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Article

Multiwalled-Carbon-Nanotubes (MWCNTs)–GPTMS/Tannic-Acid-Nanocomposite-Coated Cotton Fabric for Sustainable Antibacterial Properties and Electrical Conductivity

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Abstract: We propose a method of crosslinking multiwalled carbon nanotubes (MWCNTs) with cotton fabric. 3-Glycidoxypropyltrimethoxy silane (GPTMS) polymer was used for the stabilization and modification of the surfaces of MWCNTs. The presence of tannic acid in the finishing formulation adds a sustainable functionality to the treated surface. The formation of the GPTMS–MWCNTs nanocomposite as well as the MWCNTs–GPTMS tannic-epoxy nanocomposite on the fabric surface was confirmed by Fourier-transform infrared spectra (FTIR). The surface morphology and physical properties were investigated. An assessment of antibacterial activity, UV-protective properties, and electrical conductivity was performed. The post-treatment results of the MWCNTs–GPTMS nanocomposite fabric with tannic acid exhibited superior antibacterial character with the highest inhibition zones for Staphylococcus aureus and Escherichia coli (26 mm, 24 mm). On the contrary, the electrical conductivity was negatively impacted. The treatment of cotton fabric with tannic acid showed a great UV-protection-factor estimation of 96.2, which was additionally improved by treatment with MWCNTs 152.1. Cotton fabric treated with cotton/GPTMS/tannic acid/MWCNTs as well as cotton/GPTMS/MWCNTs recorded the highest electrical-conductivity properties. Fabrication of MWCNTs–GPTMS/tannic-acid-nanocomposite-coated cotton fabric for durable antibacterial and UV protection with improved electrical and physical properties was successfully achieved.

Keywords: cotton fabric; MWCNTs nanocomposite; tannic acid; antibacterial properties; electrical conductivity; GPTMS polymer

1. Introduction

Nanomaterials are used to design smart textiles for improving the properties of textiles such as wound healing, self-cleaning and military application [1–4]. Additionally, the utilization of nanomaterials is beneficial for the enhancement the physical characteristics of textiles in fields such as antibacterial-feature, water-repellence, soil-resistance, antistatic, anti-infrared, and fire-retardant characteristics [5–8]. The use of nanomaterials not only allows for the sufficient durability of fabrics but also has no impact on the fabric’s breathability or hand feel. This is because of the great surface-area-to-volume ratio and high surface energy of nanoparticles [9,10].

The binding of nanoparticles to cellulosic substrates occurs via a crosslinking process. Non-formaldehyde crosslinking agents such as 1,2,3,4-butane tetra carboxylic acid (BTCA), citric acid, succinic acid, and maleic acid are employed for this function. The fixation mechanism is explained through the molecular incorporation of the phosphorus catalyst in the structure of the crosslinking agent followed by the formation of an ester linkage with the cellulosic chains of the cotton [11,12]
Tannic acid (TA) is a natural product with ten gallic-acid molecules connected to a central glucose unit [13]. It is isolated from naturally occurring resources (plants of both herbaceous and woody kinds). Tannic acid has many outstanding properties. It has antimutagen and antitumor characteristics. It is active against micro-organisms (bacteria and viruses). Tannic acid, in the same way as phenolic acid, is classified in a polyphenolic group. Many surveys have been reported on the use of tannic acid as an additive to biopolymers, collagen, and polysaccharides such as chitosan, agarose, and starch as a result of its unique characteristics. On the one hand, it exhibits an antimicrobial and antiviral effects; it also indicates outstanding biological properties, namely improving cell proliferation, tissue regeneration, and wound-healing procedures [14].

Carbon nanotubes (CNTs) are one of the most durable materials known. The tensile strength of multilayer nanotubes is 63 GPa, which is much higher than that of hardened steel (1.2 GPa). CNTs have a low density of only 1.3–1.4 g/cm$^3$. The high tensile strength paired with the low density makes the use of CNTs highly desirable in various fields.

The characteristic properties of carbon nanotubes (CNTs), particularly their heat conduction, electrical conductivity, high modulus of elasticity, high strength, and resistance to chemicals, have resulted in the widespread application of CNTs.

The incorporation of CNTs into polymers has exhibited extraordinary electronic, thermal, and mechanical properties as well as chemical and physical properties [15]. More recently, simple dip-coating, drying or exhaustion methods have been used for the deposition of carbon nanotubes onto fabrics while different polymers have been used as stabilizers [16,17]. Earlier studies have argued that polymeric composites that have incorporated CNTs possess satisfactory physical, chemical, and mechanical properties [18].

Due to the fact that there is no interaction between the surface of textile fabrics and carbon nanotubes, previous studies have reported the necessity of using network-based polymers for dispersing and fixing CNTs on their surfaces. B. S. Shim et al. used poly-4-styrene sulfonate (PSS) to disperse CNTs followed by the dipping of cotton fabric, resulting in a conductive fabric that can be applied to telemedicine sensors and the detection of albumin [19]. M. in het Panhuis et al. used aqueous sulfonated polyaniline to disperse CNTs and used it as a dye for the prepared conductive textiles [20,21]. In another study, P. Xue, K. et al. used a wet-spinning technique for the coating of cotton fabric with a poly-vinyl alcohol/carbon-nanotube nanocomposite with the aim of developing yarns with conductive applications [20]. Water-soluble carbon nanotubes were functionalized in alkali and acidic solutions and then incorporated into a poly-vinyl alcohol (PVA) network followed by the coating of a polypropylene thread in order to improve its mechanical properties [21]. Recently, CNTs were dispersed in poly-vinyl pyrrolidone (PVP) medium and deposited onto cotton fabric using a curing method under UV-C irradiation [22]. In another recent study, a conductive super-hydrophobic cotton fabric was developed by assembling carboxylated and aminated multiwalled carbon nanotubes and modifying them with polydimethylsiloxane [23].

MWCNTs have been coated onto cotton fabrics by different methods for various functionalities, i.e., super-hydrophobicity, self-cleaning and flame retardancy, as well as improved mechanical resistance, electrical conductivity, and UV protection [24,25]. Durability plays a key role in the monitoring of the acquired properties. It was also reported that many carboxylic acids have been used to crosslink CNTs with cotton fabric, i.e., succinic acid as well as 1,2,3,4-butanetetracarboxylic acid (BTCA) [17,26].

To the best of our knowledge, there is no study on the crosslinking of MWCNTs with cotton fabric using GPTMS polymer and tannic acid. Herein, a MWCNTs–GPTMS/tannic-acid nanocomposite was fixed onto the surface of cotton fabric via crosslinking. GPTMS polymer was used as a stabilizing and to modify the surfaces of the MWCNTs. Additionally, it acted as a crosslinking and bridging agent for the enhancement of the deposition and fixation of the nanocomposite onto the fabric. The use of tannic acid is not only environmentally friendly and cost effective but also provides biocompatibility between MWCNTs and GPTMS and enhances the antibacterial activity of the treated fabric without affecting
the physical and mechanical properties of the coated cotton fabric. Electrical properties and antibacterial activity were also investigated.

2. Experimental

2.1. Materials

Mill-bleached pure 100% cotton fabric (138 g/m²) was supplied by Misr Company for Spinning and Weaving Mehalla, El-Kobra, Egypt.

2.2. Chemicals

3-Glycidoxypropyltrimethoxy silane (GPTMS) with a purity of 98% (supplied by Aldrich). The multiwalled carbon nanotubes (MWCNTs) were purchased from Nanotech Port Co. Ltd. (Shenzhen, China) Their purity was >95%, their length was about 10 m and their average outer diameter was 10–30 n.

2.3. Preparation of GPTMS Sol

A volume of 10 mL of GPTMS were dissolved in 100 mL ethanol before hydrolyzation using 0.01 M hydrochloric acid. The resulting solution was stirred for at least 3 h to form the base solution.

2.4. Coating of Fabrics Using MWCNTs–GPTMS Nano Sol

GPTMS solution was mixed with an MWCNTs suspension in an ethanolic solution. 1-methylimidazol (0.5 mL/10 mL GPTMS) was added as a catalyst. Fabric samples were first immersed in ethanol and sonicated for 15 min to remove organic material and detergent, then washed with distilled water and dried at 100 °C; the fabric was then dipped in MWCNTs-based solutions, each dip for 2 min. The treated samples were then dried at 80 °C and cured at 130 °C for 3 min. Finally, all samples were washed with deionized water several times and dried.

2.5. Coating of Fabrics Using GPTMS/MWCNTs/Tannic Acid Nanocomposite

Clean cotton fabric was immersed in ethanol and sonicated for 15 min to remove organic material and detergent, then washed with distilled water and dried at 100 °C; the fabrics were first dipped in solutions of tannic acid then in GPTMS–MWCNTs–based solutions, each dip for 2 min. The treated samples were then dried at 80 °C and cured at 130 °C for 3 min. The second treatment was a post-treatment of the GPTMS–MWCNTs fabric samples with tannic acid that involved being dried at 80 °C and cured at 130 °C for 3 min. Finally, all samples were washed with deionized water several times and dried.

3. Characterization

3.1. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy has been widely used in cellulose research. Because it is a very simple means of acquiring direct information on chemical changes that occur during various chemical treatments. ATR-FTIR equipment (Model IR 4700, JASCO, Tokyo, Japan) was used to scan from 4000 to 400 cm⁻¹ in ATR mode with KBr as a support material.

The software was set up to scan the background and samples at a specific number of scans (64) and at a specific resolution (4).

3.2. Scanning Electron Micrograph SEM/EDX Analysis

Samples for SEM/EDX were taken using FEI INSPECTS Company, Philips, Holland environmental scanning without coating. The elemental constitution of solid samples was investigated using elemental micro-probe and elemental distribution-mapping techniques. To provide a rapid quantitative and qualitative examination of the elemental composition, a SEM equipped with an energy-dispersive spectroscopy (EDX) with accelerating voltage of 30 kV FELCO Netherland was used to perform elemental analysis of the particles.
3.3. Antibacterial Test

The antibacterial activity of the treated samples against Staphylococcus aureus, Bacillus subtilis (G + ve), Escherichia coli, and Pseudomonas aeruginosa (G – ve) bacteria was determined using an agar plate. The antibacterial activity of the fabric samples was evaluated using (ATCC 1533) the disk-diffusion method [27,28].

3.4. UV Protection Factor

Ultraviolet-protection factor (UPF) was measured using an ultraviolet JASCO model V-750 UV/VIS Spectrophotometer apparatus (JASCO, Tokyo, Japan). UV protection and classification according to AS/NZS 4399:1996 were evaluated. The scanning range was 200–600 nm.

3.5. Electrical Conductivity Properties

A digital multimeter was used to measure the electrical conductivity of the dry textile composite at room temperature (25 °C). An electrical circuit consisting of a Hewlett Packard 6634B system DC power supply and a digital Hewlett Packard 34401A multimeter (Hewlett-Packard Company, Palo Alto, CA, USA) was used to record electrical measurements. Test Method 76-1995 of the American Association of Textile Chemists and Colorists was used to conduct the measurements [29,30].

\[
R = RS = \frac{\rho L}{A}
\]

\[
\frac{RA}{L} = \rho
\]

\[
\sigma = \frac{1}{\rho} = \frac{L}{RA} = \frac{L}{RWt}
\]

where \(R\) = resistivity, \(Rs\) = bulk resistivity of fabric, \(L\) = length of fabric, \(\sigma\) = conductivity, \(\rho\) = resistivity, \(A\) = cross-sectional area of the fabric, and \(W\) and \(t\) are width and thickness of the fabric.

3.6. Tensile Strength

The tensile strength of the fabric samples was determined by the ASTM Test Method D-1682-94 (1994). Two specimens for each treated fabric were tested in the warp direction and the average value was recorded to represent the fabric-breaking load (Lb).

3.7. Roughness

Surface roughness was monitored according to the JIS 94 standard, using a surface-roughness-measuring instrument SE 1700a made in Japan.

3.8. Statistical Analysis

Results were expressed as a mean value with its standard deviation (mean ± SD) of each sample that was repeated three times (\(n = 3\)).

4. Results and Discussion

4.1. Mechanism of Deposition for MWCNTs–GPTMS-Tannic Nanocomposite on Cotton Fabric

Figure 1 depicts the mechanism diagram whereby tannic acid/MWCNT nanocomposites were deposited and attached to the cotton fabric. Due to the hydrophobic nature of MWCNTs and their aggregation in an aqueous solution, GPTMS was added to the modified MWCNT surfaces in order to enhance their hydrophilicity [31]. GPTMS was pre-hydrolyzed for the conversion of the alkyl oxygen groups (–OCH3) to hydroxyl groups (–OH) (equation (1) in Figure 1a). After its addition, stable hydrogen bonds were formed between hydroxyl groups covering the surface of the MWCNTs and hydroxyl groups of the hydrolyzed GPTMTs (equation (2) in Figure 1a). In the next step, cotton fabric was
immersed in the previous nanotube solution followed by drying. MWCNTs–GPTMS was fixed onto the fabric by ether crosslinking with the cotton fabric via the reaction of the epoxy groups of GPTMS with the hydroxyl groups of the cellulose structure, resulting in a soft coat on the surface of the fabric (equation (3) in Figure 1a) [32]. During the last stage, the treated fabric was immersed in a tannic-acid solution using a pad–dry–cure technique. At this stage, tannic acid was adsorbed onto the surface of the modified MWCNTs, resulting in the formation of the MWCNTs–GPTMS/tannic-acid nanocomposite (equation (4) in Figure 1a). This can be explained in terms of the combination between the aromatic benzene ring in the tannic-acid molecule with the π-electron orbit perpendicular to the MWCNT’s axial direction, leading to a π–π electron interaction [33,34]. In the case of pretreatment with tannic acid, it could be adsorbed onto the surface of cotton fabric due to its hydrophilic hydroxyl groups, which make hydrogen bonds with hydroxyl groups of cotton fabric. Additionally, GPTMS allows the homogeneous distribution of MWCNTs within its formed network, while the hydroxyl groups of the tannic acid may react with GPTMS by a ring-opening addition reaction, resulting in the fixation of the nanocomposite [15,35].

Figure 1. (a) Schematic mechanism for deposition of MWCNTs–GPTMS/tannic acid nanocomposite on the surface of cotton fabric; (b) Structure of tannic acid.
4.2. IR Analysis

The presence of functional groups on the modified cotton surface was confirmed through Fourier-transform infrared spectra. Figure 2 shows FTIR spectra of the unmodified cotton (a), cotton fabric modified with the GPTMS–MWCNTs nanocomposite (b) and cotton fabric modified with MWCNTs–GPTMS-tannic nanocomposite (c). On account of unmodified cotton fabric (a), a band appeared at 3200–3500 cm⁻¹ that was assigned to O–H stretching. The bands in the range of 1500–800 cm⁻¹ appeared as a result of the existence of C–H, O–H, C–O, and C–O–C vibrations, due to the cellulose [9]. Compared to blank cotton fabric, Figure 1b shows a weak signal around 770 cm⁻¹ that was assigned to the stretching vibration of the Si–O–Si bonds, thus confirming that: (i) the fabric was modified via a ring-opening reaction between the GPTMS–MWCNTs nanocomposite and the cotton fibers [36,37] and (ii) the –OH groups of the MWCNTs could react only with the –OCH₃ groups of the GPTMS molecules. Additionally, two new bands appeared at 2910 and 2857 cm⁻¹ that were related to the stretching of the methylene groups from the GPTMS molecules. Figure 2c shows the sharp peaks observed at 1706 and 1604 cm⁻¹ that were attributed to the stretching vibrations of C=O and aromatic C=C, respectively, thus confirming the adsorption of tannic acid onto the cotton-fabric surface [15,38,39].

![Figure 2. FTIR spectra of the treated fabrics.](image)

4.3. SEM Analysis

By conforming the deposition of nanoparticles, SEM images are used to study the morphology of the fabric surface [40]. Figure 3 illustrates SEM images of the untreated cotton fabric (a), the MWCNTs–GPTMS-nanocomposite-treated cotton fabric (b), and MWCNTs–GPTMS-tannic-acid-nanocomposite-treated fabric (c). The surface of the untreated cotton fabric was clear and smooth (Figure 3a). In contrast, it is obvious that the sample treated with MWCNTs–GPTMS in Figure 3b shows a coating layer of MWCNTs on the surface of the fabric with some particulate agglomerations of carbon nanotubes. This confirms the deposition of the MWCNTs–GPTMS nano-network structure. In addition, some cracks are found on the surface of fibers because of the GPTMS-crosslinking effect. In comparison with sample in (Figure 3c) that was treated with a uniform coating of the MWCNTs–GPTMS-tannic acid nanocomposite. This could be due to the fact that the MWCNTs’ modification by tannic acid could enhance the compatibility between GPTMS and the MWCNTs [15]. On the other hand, the elemental composition of the coated fabrics was confirmed using EDX analysis. Figure 3e,f confirmed the deposition of MWCNTs, GPTMS and tannic onto surface of the cotton fabric with respect to Figure 3d of the untreated fabric.
Cotton fabric (a), the MWCNTs–GPTMS-nanocomposite-treated cotton fabric (b), and MWCNTs–GPTMS-tannic-acid-nanocomposite-treated fabric (c). The surface of the untreated cotton fabric was clear and smooth (Figure 3a). In contrast, it is obvious that the sample treated with MWCNTs–GPTMS in Figure 3b shows a coating layer of MWCNTs on the surface of the fabric with particulate agglomerations of carbon nanotubes. This confirms the deposition of the MWCNTs–GPTMS nano-network structure. In addition, some cracks are found on the surface of fibers because of the GPTMS-crosslinking effect. In comparison with sample in (Figure 3c) that was treated with a uniform coating of the MWCNTs–GPTMS-tannic-acid nanocomposite. This could be due to the fact that the MWCNTs' modification by tannic acid could enhance the compatibility between GPTMS and the MWCNTs [15]. On the other hand, the elemental composition of the coated fabrics was confirmed using EDX analysis. Figure 3e,f confirmed the deposition of MWCNTs, GPTMS and tannic onto surface of the cotton fabric with respect to Figure 3d of the untreated fabric.

Figure 3. SEM images and EDX analysis of the treated and untreated cotton fabric. (a) SEM for blank cotton (b) SEM for cotton fabric modified with GPTMS–MWCNTs nanocomposite, (c) SEM for cotton fabric modified with MWCNTs–GPTMS-tannic nanocomposite, (d) EDX for blank cotton, (e) EDX for cotton fabric modified with GPTMS–MWCNTs nanocomposite, and (f) EDX for cotton fabric modified with MWCNTs–GPTMS-tannic nanocomposite.

4.4. Antibacterial Activity

The antibacterial property of coated fabrics with different treatments including cotton/GPTMS, cotton/tannic acid, cotton/GPTMS/MWCNTs, cotton/GPTMS/MWCNTs then tannic acid, cotton/GPTMS/tannic acid/MWCNTs nanocomposites against two well-known types bacteria was evaluated. Gram-positive (S. aureus and B. subtilis) and Gram-negative (E. coli and P. aeruginosa) are broadly used as bio-detectors of pollution. Table 1 summarizes the evidence of antibacterial activity. The antibacterial action in the nanocomposites containing MWCNTs requires a closing to be attached between the MWCNTs and the micro-organisms. An effective antibacterial character was observed due to the presence of MWCNTs on the cotton surface. It is noteworthy that the highest inhibition zones for S. aureus and E. coli were observed upon the post-treatment of the MWCNTs–GPTMS-nanocomposite fabric with tannic acid (26 mm, 24 mm). Many studies have indicated that MWCNTs allow for the capability of adhesion to micro-organisms; subsequently, they can be utilized to eliminate a diverse array of biological pollutants, involving bacteria, viruses, natural organic matters, and cyanobacterial toxins. This was proposed because of their fibrous morphology, which encroaches upon the bacterial cell surface and disturbs the intracellular metabolic pathways [26,41,42].
It was also observed that the inhibition-zone diameter for \textit{B. subtilis} and \textit{E. coli} recorded the highest value among the other treated samples (26 mm, 20 mm). Similar to phenolic acid, tannic acid may be classified in the polyphonic group. It has been extensively researched in the biomedical field as it has remarkable antiviral and antibacterial properties. Tannic acid is active against Gram-positive and Gram-negative bacteria, while it also shows outstanding biological properties. The antibacterial adequacy of tannic acid is disclosed by its ability to penetrate the bacterial cell wall up to the inward layer, thereby obstructing the metamorphosis of the cell and inducing cell death. In Gram-positive bacteria, tannins are quickly dynamic. Nonetheless, in Gram-negative bacteria, the process is slower on account of the presence of the double-layer membrane. Tannic acid prevents the bacteria from binding to the surface \cite{43}. When bacteria do not adhere to the surface, bacterial cells die. Furthermore, bacterial growth is restricted by the presence of tannic acid as it prevents the absorption of sugar and amino acids. The results in Table 1 also indicate the durability of the treated cotton fabric towards repeated washing cycles. The treated samples kept their antibacterial properties after 20 washing cycles. The antibacterial character of the MWCNT-treated fabric was improved by the presence of tannic acid.

It is noteworthy that tannic acid plays a dual role in the stabilization of MWCNTs and the improvement of the functionalities of the treated fabric as well. These results are in accordance with other previous reports on other materials \cite{15,44,45}.

### Table 1. Antibacterial activity and durability properties.

| Substrate/Treatment of Fabric | G+ \textit{S. aureus} | G− \textit{B. subtilis} | G− \textit{E. coli} | G− \textit{P. aeruginosa} |
|------------------------------|-----------------------|------------------------|---------------------|------------------------|
| No. of Washing Cycle        | 1                     | 20                     | 1                   | 20                     | 1                   | 20                     |
| cotton/GPTMS                | 0.0                   | 0.0                    | 0.0                 | 0.0                    | 0.0                 | 0.0                    |
| cotton/tannic acid          | 21                    | 20                     | 23                  | 19                     | 17                  | 15                     |
| cotton/GPTMS/MWCNTs         | 15                    | 20                     | 17                  | 18                     | 17                  | 15                     |
| cotton/GPTMS/MWCNTs then tannic acid | 26 | 25 | 22 | 24 | 23 | 22 |
| tannic acid/cotton/GPTMS/MWCNTs | 18 | 16 | 17 | 16 | 15 | 18 | 17 |
4.5. UV Protection Properties

To examine the UV-radiation-protection character of the blank fabrics and the nanocomposite-coated cellulosic fabrics, the UPF (ultraviolet-protection factor) values, which are defined as the ultraviolet-light-transmittance percentage, were estimated and the results are outlined in Table 2.

Table 2. UPF values of cotton fabrics treated under different conditions.

| Treatment                          | UPF Value | UV Protection |
|------------------------------------|-----------|---------------|
| Blank                              | 7.1       | 5             | Non-ratable |
| Cotton/GPTMS                       | 6.8       | 5             | Non-ratable |
| Cotton/tannic acid                 | 96.2      | 50+           | Excellent   |
| Cotton/GPTMS/MWCNTs                | 73.6      | 50+           | Excellent   |
| Cotton/GPTMS/MWCNTs then tannic acid | 152.1    | 50+           | Excellent   |
| Tannic acid/cotton/GPTMS/MWCNTs    | 75.3      | 50+           | Excellent   |

As the table shows, the UV resistance and wash durability of the modified cotton fabrics were measured. The treatment of cotton fabric with tannic acid showed a great UV-protection factor estimated at 96.2, which was additionally improved by treatment with MWCNTs. The cotton fabric treated with GPTMS/MWCNTs then tannic acid displayed a UV-protection factor estimated up to 152.1. Tannic acid afforded protection against UV-B [46,47]. “Dark” colors (such as dark green, red, navy blue, and black) offer greater protection than “light” colors. Treatment with MWCNTs endows the black color to cotton fabric, which provides excellent UV protection. This may be the result of the black color absorbing the radiation and altering the transmitting effect. Thanks to the post-treatment with tannic acid, a higher load and a more uniform dispersal of the MWCNTs were obtained. Furthermore, it was found that the optical behavior of the MWCNTs is due to their homogeneity and alignment. Aligned nanotube networks can brief rate and strongly absorb visible light [17].

4.6. Analysis of Conductivity

Table 3 shows the measurement of the electric properties of the MWCNT-based cotton-fabric hybrids. The resistivity relative to the different treatments was recorded. However, the introduced results show a conspicuous contrast in the sorption of the nanotube suspension by the treated textile. Furthermore, the measurement of carbon nanotubes deposited onto the surface of the cotton samples was generally influenced by the formulation. The increase in electrical conductivity followed the order cotton/GPTMS/tannic acid/MWCNTs > cotton/GPTMS/MWCNTs > cotton/GPTMS/MWCNTs then tannic acid > cotton/GPTMS > cotton/tannic acid.

Table 3. Electrical properties of untreated and treated cotton fabric.

| Treatment                           | Resistivity Ω/cm |
|-------------------------------------|------------------|
| Untreated                           | 245              |
| Cotton/GPTMS                        | 148              |
| Cotton/tannic acid                  | 150              |
| Tannic acid/cotton/GPTMS/MWCNTs     | 115              |
| Cotton/GPTMS/MWCNTs                 | 120              |
| Cotton/GPTMS/MWCNTs then tannic acid| 145              |

In the case of the cotton-based (cotton/MWCNTs) hybrid materials, particularly those with coatings, a large amount of the nanotube suspension defused and then stilled inside
the fiber structure, which affected the fiber conductivity. When GPTMS was present, it acted as a network for the homogeneous distribution of CNTs on the fabric surface. The surface deposition of MWCNTs was increased by this. The MWCNTs deposition was accompanied by an improvement in the thickness of the surface layer. This directly contributed to a decrease in the threshold for percolation and an increase in the surface conductivity. Therefore, as a result of decreasing electrical resistivity, the surface electrical conductivity increased; in the meantime, the tannic-acid adsorption allowed the nanotube suspension to effectively penetrate the surface of the cotton fibers, infiltrating their porous construction and leading to a highly conductive fabric structure. While the adsorption of the layers of tannic acid onto the surface led to a lower effect of the MWCNTs, the fabric conductivity was determined to be smaller than in the other treatments, and the conductivity of such a composite was relatively low. The above outcomes show potential for controlling the permeation edge and conductivity estimates of hybrid materials simply by applying carbon nanotubes not only to the surface but also within the material.

4.7. Mechanical Properties

There are few reports of the impact of MWCNT deposition on cellulosic fabric’s mechanical characteristics [48]. Table 4 shows the roughness and tensile strength of the coated surface of the cotton fabric. Table 4 clearly shows the improvement in tensile strength and a slight increase in roughness values for the fabric treated either by MWCNTs–GPTMS or by tannic-MWCNTs–GPTMS nanocomposites compared to the untreated fabric. This proves the homogeneous coating of MWCNTs on the surface of the fabric and could be explained by the strengthening effect of the carbon nanotubes dispersed in the nanocomposite [49]. In addition, the mechanical properties of the polymer-microscalized fibers were significantly improved by using nanomaterials such as carbon nanotubes as fillers or reinforcements in composite materials. Moreover, the modified CNTs formed nanoscale surface roughness on the microscale cellulose fabric, resulting in the formation of an artificial lotus-leaf structure on the cotton [48]. On the other hand, samples treated with only GPTMS or with tannic acid exhibited a decrease in tensile strength as well as an improvement in roughness values compared with the untreated samples. This could be attributed to the effect of the ether crosslinking or the acidity of the crosslinking agent’s cellulose structure leading to a degradation of the cellulose polymer chains, thereby resulting in the reduction of tensile strength.

Our results were compared to other reported results that indicate a negative impact of using carboxylic acid as a crosslinking agent on tensile strength. The results in Table 4 demonstrate the importance of using GPTMS/tannic acid in the finishing formulation in a certain sequence in order to enhance the performance of the MWCNT-treated cotton fabric without affecting the physical properties [17]. Finally, Table 5 shows a comparative study between the results of our work and previous work indicating the importance of using tannic acid as we as GPTMS in the finishing formulation with MWCNTs to improve fabric performance.

Table 4. Tensile strength and roughness of treated and untreated cotton fabric.

| Treatment                                           | Tensile Strength (Kg f) | Roughness (µm) |
|-----------------------------------------------------|-------------------------|----------------|
| Untreated cotton fabric                             | 55 ± 0.86               | 14.5 ± 0.41    |
| Cotton-GPTMS                                        | 46 ± 0.76               | 12.3 ± 0.37    |
| Cotton-tannic acid                                  | 52 ± 1.50               | 12.7 ± 0.25    |
| Cotton-GPTMS–MWCNTs                                 | 78 ± 0.36               | 15.4 ± 0.35    |
| Cotton-GPTMS–MWCNTs drying then tannic acid         | 75 ± 0.5                | 14.9 ± 0.26    |
| Tannic acid-cotton-GPTMS–MWCNTs                     | 72 ± 0.65               | 15 ± 0.21      |
Table 5. Comparison between previous work and our work.

| Previous Work | Our Work |
|---------------|----------|
| **Treatment** | **Functionalities** | **Treatment** | **Functionalities** |
| Cotton fabrics were treated with nano titanium dioxide and multiwalled carbon nanotubes (MWCNTs) using succinic acid as a crosslinking agent [26] | -The abrasion resistance and UV blocking capability are improved, | Treatment of cotton fabric in Presence of ecofriendly tannic acid as well as GPTMS is the mean key role in improvement of functions | Extra antibacterial, UV protection, improvement in tensile strength, electrical conductivity |
| A dip–dry–cure finishing process was used to coat cotton fabric with MWCNTs functionalized with poly(butylacrylate) [48]. | -Durable superhydrophobicity, -self-cleaning and flame retardancy, -improved mechanical resistance and UV protection | | |
| Coating of MWCNTs onto cotton by ultrasonic irradiation followed by the dipping method [24] | Hydrophobicity to the fabric, this property was not durable | | |
| MWCNTs were coated with tetraethyloorthosilicate and a fluoroalkoxysilane after being noncovalently functionalized with an organic–inorganic hybrid consisting of silica and an amphiphilic copolymer of styrene and maleic anhydride [50]. | Hydrophobicity and improved conductivity | | |
| The exhaustion method was used to coat carbon nanotubes (CNTs) and fix them on a cotton surface utilising 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent [17] | Increase the thermal stability of the substrate. | | |
| A dyeing-like method was used to successfully incorporate MWCNTs into cotton and polyester substrates [51]. | Superhydrophobic behavior, flame-retardant | | |
| MWCNTs were stabilized on a cotton surface using vinylphosphonic acid via UV irradiation [52] | High-efficient flame retardant finishing of cotton fabrics and improvement of its thermal properties. | | |
| (BTCA) and ZnO-BTCA-carbon nanotube (CNT) composites were fabricated and coated on cotton fabric by pad-dry-cure [53] | Very good antibacterial activity | | |

5. Conclusions

Cotton fabric was treated with a high-performance MWCNTs–GPTMS nanocomposite. Tannic acid was added to the finishing formulation in different sequences to enhance the sustainable functionalities of the treated fabric. GPTMS had no effect on the biological activity of the treated cotton fabric. There was an improvement in tensile strength and a slight increase in roughness values for the fabric treated either by MWCNTs–GPTMS or by tannic-MWCNTs–GPTMS nanocomposites compared to untreated fabric. Outstanding antibacterial properties were recorded in all the treated fabrics while superior properties were achieved upon the post-treatment with tannic acid for both *S. aureus* and *E. coli*, i.e., large inhibition-zone diameters (26 mm, 24 mm). The post-treatment of cotton/GPTMS/MWCNTs with tannic acid afforded a maximum UV-protection factor value.
of 152.1. Modification with carbon nanotubes imparted high electrical conductivity only in the case of pretreatment with tannic acid, which had the lowest recorded resistivity value of 115 Ω/cm, while post-treatment with tannic acid negatively affected the electrical conductivity and resulted in the high electrical-resistivity value of 145 Ω/cm.

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