

Radiation synthesis of silver nano- and microparticles in cellulose fibers

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Abstract. Polymer nanocomposites containing metal nanoparticles have attracted a great interest due to their unique chemical and physical properties. “Green” chemistry promotes application of natural fibers in such structures, among them cellulose is one of the most frequently used. However, cellulose fabric have ability to absorb moisture, so under certain conditions of humidity and temperature they can be subjected to microbial attack. One of the most popular and best known antibacterial agents is silver, which serves as a potential antibacterial material acting against an exceptionally broad spectrum of bacteria including activity against antibiotic-resistant bacteria. Silver nanoparticles (Ag NPs) were grown at the cellulose fibers surface by direct reduction of AgNO_3 with electron beam (EB) application. Nanocomposites obtained according to the method described in the text were investigated with X-ray diffraction (XRD), scanning electron microscope with back-scattered electrons detector (SEM-BSE) and energy dispersive spectroscopy (EDS) as well as thermogravimetric analysis (TGA) in order to determine influence of different size silver particles on fibers thermal properties.

Key words: silver particles • cellulose • EB irradiation

Introduction

Polymer nanocomposites containing metal nanoparticles have attracted a great interest due to their unique chemical and physical properties. The need of elaboration of non-toxic and cost-effective antimicrobial finishing of fabrics grows with progressive production increase of medical, healthcare and protective materials [8]. Cellulose and its derivatives have been used in a variety of applications in several areas such as the textile industry, the paper industry, and in the biomedical field as tissue engineering materials due to their good biocompatibility, mechanical properties and easy fabrication of demanded shapes and forms [14]. Cellulose fabric have ability to absorb moisture, so under certain conditions of humidity and temperature it can be subjected to microbial attack [8, 12]. The organic matter that may be incorporated between the fibers could become a nutrient for microbial growth as well. In the case of filter it may lead to unpleasant smell or even bioaerosol generation. Various chemicals have been already incorporated into fibers to prevent harmful activity of the microorganisms [7, 13, 18]. One of the most popular and best known antibacterial compound is silver [16]. Silver serves as a potential antibacterial agent acting against an exceptionally broad spectrum of bacteria including activity against antibiotic-resistant bacteria [10] while exhibiting low toxicity to mammalian cells [20]. In general, the nanosized inorganic particles

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posses very high surface area and shows unique chemical and physical properties. The immobilization of Ag NPs onto different fibers has attracted a great deal of attention [11, 17] recently. The mechanism of the antibacterial action of silver depends on state of the silver [5]. The atomic oxygen adsorbed onto the surface of silver exposed to aqueous media rapidly reacts with pairs of sulfhydryl (-S-H) groups on the surface of bacteria or viruses by replacing the hydrogen atoms (as water) resulting in the coupling of the sulfur atoms to form an R-S-S-R bond which completely blocks respiration and electron transfer. Monovalent silver ions have an affinity for sulfhydryl groups exposed outer bacteria or viruses. The resulting stable -S-Ag group inhibits hydrogen transfer. Antelman [1] observed that when the reproductive rates of organisms are high as in the case of bacteria with their exposed sulfhydryl and amino sites, this action will attract oxidation by the silver ions (III) and the organism will be oxidized.

Silver nitrate is the most common silver compound used as an effective antibacterial agent in clinical practice. There is a strong evidence in the literature that the active component of this silver salt is the silver itself [3]. Silver nitrate is a substance that releases silver ions rapidly while adequately activated.

The application of Ag NPs to different materials gains a great deal of attention particularly because of their high resistance to microbes. Vigneshwaran *et al.* developed *in situ* synthesis of Ag NPs on cotton fabrics where the aldehyde groups of starch molecules reduce the silver nitrate to silver metal, simultaneously stabilizing the Ag NPs formed on the fabric [19]. Perelshtein *et al.* have elaborated sonochemical coating of Ag NPs using the ultrasound irradiation [15]. Durán *et al.* obtained cotton fabrics with good antibacterial properties using the Ag NPs produced by biological process directly on the cotton fabrics [6].

The present study is carried out to elaborate and investigate the formation of Ag NP on cellulose fibers. Our approach relies on the loading of cellulose fibers with Ag NPs which were obtained from silver nitrate aqueous solution with the EB application. Obtained materials with different Ag NPs concentration were investigated by using XRD, SEM-BSE and EDS. TGA analysis was performed to evaluate the influence of different size of Ag NPs and the effect of EB irradiation on fibers thermal properties.

Materials

Silver nitrate (AgNO_3 ; > 99.5% purity) was purchased from Fluka (Switzerland). 2-propanol was purchased from POCH S.A. (Poland). All chemicals were of analytical reagent grade and were used without further purification. Discs of cellulose filter paper (surface density 65 g/m², 30 mm dimension) were prepared.

Instrumentation

Morphology of the samples was studied using a scanning electron microscope with a detector of back-scattered electrons (SEM-BSE) DSM 942 (Zeiss Instrument,

Leo, Germany) equipped with an energy dispersive spectrometer (EDS) which allows to determine precisely elemental composition of materials. Samples for SEM-BSE were prepared according to the standard procedure, fixed with conductive glue and covered with a thin gold layer.

The thermal investigation of cellulose fibers with silver particles was carried out with Q 500 TGA (T. A. Instruments) from 30 to 600°C at a heating rate of 10°C per min, under a constant flow (60 ml/min) of nitrogen gas.

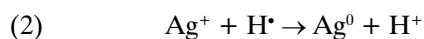
The XRD pattern of silver particles in cellulose fibers was recorded using a Bruker-AXS D8 advance X-ray diffractometer. Cellulose samples were placed in silver nitrate solutions of different concentrations and were exposed to EB irradiation using a 10 MeV – 8 kW linear electron accelerator “Elektronika”.

In situ synthesis of cellulose/silver composites

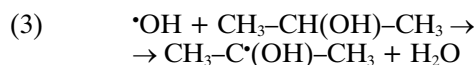
Adequate volumes of 0.1% silver nitrate solution and distilled water were used to obtain solutions of the required AgNO_3 concentrations ($4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ and $4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$). Discs of cellulose filter paper of 30 mm dimension were immersed in the AgNO_3 solutions. Ag NPs were grown at the cellulose fiber surface by direct reduction of Ag^+ with EB application. Isopropyl alcohol (1.5 mM) was added to convert OH radicals into the isopropyl radical. Samples prepared in this way were irradiated with EB with a dose of 25 kGy.

When cellulose fibers, placed in the aqueous silver nitrate solution are irradiated with EB radiation, most of the energy is absorbed by water what results in the formation of reactive products like hydrated electron (e_{aq}^-), hydrogen atom (H^\bullet) and hydroxyl radical (OH^\bullet).

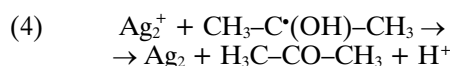
Hydrated electron (e_{aq}^-) and hydrogen atom (H^\bullet) are very powerful reducing agents ($E^0 \text{H}_2\text{O}/e_{\text{aq}}^- = -2.87 \text{ V NHE}$, $E^0 \text{H}^\bullet/\text{H}^\bullet = -2.3 \text{ V NHE}$) and reduce Ag^+ ions on the cellulose fibers surface to zerovalent Ag due to the following reactions:



Silver cations can be also reduced by isopropanol radicals which are formed in the reaction of hydroxyl radical (OH^\bullet) with isopropanol molecules [2]:



Silver atoms immobilized on the cellulose fibers react with Ag cations from solution, forming silver dimers Ag_2^+ which are next reduced by e_{aq}^- , H^\bullet or isopropanol radicals yielding neutral silver dimers Ag_2^0 .



This process continues and leads to the formation of large Ag clusters on the cellulose fibers surface.

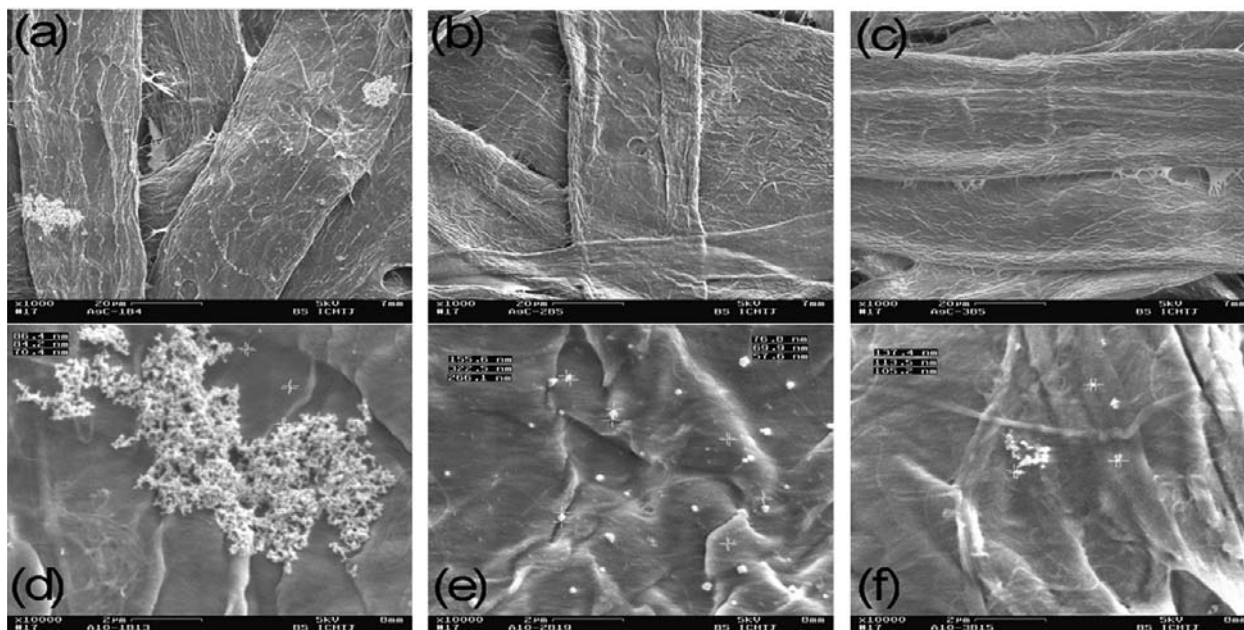
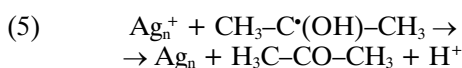


Fig. 1. SEM images of silver particles embedded in cellulose fibers: AgNO_3 concentration $4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, magnification $1000\times$ (a); AgNO_3 concentration $4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, magnification $1000\times$ (b); AgNO_3 concentration $4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$, magnification $1000\times$ (c); AgNO_3 concentration $4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, magnification $10\,000\times$ (d); AgNO_3 concentration $4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, magnification $10\,000\times$ (e); AgNO_3 concentration $4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$, magnification $10\,000\times$ (f).



The surface hydroxyl groups present in cellulose structure are favourable to effective adsorption of silver onto cellulose fibers [9].

Change in the cellulose fibers color from white to yellow during irradiation of samples was observed, confirming the reduction of the Ag^+ ions and a subsequent formation of Ag particles.

Results and discussion

Figure 1 depicts the SEM-BSE micrographs of silver particles–cellulose composites obtained for different concentrations of the applied AgNO_3 solution. These micrographs evidence the silver nano- and microparticles presence on the surface of cellulose fibers. Distribution, size and shape of the silver particles depend on the concentration of AgNO_3 solution. For the highest concentration of AgNO_3 solution ($4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$) (Figs. 1a and 1d) a large amount of Ag NPs, which agglomerated in big clusters with no defined morphology, were observed. Smaller concentration of Ag^+ ions ($4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution) seems to be the most suitable for homogeneous distribution of silver particles. In Figs. 1b and 1e silver particles with diameter in the range between 57 and 322 nm with an approximately spherical shape and homogeneous distribution on the cellulose fibers surface are observed. Application of the lowest AgNO_3 solution concentration ($4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$) resulted in the formation of small silver clusters composed of Ag NPs with narrow size distribution ($\sim 100 \text{ nm}$). These silver clusters are not dispersed homogeneously within the cellulose fibers, but only few agglomeration centers are observed at the fiber surface (Figs. 1c and 1f). These results

show that there is an optimal concentration of silver nitrate solution which ensures homogeneous and most narrow size distribution of silver particles obtained in the cellulose fibers.

Quantitative assessment of the amount of the elemental Ag was conducted with the use of EDS. The content of silver in cellulose fibers depends on the concentration of AgNO_3 solutions applied. The Ag concentrations determined in the samples were as follows: 0.71% (for $4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution), 0.18% (for $4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution) and 0.02% (for $4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution) and correspond to a percentage error level (Table 1).

Figure 2 shows the thermograms of the non-modified cellulose fiber, non-modified cellulose fiber after treatment with EB with a dose of 25 kGy and cellulose fibers modified with AgNO_3 solutions of different concentrations and irradiated with EB at a dose of 25 kGy. Cellulose fibers show a good thermal stability until 270.59°C and maximum decomposition takes place at 369.63°C . It was observed that a small amount of silver particle addition as well as EB irradiation do not influence thermal stability of the cellulose fibers. The maximum decomposition temperature decrease only slightly for the fibers with the highest silver concentration and the weight loss is lower than 10% in comparison to control

Table 1. Concentration of different elements in cellulose samples treated with AgNO_3

Element	Concentration (wt.%)
Sample: Cellulose + $4.3 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution	
Silver	0.71
Sample: Cellulose + $4.3 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution	
Silver	0.18
Sample: Cellulose + $4.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 solution	
Silver	0.02

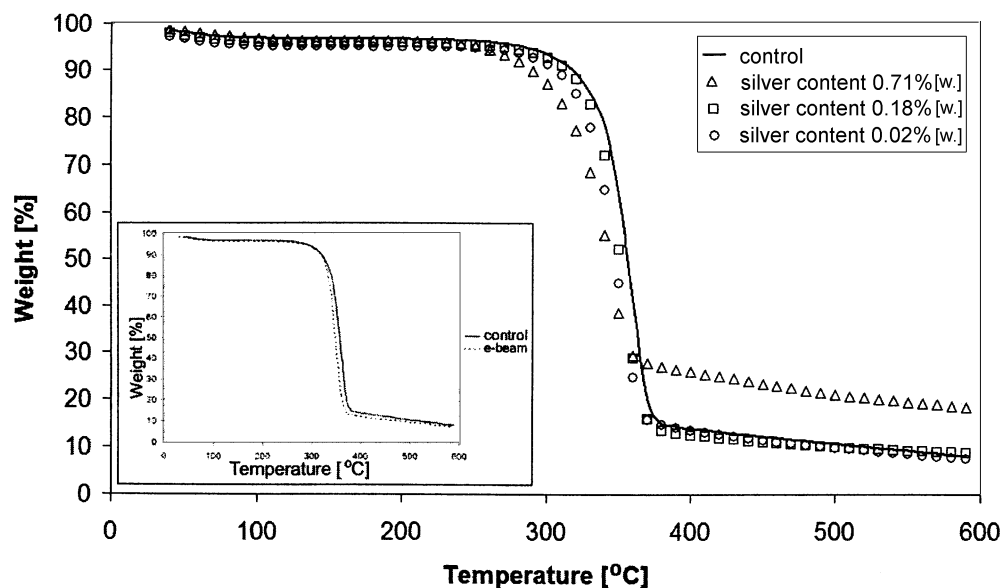


Fig. 2. Thermograms of non-modified cellulose fiber and cellulose fibers modified with silver obtained with EB irradiation. Insert: comparison of thermograms of non-modified cellulose fiber and non-modified cellulose fiber after treatment with EB.

sample. The residual mass (17%) obtained for temperature 600°C is related to silver particles.

Figure 3 shows the XRD pattern for the sample with the highest silver concentration. It shows peaks at 38.33° and 44.53° assigned to diffraction from the (111) and (200) planes of fcc silver. The crystalline size can be determined by the Debye-Scherrer equation [4] from diffraction peak of XRD results. The calculated average crystalline size is 280 Å. Taking into consideration SEM-BSE image, we assumed that this is an average size of smaller silver particles which agglomerate in big clusters. No diffraction lines could be obtained for two samples with smaller silver concentrations, because the average silver particles are too small to be observed with the XRD method.

Conclusion

The silver ions are reduced effectively by EB irradiation and are stabilized onto the surface of cellulose fiber. Reduction of silver with EB irradiation gives the possibility to control silver particles size and distribution in the material with application of different concentration of the silver salt solution. Addition of silver particles as well as EB irradiation do not significantly influence the thermal stability of cellulose fibers, so such fibers have a great potential for the application as antibacterial filters or finishings. Further investigation will be carried out to determine the influence of irradiation dose on the size and distribution of silver particle in this material.

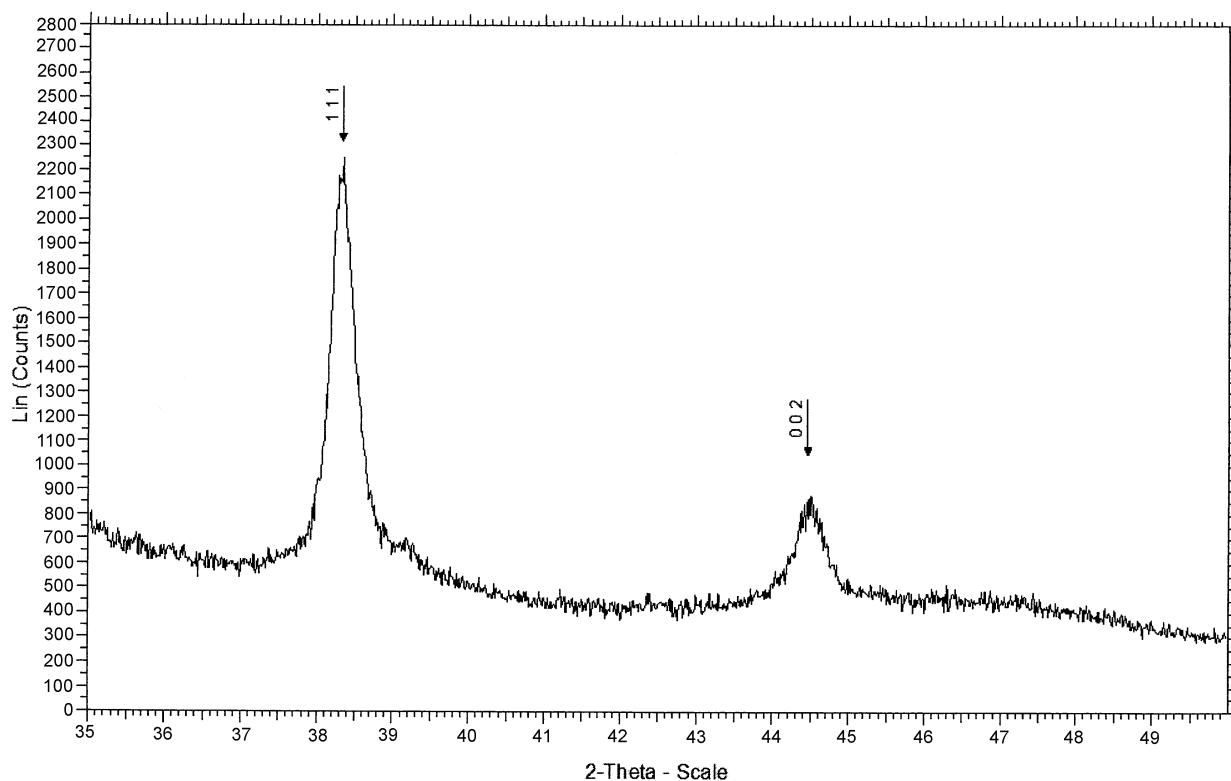


Fig. 3. XRD patterns of cellulose fibers modified with silver obtained with EB irradiation (concentration 0.71% w.)

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