretching. [43] Bands at 901.6 and 1161 cm^{-1} are designated for C-O-C stretching.

Figures (16–18) represent FTIR of treated cellulose acetate with TiO_2 NPs in different media; ethanol, ethylene glycol, and glycerol media (50% v/v) respectively, while Fig. 19 represents the treated sample with laser/TiO_2 NPs in ethanol solution (50% v/v). It was observed that the absorption peak of OH vibration (3391 cm^{-1} for untreated CA) is shifted to a lower wavelength (3371.9, 3344, 3323, and 3363 cm^{-1}) for treated CA with the aforementioned reagents in Figs (16-19) respectively. This shift in the absorption bands confirmed some change in the material structure due to treatment with TiO_2 NPs. It is also observed that peaks of the C=O group at 1734 do not shift and are almost the same for all samples. The absorption peak of 1367.3 cm^{-1} may be due to the vibration of the - OH group and almost it was the same for all samples. A slight shift was noticed from 1367.23 to about 1368 cm^{-1} and the intensity of this peak increases to about 82% compared to 69% for untreated one. It comes from the alcoholic media used for treatment. [44].

The further absorption band at 485 cm^{-1} may be due to the superposition of metal-oxygen stretching vibration confirming the binding between CA and metal oxide. [44] The absorption peak at 485 cm^{-1} corresponds to the absorption of TiO_2. The peak at 598 cm^{-1} in all treated CA samples with TiO_2 was within the range of the Ti-O bond absorption peak and represented a characteristic absorption peak of TiO_2. This peak does not appear in untreated CA Fig 15. The intensity of the TiO_2 peak (598 cm^{-1}) was found to be the highest for samples treated with laser/TiO_2 NPs (Fig.19).

The noticed peak in the range of 3000-3500 cm^{-1} for CA and CA- TiO_2 is assigned to the OH group. The observed vibrational could be related to the bonding of the O-H group in CA and the Ti-O bond in TiO_2 NPs. The decrease in the absorption band of the OH peak may be due to weak bonding between OH and NPs. [43] This may indicate that the probability of occurring chemical reactions in this process is unexpected. [43] Also, the results are matching with SEM and EDX analysis.

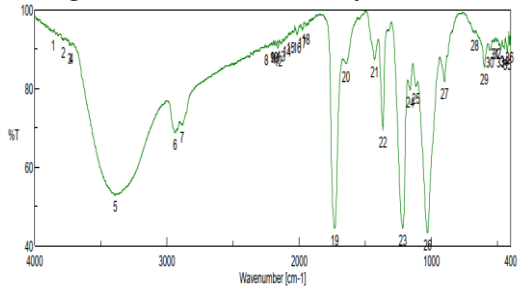

Fig 15: FTIR for untreated CA

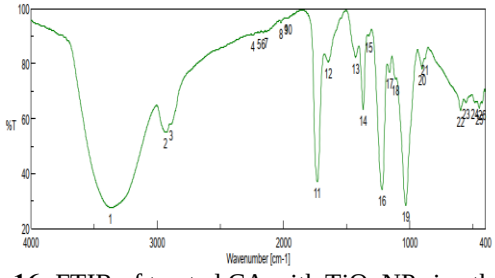

Fig 16: FTIR of treated CA with TiO_2 NPs in ethanol medium

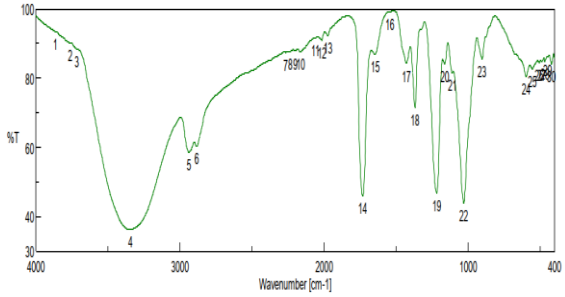

Fig 17: FTIR of treated CA with TiO_2 NPs in ethylene glycol medium

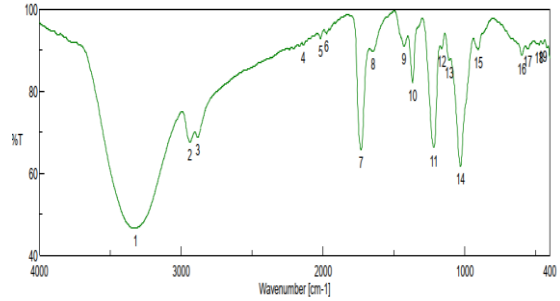

Fig 18: FTIR of treated CA with TiO_2 NPs in glycerol medium.

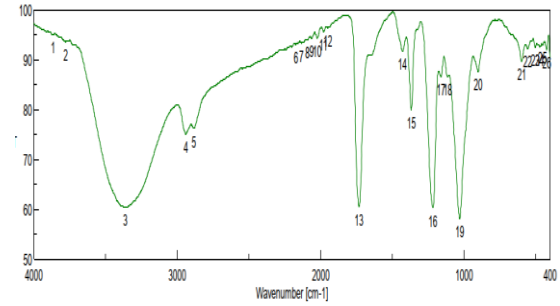

Fig 19: FTIR of treated CA with laser/TiO_2 NPs

Exposure of skin to ultraviolet irradiation (UV) may be dangerous and cause cancer. Textile and sun-blocking creams could decrease the danger of UV radiation. UV blockers either organic or inorganic may be used as UV absorbers. Such inorganic UV blockers are TiO_2, ZnO, SiO_2, and Al_2O_3. Inorganic UV blockers are preferred over organic ones because of the non-toxicity of most of them. TiO_2 provides very good protection against UV irradiation by reflecting or scattering UV rays. TiO_2 NPs can also absorb UV rays because it is considered semiconductor. [45] Table (7) shows the values of the UV protection factor (UPF) of TiO_2 treated cellulose acetate fabric in both ethylene glycol and glycerol solutions of different ratios (10-50% v/v). The media of treatment becomes effective in enhancing the UPF at 50 % v/v alcoholic medium. This may be a reflection of the absorption of enough concentration of TiO_2 by the fiber. It is also clear that ethylene glycol is better than glycerol medium in improving fiber protection against UV rays.

Table 8 illustrates the values of UPF of treated CA with TiO_2 NPs in different media and then printed with turmeric natural dye. It is clear that the presence of NPs with turmeric natural dye enhanced markedly the UPF of cellulose acetate fabric and gives excellent protection against UV rays. This improvement in UPF may be due to the absorption of UV irradiation by TiO_2 NPs and reinforced fiber. Also, it is noticed that the sample treated with laser/TiO_2 in alcoholic media has the maximum UV protection factor 59 for the white sample and 76 for the printed sample with turmeric dye]. This may be due to increasing the surface roughness of cellulose acetate as shown in SEM images and resulting in increasing UV blocking efficiency.

3.9 UV Protection Factor (UPF)

Table 7: UPF of TiO_2 treated CA concerning different concentrations of alcoholic media

Type of Sample	UPF	
	Ethylene glycol	Glycerol
-Untreated CA	2.7	2.7
-Treated CA with TiO_2 NPs in:		
10:90		
20:80	5.4	4.3
30:70	5.8	4.7
40:60	7.7	5
50:50	9.3	5.8
	24	20

Treatment : padding, pick up 100%, 25°C, TiO_2 0.5% (o.w.f), Curing : 110 °C, 5 min

3.10. Anti-microbial Activity

The uses of nanoparticle treatment for textiles are promising for giving functionality and add-value to textile fibers. One of these good properties is improving the antibacterial activity of textiles. When cellulose acetate is exposed to moisture, aging, or some conditions, some microorganisms grow and cause the decay of the fabric. Treating acetate fabric with antimicrobial agents could prevent or decrease the effect of these microorganisms. So, cellulose acetate treated with 0.5 % (o.w.f) TiO_2 NPs in glycerol/water mixture 50% (v/v) and that treated sample printed with turmeric are tested against both

Gram (+ve) and Gram (– ve) strains. The Gram (+ve) strain is the staphylococcus strain (S. aureus) [ATCC 6538] and Gram (-ve); Escherichia coli strain (E. coli) [ATCC 2592]. The fabric is also tested against single-cell fungi (Candida albicans) and also against Aspergillus Nigar fungi. The % reduction in these microorganisms is illustrated in Table (9) for untreated and treated cellulose acetate fabric.

So, combined laser and nanoparticles treatment is a promising method for improving UV protection properties, and this new opportunity for the production of high-performance and functional materials and opening a new market for cellulose acetate fabric. For Example, TiO_2 NPs treated CA fabrics have a photocatalytic activity and consequent high degradation rate of organic pollutants making them suitable for filters or membranes to reduce chemical oxygen demand (COD) and total organic carbon (TOC) in wastewater [34].

Table 8: UPF of TiO_2 treated CA versus colored ones with Tumeric natural dye.

Type of Sample	UPF	
	White	Colored
-Untreated CA	2.7	3.6
Treated CA with TiO_2 NPs		
- Ethanol /water	55.3	75.3
- Ethylene glycol/water	24	44.3
- Glycerol/water	20	29.8
Treated with laser/TiO_2 in ethanolic medium	59.0	76.0

Treatment: padding, pick up 100%, 25°C, TiO_2 0.5% (o.w.f), 50% (v/v) alcohol. Curing: 110°C, 5 min. Printing: Tumeric natural dye, steaming: 110°C, 20 min

It was found that treatments of CA with TiO_2 NPs at the aforementioned conditions either printed with turmeric natural dye or not, give the high antibacterial activity of cellulose acetate for both Gram (+ve) and Gram(-ve) bacteria strains. The printed cellulose acetate sample with turmeric natural dye after treatment with TiO_2 NPs in glycerol medium (50% v/v) was found to be more effective in increasing the reduction% of tested microorganisms and consequently enhancing the antimicrobial activity of cellulose acetate fabric. It is also observed that the maximum reduction (98%) could be attained for cellulose acetate printed with turmeric natural dye after treatment with TiO_2 NPs against G +ve strain (S. aureus).

Table 9: The antimicrobial activity of treated and printed CA fabric

Type of Sample	% Reduction			
	S. aureus (G+ve)	E. coli (G-ve)	Aspergillus Niger	Candida albicans
-Untreated CA	0.0	0.0	0.0	0.0
-Treated CA with TiO_2 NPs	70.1	63.1	93.96	87.55
- Treated CA printed with Tumeric	98.0	76.3	94.0	87.6

Treatment: padding, pick up 100%, 25°C, TiO_2 0.5% (o.w.f), 50% (v/v) alcohol. Curing in the microwave: 60 seconds. Printing: Tumeric natural dye, steaming: 110°C, 20 min

It also gives excellent anti-fungi properties against both Aspergillus Niger and Candida albicans which may be attributed to turmeric natural dye. TiO_2 NPs are reported [36] to be an antibacterial agent as well as turmeric natural dye. TiO_2 NPs lead to bacterial cell death. It is also known that alcoholic media and organic solvents increase the accessibility of fabric-absorbing TiO_2 NPs. The durability was tested after 5 washing cycles. It was observed that the TiO_2 NPs treated samples keep their antibacterial activity good and the decrease in % reduction was a little about 5-6 % decrease. Such antibacterial finishes could be applied to the medical textile.

4. Conclusion

It can be concluded that: Examining some of the attributes of treated cellulose acetate results in a minor increase in shrinkage and weight loss. According to this study, treatments can increase the tensile strength of cellulose acetate fabric. FTIR gives the composition of acetate textiles and detects the presence of TiO2 NPs as well as indicated in SEM and EDX. • After these treatments, the fabric

becomes more wettable, whereas laser treatment somewhat hydrophobes the fibre.

According to this research, the applied treatments may improve the cellulose acetate fabric's functional qualities, such as its antibacterial and UV protection factors. Overall, improving the functionality and performance of acetate fibres using laser/NPs treatments of cellulose acetate fabric is a promising topic.

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There is no available fund

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7. Author Declarations

The authors declare that the data supporting the findings of this study are available in the article

The authors declare that there is no conflict of interest.

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