METHODS FOR MODIFICATION OF COTTON FABRICS WITH GELATIN – GLUTARALDEHYDE AND ZNO NANOPARTICLES

DARINA ZHELEVA[1], MARGARITA KOLEVA[1], DESISLAVA ANGELOVA[1], DESISLAVA GRABCHEVA[1], PETAR TODOROV[2]

[1]*University of Chemical Technology and Metallurgy - Textile and Leather Department*

[2]*University of Chemical Technology and Metallurgy - Organic Chemistry Department*
Sofia, Bulgaria, e-mail: darinajeleva@abv.bg

Cotton fabrics have good water absorption properties, air permeability, non-toxicity, but microorganisms easily damage them. Collagen is a commonly used biomaterial that has properties such as biocompatibility, biodegradability, non-toxicity, but with poor mechanical properties. Glutaraldehyde is the main cross-linking agent for collagen and characterized by antimicrobial properties. ZnO nanoparticles exhibiting antibacterial, antifungal, anticorrosive and protective properties against UV, is widely applicable in medicine. The combination of all these components in one biocomposite with potential antimicrobial properties and healing effect can find application in medical practice. In this study, an attempt was made to improve the properties of cotton fabric by impregnating it with gelatin hydrogel cross-linked with glutaraldehyde and containing ZnO nanoparticles. Three methods of modification were applied, varying the mixing regimes of the components and the conditions. The composite materials were investigated by means of SEM, FTIR, and fluorescence analysis. The morphological analyzes of the samples modified by different methods show that the spherical particles of ZnO have changed into a flower-like structures; the particles are covered by the collagen film; and dispersed and agglomerated in certain places. FTIR analyzes prove interactions between the organic and inorganic components. This is also confirmed by the observed fluorescent properties, which are of different intensity. All these observations suggest good antibacterial properties that will be the subject of future research.

Keywords: biocomposites, cotton, gelatin, ZnO nanoparticles

INTRODUCTION

In biomedical industry, collagen has been employed to modify and functionalize different types of materials for wound treatments applications. Various forms of collagen including fibers, films, membranes, coatings, 3D printed constructs, and hydrogels have been used as scaffold for medical applications. Therefore, it is fundamental to develop wound dressings that are capable of preventing bacteria penetration into the wound or avoid microorganisms' growth (Cortés *et al.*, 2019; Dong and Lv, 2016). As a biomaterial, gelatin has advantages such as: it is a natural polymer which has not shown antigenity, it is completely resorbable *in vivo* and its physicochemical properties can be suitably modulated. Due to the large number of functional side groups it contains, gelatin readily undergoes chemical cross-linking, which is very important for its possible use as a biomaterial. One of the main disadvantage of gelatin as a material is its poor mechanical properties. Glutaraldehyde is by far the most widely used agent, due to its eficiency to stabilize collagen-based biomaterials (Khor, 1997). Cotton fabric is the most popular raw materials in textile industry due to the properties such as wearing comfortability, flexibility, water absorptivity, breathability. However, cotton products are easily damaged by microorganisms on account of its moisture retaining nature, and therefore not only cause discoloration, loss in mechanical strength, and foul odor but also result of negative health effects (Irfan *et al*, 2017). Current wound dressings have some major deficiencies including low absorption of wound fluids, low flexibility, a tendency to adhere onto the wound surface, poor mechanical strength and lack of a suitable and moist environment for wound healing. In addition, the majority of current wound dressing do not harbor antimicrobial activity. In this context, hydrogel-based wound dressings would provide a cooling sensation, a moisture environment as well as a barrier to microorganism colonization. Nanoparticles have emerged as potent treatment for bacterial infections and are routinely combined with hydrogels to form hybrid biomaterial systems (Wahid *et al.*, 2017; Tauhiduzzaman *et al*., 2021; Ayanoglu *et al*.,

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2022). Among various metallic oxides, ZnO nanoparticles have been widely applied as antimicrobial agents, which exhibits efficient bactericidal activity against Gram-positive and Gram-negative pathogens, as well as high-pressure and heat-resistant bacteria. Some reported antibacterial mechanisms are as follows: ZnO can bind to the cell membrane and induce increased membrane permeability and cell lysis. Meanwhile, it could produce ROS (reactive oxygen species) such as singlet oxygen ($^1O_2$) and hydroxyl radicals (HO•) and inactivate pathogens. Besides, the released zinc ions could promote the growth of fibroblast and the migration of keratinocytes, thus enhancing tissue repair during wound healing. In textile fabrication, metal oxides: ZnO, TiO_2, CuO, MgO can be used to protect fabrics from UV, microbes, retard flame, conduct electricity, repel water, self-clean, etc. The nanostructures of metallic oxides release ions, and these ions cause the inactivation (Sawhney *et al.*, 2008; Raut *et al.*, 2010; Stankic *et al.*, 2016; Verbic *et al.*, 2019; Kolodziejczak-Radzimska and Jesionowski, 2014). Considering the Collagenic nature of the skin and the beneficial properties of Chitosan, the two polymers were proposed to be used in developing nanostructured wound dressing loaded with ZnO nanoparticles. These nanostructured materials confer promising characteristics to be used as anti-infectious wound dressing being biocompatible, antimicrobial against *C. albicans* and *S. aureus*, and highly hydrophilic able to absorb over 2300% water, which confer the premises of maintaining proper humidity and exudate absorption during wound healing (Tiplea *et al*., 2021). The new Collagen/(RGO/ZnO/TiO_2/SiO_2) composites demonstrate an antimicrobial activity dependent on the agent loading level (RGO is reduced graphene oxide). It is specific in respect to Gram-negative, Gram-positive bacteria and fungi (Staneva *et al.*, 2020). ZnO nanostructures have been applied on textile materials through different methods such as hydrothermal route, layer-by-layer deposition, pad-dry procedure, ultrasonic irradiation technique, and sol-gel process (Li *et al.*, 2011; Uğur *et al*, 2010; Vihodceva and Kukle, 2013). There are two main methods of chemical production of ZnO-NP and their application on textiles, i.e., *ex situ* and *in situ* synthesis (Shubha *et al.*, 2019; Montazer and Amiri, 2014). Zinc nitrate hexahydrate and potassium hydroxide were used as starting materials and the reaction was performed at 50°C. The *in situ* growth of ZnO nanostructures on cotton fabric occurred in a single-stage process. The cotton fabrics coated with ZnO nanostructures presented an antibacterial efficiency (Souza *et al.*, 2018). Pomegranate peel extract was used as a reducing agent and wood ash extract was used as an alkali source for the formation of ZnO-NP from zinc acetate. Four different methods, which varied in drying between immersion of fabric in the active solutions for synthesis and the use of padding and ultrasonication, were investigated to evaluate the most suitable one to achieve excellent UV properties of the textile (Verbic *et al.*, 2021). The authors (Hong *et al.*, 2020) reported on hydrothermal application for seedless growth of ZnO on different fabrics using [$Zn(NO_3)_2 \cdot 6H_2O$] as precursor (with nano rod structure).

The aim of this study is to prepare biocomposites from modified cotton fabric with glutaraldehyde-crosslinked gelatin and ZnO particles and to investigate the methods of modification, varying mixing regimes of the components and the conditions.

MATERIALS AND METHODS

Materials

A bleached and unmercerized, plain-woven, 100% cotton fabric, with a surface weight of 145±5 g/m^2 was used. $Zn(NO_3)_2 \cdot 6H_2O$ (CAS:10196-18-6) and NaOH were purchased from Sigma-Aldrich (Darmstadt, Germany); glutaraldehyde (25% aqueous solution) from Sigma-Aldrich (Darmstadt, Germany); citric acid monohydrate (CAS: 5949-29-1) and Gelatin (CAS: 9000-70-8), from Merck KGaA (Darmstadt, Germany). All solutions were prepare with distilled water.

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Methods for Preparation of Composite Materials

Method 1

The gelatin (5% w/v) was dissolved in water under stirring and is added the glutaraldehyde water solution (2.5 % w/w to gelatin) for the crosslinking during 24 h. Then cotton substrates (untreated and pretreated with citric acid) was impregnated with the solution containing cross-linked gelatin and staying the immersed samples for 24 h. Then the samples were immersed in water solution of $Zn(NO_3)_2 \cdot 6H_2O$ and dried at 90°C for 30 min. Finally, the samples were soaked in sodium hydroxide solution with a ten-time stoichiometric excess to zinc ions and treated thermally at 90°C for 30 min. The obtained composites were washed with water and dried at a room temperature.

Method 2

The gelatin (5% w/v) was dissolved in water under stirring. Preparing of water solution of $Zn(NO_3)_2 \cdot 6H_2O$. Cotton substrates (untreated and pretreated with citric acid) were impregnated with solution containing gelatin and was added the solution of $Zn(NO_3)_2 \cdot 6H_2O$ and then dried at 90°C for 30 min. Next, the samples were impregnated with a glutaraldehyde water solution (2.5 % w/w to gelatin) and dried again (90°C for 10 min). Finally, the sample was soaked in sodium hydroxide solution and treated thermally at 90°C for 30 min. The obtained composite materials were washed with water and allowed to dry at a room temperature.

Method 3

The gelatin (5% w/v) was dissolved in water under stirring and cotton samples were impregnated with gelatin solution. Preparing of water solution of $Zn(NO_3)_2 \cdot 6H_2O$ and sodium hydroxide solution. Then, the solution of NaOH was added drop-wise, vigorously stirred with the solution of $Zn(NO_3)_2 \cdot 6H_2O$ at heating of 80ºC during 10 min. A white precipitate of ZnO was obtained. Then cotton substrates (untreated and pretreated with citric acid) was impregnated with the solution then dried at 90ºC for 1h and staying the immersed samples for 24 h. Finally, the samples were crosslinked with glutaraldehyde water solution and treated thermally at 90ºC for 30 min. The obtained composites were washed and dried.

Analysis

The surface morphology of the composite materials and the formation of ZnO particles were analyzed using a scanning electron microscope (SEM) JSM-5510 (Jeol Ltd., Tokyo, Japan) operated at a 10-kV acceleration voltage. FTIR analysis was carried out on an Infrared Fourier Transform spectrometer (IRAffinity-1, Shimadzu, Japan) equipped with a diffuse-reflectance attachment (MIRacle Attenuated Total Reflectance Attachment). Measurements were done using a spectral range of 600–4000 cm^{-1}. X-ray fluorescence (XRF) spectrometry was used to define the amount of ZnO in composite materials. A wavelength dispersive (WDXRF) technique was used and Rigaku Supermini200 (Bruker, Hanau, Germany) equipment was used.

RESULTS AND DISCUSSIONS

Morphological Properties of Composites

Fig.1 shows micrographs of the cotton fabric and of composite materials obtained at different modification methods. As can be seen on fig.1b the cotton material is covered by crosslinked gelatin. The micrographs of the composite obtained by *Method 1* on

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fig.1c show that the spherical particles have changed into a flower-like shape with needle-like ends. In composite material obtained by *Method 2* on fig.1d, the individual fibers are covered with a layer with a granular structure of white spherical ZnO particles, distributed relatively homogeneous on the surface. The micrographs in fig.1e for a composite obtained by *Method 3* show crowding and agglomeration of the zinc oxide particles in certain places of the cellulose matrix. This agglomeration of the particles is likely to show a better effect due to the larger surface area of the ZnO.

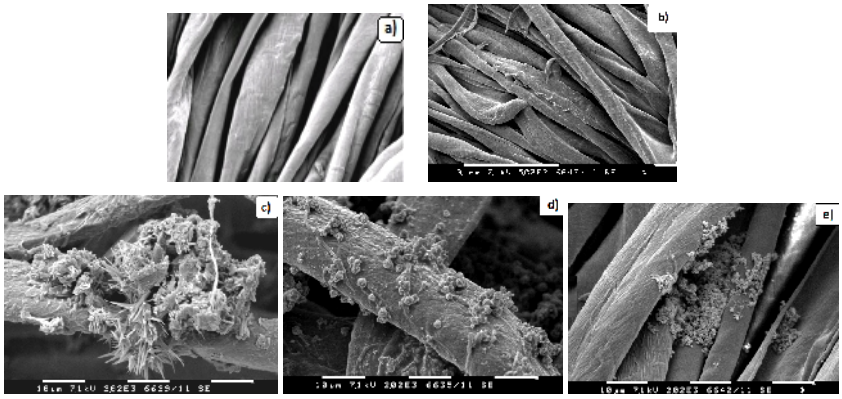

Figure 1. SEM images of the surface of a cotton fabric a) Cotton; b) Cotton-Gelatin-GA and fabrics modified by different methods: c) Modified Cotton–Method 1; d) Modified Cotton–Method 2; e) Modified Cotton–Method 3

Fluorescence Analysis of the Composites

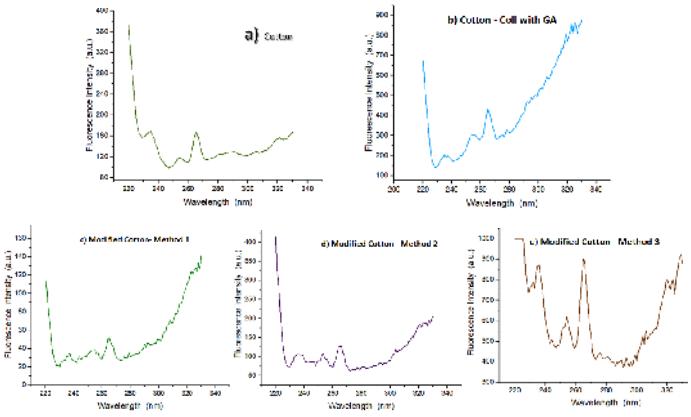

Figure 2. Fluorescence analysis of cotton fabrics: a) Cotton; b) Cotton-Gelatin-GA; c) Modified Cotton–Method 1; d) Modified Cotton–Method 2; e) Modified Cotton–Method 3

Fig.2 shows the photoluminescence spectra of samples in the solid state. After crosslinking with glutaraldehyde, collagen emits a blue–green fluorescence with higher peak intensity. The presence of zinc oxide in the crosslinked collagen film is the reason for the weakening of the fluorescence emission of collagen and for the appearance of a

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new peak. The peak arises due to a transition between interstitial zinc and the zinc vacancy level (Samanta *et al.*, 2012). The most significant differences in the fluorescence analysis were observed in the samples modified by method 3, which is most likely due to an increase in the amount of zinc oxide and it could produce reactive oxygen species such as singlet oxygen ($^1O_2$).

FTIR Analysis

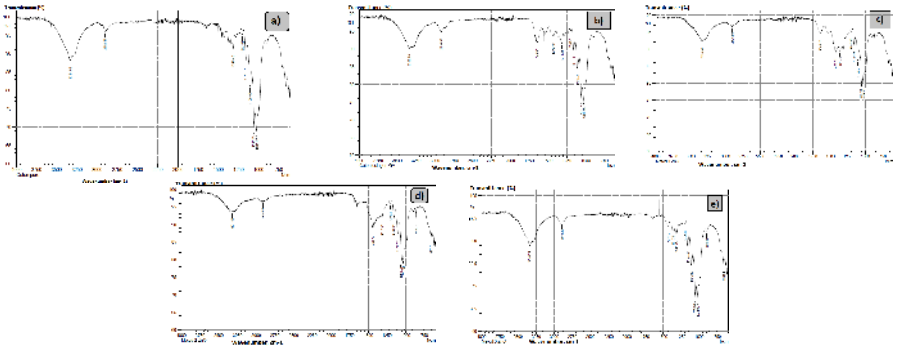

Figure 3. FTIR analysis of cotton fabrics: a) Cotton; b) Cotton-Gelatin-GA c) Modified Cotton–Method 1; d) Modified Cotton–Method 2; e) Modified Cotton–Method 3

Oxycellulose has many reactive aldehyde groups which can react with amino groups from collagen molecule to form Schiff bonds (Hu, 2015). This can be seen from the FTIR spectrum on fig.3b with the appearance of a new peak at 1450 nm^{-1}, resulting from the cross-linking of collagen with glutaraldehyde.

As reported in (Verbic *et al.*, 2021), the peak at 854 cm^{-1} confirms the formation of tetrahedral coordination of ZnO. This peak present in our spectra (fig.3c,d,e) and these peaks are most clearly expressed in the composite obtained by Method 3 (fig.3e).

CONCLUSIONS

In this study, biocomposites were obtained by modifying cotton fabric with crosslinked glutaraldehyde gelatin containing zinc oxide particles. Three methods of synthesis of ZnO by varying the components and processing conditions were investigated. It was proved that the composites obtained by method 3 show the best characteristics and exhibited promising results for antibacterial properties, which will to be investigated in the future.

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