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METHODS FOR THE SYNTHESIS OF TiO_2 NANOPARTICLES. PROPERTIES OF TEXTILE MATERIALS TREATED WITH TiO_2 NANOPARTICLES

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ABSTRACT

In recent decades, interest in oxide nanomaterials with multifunctional properties has grown significantly. Titanium dioxide undoubtedly belongs to them, characterized by exceptional photocatalytic activity, non-toxicity, high availability, biocompatibility, antibacterial properties, and low cost. The treatment of textile materials with TiO_2 *nanoparticles is relatively simple, but the insufficient bonding efficiency between certain fibers and* TiO_2 *nanoparticles creates a problem regarding the stability and durability of the nanocomposites.*

In this study, an attempt was made to improve the properties of cotton modified with gelatin hydrogel, which was cross-linked by glutaraldehyde, and incorporated titanium nanoparticles. Three modification methods were applied, varying the mixing regimes of the components and the conditions. The composite materials were investigated via SEM, FTIR, UV-Vis and elemental analysis.

For the first time, titanium nanoparticles obtained by the reduction of TiO_2 *with oxalic acid were used to modify cotton. Cotton samples were modified with gelatin hydrogel cross-linked with glutaraldehyde to increase the active groups of cellulose fibers that bind to Ti ions. Using the hydrogel, the nanoparticles are deposited on the surface of the textile substrate. The elemental analysis shows the presence of* TiO_2 *nanoparticles. Lines for Ti atoms appear, which is evidence that the particles retain their composition after immobilization. Microscopic analyzes showed that* TiO_2 *nanoparticles were distributed unevenly in the cotton matrix. In the UV analysis, the appearance of a new absorption at 890* cm^{-1} *was observed due to the attachment of Ti-NPs. The appearance of the IR peak at 878* cm^{-1} *confirms the formation of chelate complexes of the nanoparticles in the composite material.*

Keywords: biocomposite, cotton fabric, gelatin, TiO_2 *nanoparticles.*

INTRODUCTION

The development of textile materials with antibacterial and antiviral activity that have self-cleaning properties is of a great interest to modern engineering technologies. Numerous studies have indicated that inorganic nanoparticles (NPs) can inactivate viruses due to the disruption of the viral envelope by the generation of oxidative species. Well-known effective antimicrobial agents are metal nanoparticles and metal oxides, namely: titanium dioxide (TiO_2), zinc oxide (ZnO), silver (Ag) and copper (Cu) [1 - 4]. The incorporation of TiO_2 NPs on textile fibers provides antiviral properties and UV protection, acts as flame retardants, increases surface hydrophobicity/hydrophilicity, and possesses self-cleaning properties [5 - 7].

Cotton fabrics covered by TiO_2 NPs have been shown to exhibit bactericidal properties against Gram-negative and Gram-positive bacteria. The antibacterial activity of TiO_2 NPs is due to the fact that they can produce reactive oxygen species (ROS) in the presence of UV radiation. Intracellular enzyme Coenzyme A supports the transfer of electrons between bacterial cells and semiconductors [8]. Oxidation of coenzyme A leads to a decrease in respiratory activity and, accordingly, to cell death of bacteria as a result of the destruction of the cell membrane and subsequent destruction of the cell wall. Photocatalytic action has also been observed in the absence of light, but its mechanism is still not fully understood and is being investigated [9]. UV-exposed TiO_2 not only causes bacterial cell death, but also endotoxin degradation. Scientists believe that the increase in UV resistance is due to the formation of a covalent bond between TiO_2 and the hydroxyl groups of cellulose as a result of a dehydration reaction [10, 11].

The antibacterial effectiveness of composite materials with the participation of TiO_2 NPs depends mainly on the method used for their synthesis [12, 13]. The modification of textile materials with TiO_2 NPs turns out to be comparatively simple, but with insufficient bonding between fibers and TiO_2 NPs. Nanostructures can be deposited to textile materials by diverse methods: hydrothermal; deposition layer by layer; drying methods; ultrasonic irradiation technique; and sol-gel processes. Due to the high cost, the need for highly specialized technical equipment and complex procedures, the impregnation of textile materials with TiO_2 NPs is often carried out by the immersion method. The stability of the formed complexes and the durability of the nanocomposite systems during their operation appear as a problem. For this reason, recent research is aimed at physico-chemical modification of the textile fibers surface in order to improve the efficiency of their bonding to the material. Based on the known fact, the carboxyl group is the best bonding group for TiO_2. With each of its two oxygen atoms, it binds to one Ti atom (bidentate chelation) or both Ti atoms (bridging bidentate) and this proceed to introduce new carboxyl groups into the structure of various fibers [14 - 16]. Appropriate initiation would provide not only increased efficiency but also better stability of the textile nanocomposite [17].

Cellulose fibers have been widely applied in medical textiles such as wound dressings, transdermal drug delivery, because they possess unique medical properties such as biodegradability, softness, good absorption, high hygroscopicity, flexibility, water absorption and breathability. However, cellulose fibers, due to their large surface area and ability to retain moisture, create a favorable environment for the expansion of microorganisms like bacteria, viruses and fungus, which are easily contaminated and difficult to clean [18 - 20].

A number of studies have shown that collagen-based matrices provide bioactive properties, but also stimulate cell migration into a scaffold, and in the form of hydrogels provide three-dimensional conditions for scaffold formation. Despite their good film-forming properties, there are limitations as hydrogels soon degraded hydrolytically and enzymatically [21 - 24]. A biomaterial characterized by distinctive properties, a natural polymer that does not show antigenicity, fully resorbable “*in vivo*”, possessing physico-chemical properties that are suitable for modulation, this is gelatin, which is also the subject of the present research. As a result of a large number of functional side groups in its structure, gelatin easily undergoes chemical cross-linking, which is important for its possible use in medical textiles [25 - 27]. Glutaraldehyde is often used as a cross-linking agent for collagen (GA), possessing good antibacterial properties to control the physical and biological properties of the collagen structure. GA cross-linked tissues retain many of the highly elastic properties of the native collagen fibrillar network and this makes them suitable even for bioprostheses [27].

The aim of the present study is to modify cotton textile fabrics with glutaraldehyde cross-linked gelatin hydrogel and incorporated titanium nanoparticles.

EXPERIMENTAL

Materials

A bleached, non-mercerized, plain fabric with a composition of 100 % cotton and weight of 145 ± 5 g m^{-2} was used for the purpose of modification, TiO_2 from Sigma-Aldrich (Darmstadt, Germany), Glutaraldehyde (25 % aqueous solution of $(CH_2)_3(CHO)_2$,) from Sigma-Aldrich (Darmstadt, Germany), Gelatin from Merck KGaA (Darmstadt, Germany) and Oxalic acid ($H_2C_2O_4$) from Merck KGaA (Darmstadt, Germany).

Three modification methods were applied - method 1, method 2 and method 3. The samples were modified by immersion in the different solutions in different sequences and at different temperatures. For each sample, 5 % gelatin solution, 2,5 % GA solution, 0.1 M TiO_2 solution, and 0.1 M $C_2H_2O_4$ solution were prepared in advance.

Methods for Preparation of Composite Materials

Method 1

Cotton samples size 50 x 50 mm were immersed in a 5 % aqueous solution of gelatin and cross-linked with 2.5 % aqueous solution of glutaraldehyde (GA) for 24 hours at room temperature. After draining, the samples were immersed in a 0.1 M solution of TiO_2 for 30 min and heated at t = 90°C. The next stage is immersion in a 0.1 M solution of oxalic acid ($C_2H_2O_4$) for 30 min and gradually heated to 90°C. After removing from the bath, the samples were rinsed with distilled water and dried at 90°C.

Method 2

Cotton samples size 50 x 50 mm were immersed in a 5 % gelatin solution for 30 min and heated at t = 90°C. After draining, they were immersed in a previously prepared solution of TiO_2 and $C_2H_2O_4$ for 30 min and t = 90°C. This was followed by a step of immersion in a 2.5 % GA solution for 30 min and drying at room temperature.

Method 3

Cotton samples 50 x 50 mm were immersed in a previously prepared solution of TiO_2 and $C_2H_2O_4$ for 30 min and heated at t = 90°C. After draining, the samples were immersed in a 5 % gelatin solution for 30 min at a temperature of 70°C. This was followed by a step of immersion in 2.5 % GA solution for 30 min and heating at t = 90°C. After draining, the samples were rinsed and dried at room temperature.

Analysis

The properties of the obtained composite materials are studied by various methods: UV -Vis spectral analysis, FTIR, SEM and elemental analysis. The surface morphology of the modified cotton fabric was analyzed with a Philips ESEM XL30 FEG SEM. The size, shape and distribution of the nanoparticles were determined by elemental quantitative and qualitative analysis in a 1 μm^3 area. Spectral characteristics are taken on, using UVA/ VIS/ NIR spectrophotometer Lambda 750S PerkinElmer, USA, in range of length $\lambda = 2500$ nm - 250 nm. FTIR analysis was performed on a Fourier transform infrared spectrometer (IRAffinity-1, Shimadzu, Japan) equipped with a diffuse reflectance sphere (MIRacle Attenuated Total Reflectance Attachment), the spectral range of 4000 - 600 cm^{-1}.

RESULTS AND DISCUSSION

Morphological Properties of Composites

Micrographs of cotton fabric and of the studied composite materials obtained by different modification methods are presented in Fig. 1. From the micrographs, it can be seen that the TiO_2 NPs are impregnated into the hydrogel structure on the cotton fabric. Microscopic studies (SEM) of the modified fabric by the method 1 showed that the nanoparticles were incorporated into the hydrogel structure and distributed into small film-forming structures on the cotton fabric surface. In the micrographs of the composites, obtained by the method 2, there is a complete surface gel film on the cotton sample. In method 3, TiO_2 NPs are unevenly agglomerated.

Elemental Analysis of Composites

Elemental analysis was carried out, which allows the most accurate determination of carbon, hydrogen, nitrogen and titanium atoms in the investigated composite cotton fabric/ gelatin/TiO_2 by method 1 and 3. The results are presented in Table 1 and Fig. 2.

In the composites obtained by method 3, a more uniform distribution of Ti nanoparticles is observed, while in the composites obtained by method 1, differences are observed in the individual investigated areas. The amount of atoms of the elements are defined in 1 μm^3.

FTIR Analysis of Composites

Fig. 3 shows the IR spectra of the hydrogel-modified cotton fabrics in the region from 4000 cm^{-1} to 750 cm^{-1} for the different methods.

Valence vibrational oscillations are observed, which are related to the OH hydroxyl groups with a maximum of 3377 cm^{-1}. There are peaks in the range 3200 - 3306 cm^{-1}, as a result of the interaction of the nanoparticles with -NH and OH- groups of the gelatin hydrogel and cellulose. The valence vibration of the C=O carbonyl group at the samples treated with TiO_2 NPs are observed at 1631 cm^{-1}, and it decreased in intensity. The appearance of a peak at 878 cm^{-1} in samples obtained by method 2 and by method 3 confirms the formation of chelate complexes of the nanoparticles in the composite material.

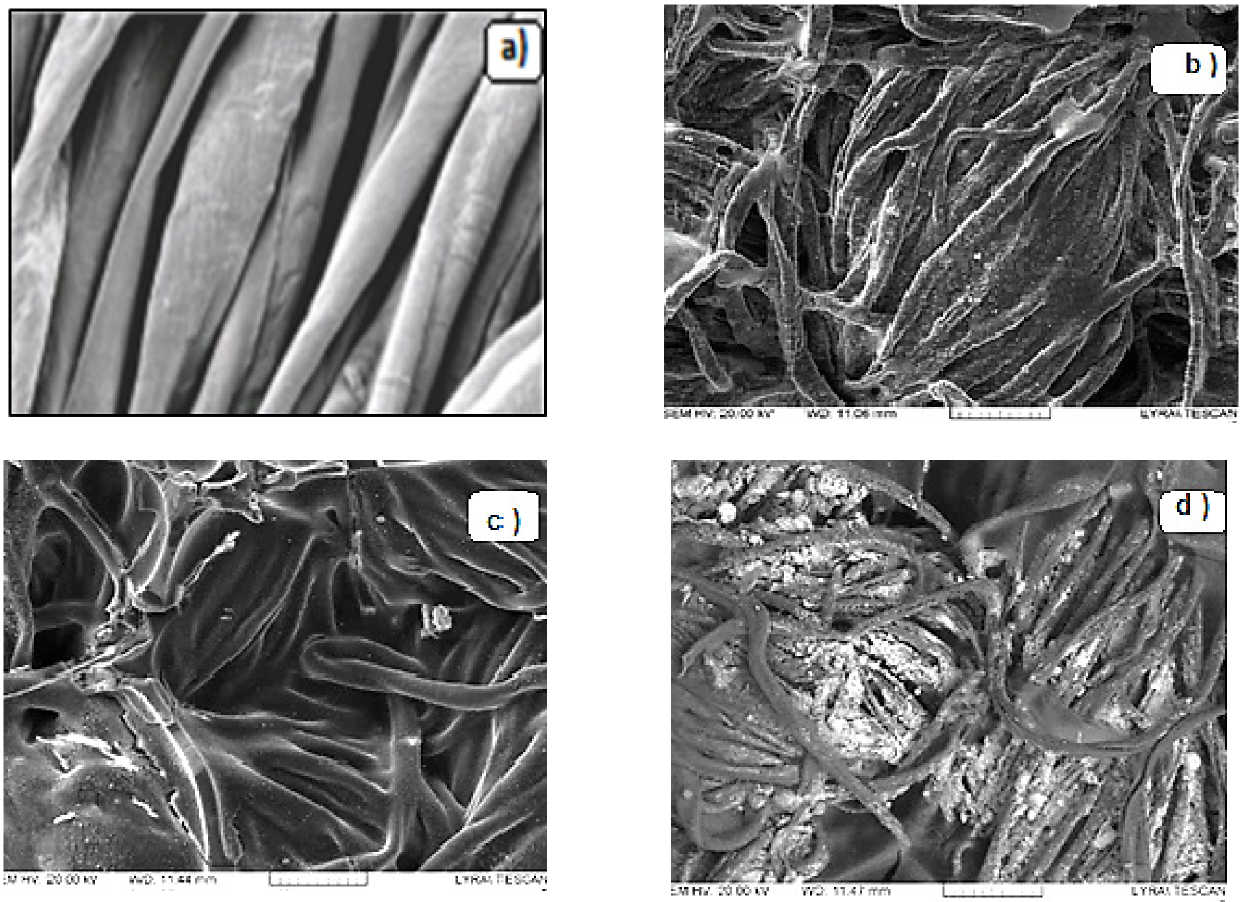
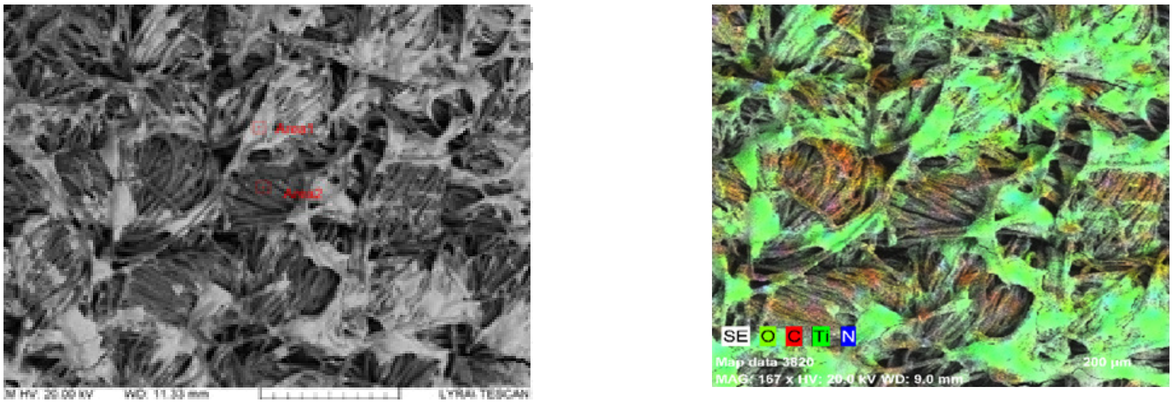


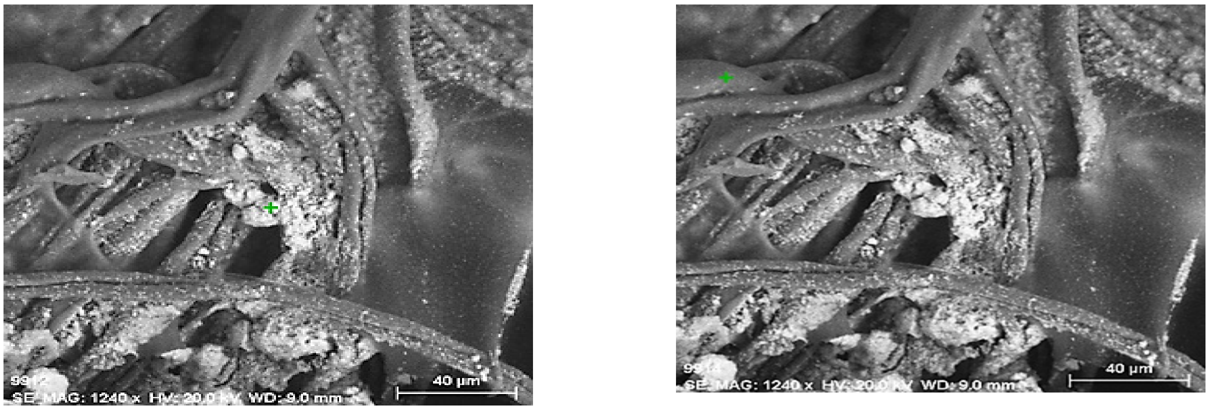
Fig. 1. SEM images of the surface of cotton fabric: a) Cotton; b) Modified Cotton - Method 1; c) Modified Cotton - Method 2; d) Modified Cotton - Method 3.

Table 1. Elemental analysis of a cotton fabric and composites.

	Element	unn. C [wt. %]	norm. C [wt. %]	Atom C [wt. %]
Method 1, Area 1	O	32.74	32.65	56.43
	Ti	64.77	64.60	37.31
	C	2.52	2.51	5.78
	N	0.25	0.25	0.48
Method 1, Area 2	O	59.96	59.96	59.00
	Ti	24.02	24.02	31.49
	C	5.34	5.34	6.00
	N	10.68	10.68	3.51
Method 3, Area 1	O	37.04	37.04	43.51
	Ti	48.31	48.31	42.60
	C	13.44	13.44	13.53
	N	1.21	1.21	0.36
Method 3, Area 2	O	47.44	43.71	61.41
	Ti	51.22	47.19	22.15
	C	7.47	6.88	12.87
	N	2.41	2.22	3.57

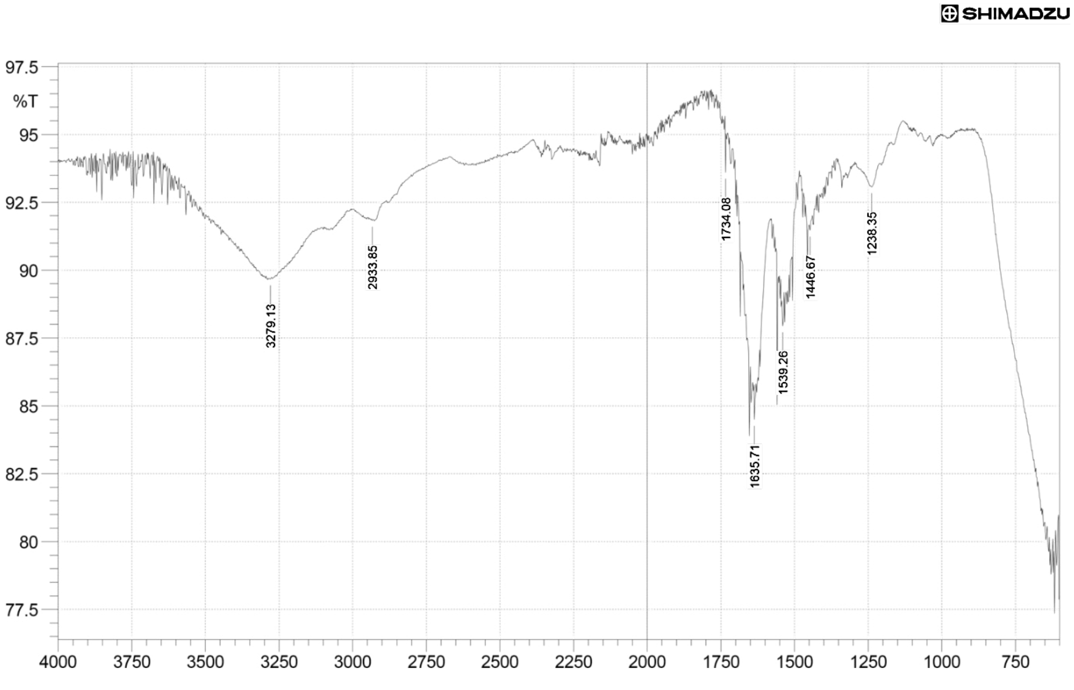


Method 1, area 1 Method 1, area 2

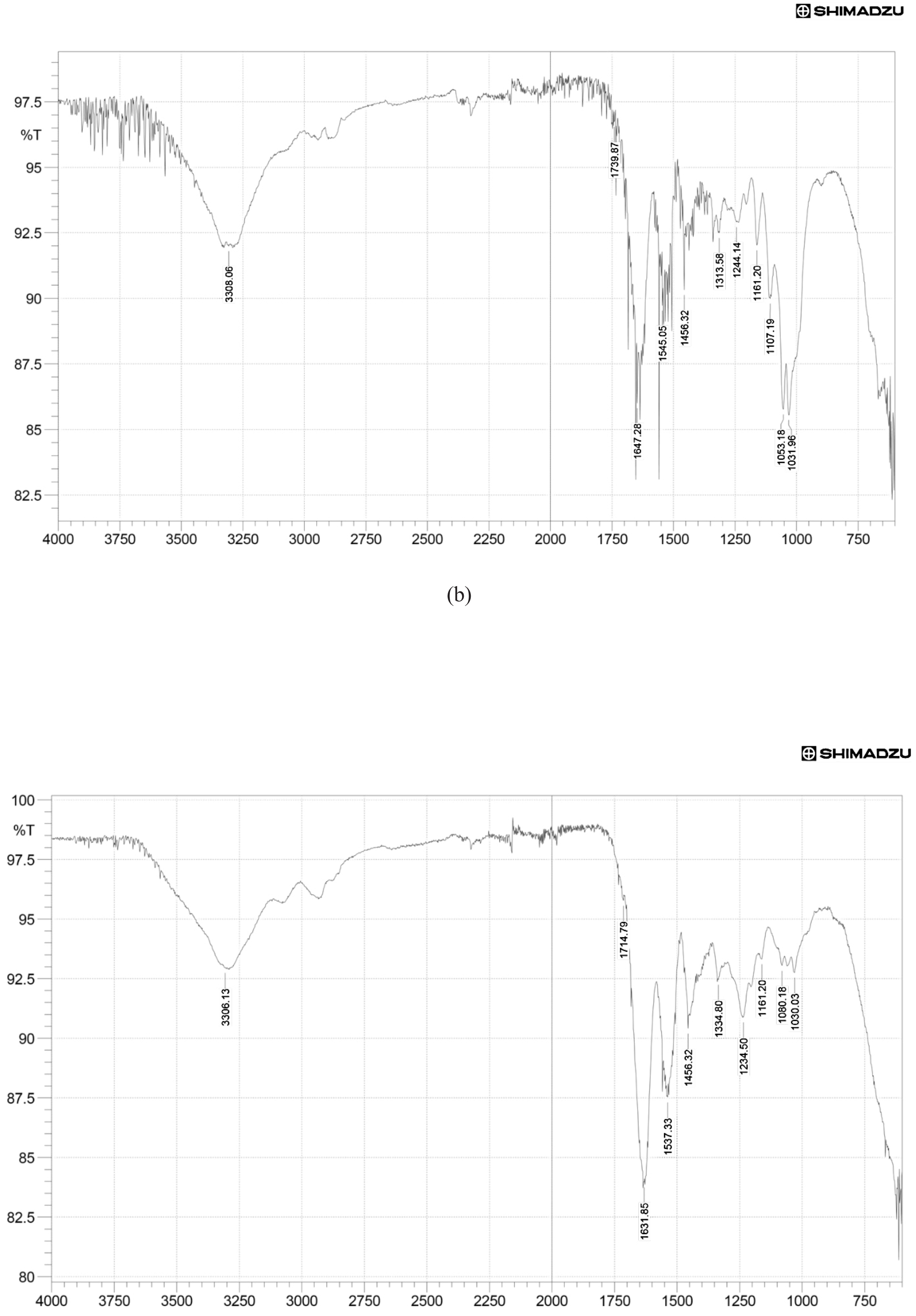


Method 3, area 1 Method 3, area 2

Fig. 2. Elemental analysis of cotton fabric: a) Modified Cotton - Method 1; b) Modified Cotton - Method 3.



(a)



(b)

(c)

Fig. 3. FTIR of cotton composites: a) Modified Cotton - Method 1; b) Modified Cotton - Method 2; c) Modified Cotton - Method 3.

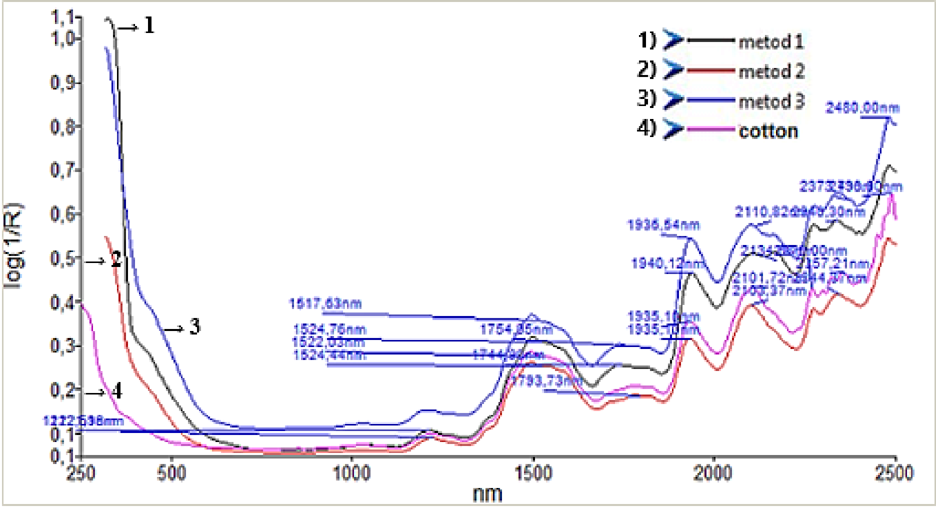


Fig. 4. Absorption spectrum of: cotton; cotton modified by method 1, method 2, method 3.

UV - VIS - NIR Absorbance spectral analysis

An absorption at 890 cm^{-1} due to the attachment of TiO_2 NPs was observed (Fig. 4). The shifts of the peaks in the different methods are related to asymmetric and symmetric stretching vibrations of the C=O group, which can be attributed to the TiO_2 NPs precursor. Elevations in the UV regions are most pronounced in the composite obtained by method 1.

CONCLUSIONS

In the present study, biocomposite materials were obtained by modifying cotton fabric with gelatin cross-linked with glutaraldehyde and containing titanium dioxide particles. Three methods for the synthesis of TiO_2 NPs were applied, varying the components and processing conditions. Using the obtained hydrogel, the nanoparticles were deposited on the surface of the studied samples. A few analyzes were performed to determine the most appropriate method. An uneven distribution of TiO_2 nanoparticles was found at the different methods used. The highest amount of TiO_2 hydrogel was found in Method 3, and the obtained samples had the best characteristics of the three methods. This promises good future results in the next planned analysis of antibacterial properties.

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