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In situ preparation of silver nanocomposites on cellulosic fibers – Microwave vs. conventional heating

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ABSTRACT

A green approach for the preparation of silver nanocomposites on viscose fibers using microwave and conventional heating is presented. Reduction of silver nitrate is induced by addition of 6-O chitosan sulfate (S-Chi) in aqueous media which provides steric protection and electrostatic stabilization to prevent agglomeration of the nanoparticles. The particles are formed in close spatial proximity to the fibers and adsorption of the particles via structural similarity takes place to create silver nanocomposites. All nanocomposites have been subjected to antimicrobial tests and high antimicrobial activity toward *Escherichia coli* bacteria has been determined. Further, the nanocomposites are characterized using different analytical techniques which reveal very similar results for both heating techniques. The only significant difference is observed concerning the shape of the nanoparticles on the viscose fibers which are slightly elongated for the microwave method in comparison to spheres observed by conventional heating. Therefore, detailed investigations on the formation of colloidal silver nanoparticles have been performed, comparing microwave dielectric and conventional heating at the exact same temperature and reaction times. These experiments resulted in nearly identical nanoparticle shape and size for both heating methods as demonstrated by dynamic light scattering, UV–vis spectroscopy and transmission electron microscopy. A wide range of parameters has been varied (temperature, $AgNO_3$ to S-Chi ratio, reaction time, and stirring speed) to study the nanoparticle formation under microwave and conventional conditions. No evidence for the existence of so-called specific microwave effects was obtained.

1. Introduction

In the past decade, the demands on textile fibers have significantly increased. Large efforts have been made to implement additional functionalities on fibers which can be summarized by the term smart textiles. Such smart textiles can offer thermoresponsive behavior, conductivity, self cleaning effects, or magnetism to mention only a few (Daoud, Xin, & Zhang, 2005; Gonçalves, Marques, Tito Trindade, Neto, & Gandini, 2006; Malmström & Carlmark, 2012; Small & Johnston, 2009; Sun et al., 2008). While conducting fibers used in heating mats (Niemz, Riedel, & Knobelsdorf, 2009) provide a high degree of safety and durability in comparison to older devices based on iron wires, other approaches aim at modifying fibers with nanoparticles (NPs) exhibiting specific properties. For the treatment of chronic skin diseases for instance, fibers loaded with ZnO NPs have shown promising results (Boateng, Matthews, Stevens, & Eccleston, 2008) while the incorporation of silver NPs has proven to induce antimicrobial activity (Dastjerdi & Montazer, 2010; Hebeish et al., 2011; Johnston & Nilsson, 2012; Kelly & Johnston, 2011; Klemencic, Simoncic, Tomsic, & Orel, 2010; Lottermoser, 1903; Marambio-Jones & Hoek, 2010; Pivec et al., 2012; Ravindra, Mohan, Reddy, & Raju, 2010; Ristic et al., 2011; Sharma, Yngard, & Lin, 2009; Simoncic, 2010; Smiechowicz, Kulpinski, Niekraszewicz, & Bacciarelli, 2011; Tang et al., 2011; Travan et al., 2009; Vijayaraghavan & Nalini, 2010; Wendler, Meister, Montigny, & Wagener, 2007). Currently, there

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are numerous textiles on the market, in particular sportswear and socks, which have been treated with silver NPs in order to prevent bad odors stemming from bacterial growth as well as several medical products for wound care (e.g. AQUACEL®, SILVERCEL™). In most of the cases, the manufacturing process involves a separate silver NP synthesis step followed by a loading of the particles onto the fibers using crosslinking agents or adsorption e.g. via electrostatic interactions. In the course of the silver NP synthesis, the reduction of silver (I) species is usually achieved using an excess amount of an external reducing agent such as $NaBH_4$, hydrazine or dimethylformamide using elevated temperatures (Dahl, Maddux, & Hutchison, 2007; Raveendran, Fua, & Wallen, 2006) The high costs and the environmental impact caused by the use of reducing agents can be avoided by replacement with reducing polysaccharides for silver NP synthesis (Donati et al., 2009; Kemp et al., 2009; Kemp & Linhardt, 2009; Raveendran, Fu, & Wallen, 2003; Sharma et al., 2009; Travan et al., 2009). In order to prevent aggregation, stabilizing and capping agents have to be employed which can be of environmental concern due to the toxic nature of the used stabilizers. Polysaccharides offer a wide range of structural diversity, they are renewable and many congeners are soluble in water; factors which are able to clearly improve the environmental performance. As a consequence, many different types of polysaccharides have been used for silver nanoparticle synthesis using conventional heating methods (Dahl et al., 2007; Donati et al., 2009; Kemp et al., 2009; Kemp & Linhardt, 2009; Sharma et al., 2009; Travan et al., 2009; Vijayaraghavan & Nalini, 2010). Nevertheless, these methods have proven to be inefficient in terms of energy input and have a quite modest life cycle assessment. A more elegant and efficient way is to use microwave heating in the course of the NP synthesis.

During last decade microwave heating has received considerable attention as a promising method for the synthesis of nanomaterials (Klinowski, Paz, Silva, & Rocha, 2011; Polshettiwar, Nadagouda, & Varma, 2009; Tompsett, Conner, & Yngvesson, 2006; Vanetsev & Tretyakov, 2007). Among the different types of nanomaterials, the microwave-assisted synthesis of colloidal inorganic nanocrystals has become an area of intense interest, growing significantly over the past few years as a powerful alternative to more traditional synthetic methods (Baghbanzadeh, Carbone, Cozzoli, & Kappe, 2011; Bilecka & Niederberger, 2010; Tsuji, Hashimoto, Nishizawa, Kubokawa, & Tsuji, 2005). The motivation for the use of microwave energy has mainly been to design processes with dramatically reduced reaction times, higher yields, and improved materials properties. If efficient agitation can be ensured (Herrero, Kremsner, & Kappe, 2008), and the temperature is monitored/controlled by fast-responding internal probes (Herrero et al., 2008; Obermayer & Kappe, 2010), rapid "in core" volumetric heating without significant temperature gradients will occur. Similar to the situation for many other metallic NPs, microwave dielectric heating is a well established technique for the synthesis of silver NPs (Chen, Wang, Zhang, & Jin, 2008; Dzido & Jarzebski, 2011; Gao, Lu, & Komarneni, 2005; Komarneni, Li, Newalkar, Katsuki, & Bhalla, 2002; Kundu, Wang, & Liang, 2009; Li et al., 2012; Liu, Huang, Chu, & Ko, 2005; Liu, Tian, Wang, & Sun, 2011; Luo & Sun, 2007; Nadagouda, Speth, & Varma, 2011; Nadagouda & Varma, 2008; Tsuji et al., 2006, 2010; Zhu & Zhu, 2006). Simple reducing sugars such as glucose, maltose and sucrose have often been used for the microwave assisted synthesis of silver NPs; reports on polysaccharides involve carboxymethyl cellulose (CMC), starch and β-cyclodextrins which can act as stabilizers and reductants in the course of the silver NP preparation have also appeared in the literature (Virkutyte & Varma, 2011). Despite the large number of reports that have described the microwave-assisted synthesis of silver NPs, the real role of microwave irradiation in these processes is still a controversial question. In most of the published examples, not only were the preparations more rapid using microwave technology, but in addition a significant difference between the materials obtained by microwave dielectric heating and conventional heating was observed. Unfortunately, in many of these reports a domestic microwave oven has been utilized, which makes controlling of reaction temperature virtually impossible. Independent of the employed microwave instrument, it has been suggested that these discrepancies were due to the occurrence of some type of "microwave effect", including claims of selective heating (Nishioka et al., 2011a; Silva & Unali, 2011; Wada et al., 2007; Xia et al., 2008), the elimination of wall effects (Horikoshi, Abe, Torigoe, Abe, & Serpone, 2010; Nishioka et al., 2011b; Tsukahara, Nakamura, Kobayashi & Wada, 2006), or apparent nonthermal effects (Baruwati, Polshettiwar, & Varma, 2009).

In this manuscript we investigate the in situ preparation of silver NPs on cellulosic fibers to create silver cellulose nanocomposites. Toward this goal we utilized silver nitrate as silver precursor and 6-O chitosan sulfate (S-Chi) as a reducing and capping agent. The synthesis is performed in aqueous medium using controlled sealed vessel single-mode microwave technology. The formation of silver NPs under microwave dielectric heating has been studied in detail and an in-depth comparison between the materials obtained by conventional heating and microwave dielectric heating was performed.

2. Experimental

2.1. Materials

Sulfated chitosan (S-Chi) ($M_r \sim 20{,}000$ g/mol) was synthesized in our labs according to a published literature procedure (Fasl et al., 2010). The degree of deacetylation (DA) was determined conductometrically and yielded a DA of 82.5%. The degree of sulfate substitution (DS) was determined to be 0.86 based on sulfur content determinations using ICP/MS. IR (KBr, cm^{-1}): 3440 ν_s(O—H), 2800–2900 ν_s(C—H), 1625 ν_s(C=O), 1525 $\nu_s(NH_2)$, 1218 ν_{asym}(O=S=O), 1063 ν_{sym}(O=S=O), 796 ν_s(C—O—S). ^{13}C NMR (D_2O, 75.4677 MHz, ppm): δ 55.18 (C-2), 66.54 (C-6), 72.67 (C-5), 73.02 (C-4), 74.76 (C-3), 101.72 (C-1).

Silver nitrate (99%) was purchased from Merck and used without further purification. Viscose fibers were obtained from Lenzing AG (Lenzing, Austria). Bidistilled water was used in all the experiments

2.2. Microwave instrumentation

Microwave irradiation experiments were performed using a dedicated single-mode microwave reactor (Monowave 300, Anton Paar, Graz, Austria) with 850 W maximum magnetron output power, allowing sealed vessel processing up to 300 °C and 30 bar of pressure in combination with an efficient magnetic stirring system. For the syntheses described herein, the reaction temperature is monitored by an internal fiber-optic (FO) temperature probe (ruby thermometer).

Some experiments were additionally conducted in a CEM Discover (Matthews, NC, USA) single mode microwave reactor equipped with a fiber-optic (FO) probe provided by the instrument manufacturer for directly controlling and monitoring the internal reaction temperature (Hosseini, Stiasni, Barbieri & Kappe, 2007). These experiments were performed in constant power mode under reflux conditions and magnetic stirring, monitoring the temperature of the reaction mixture by the FO sensor. A constant magnetron power of 28 W was used to achieve reflux temperature (100 °C) and also ensured a steady reflux of the reaction mixture for the duration of the experiment.

2.3. Silver NP cellulose fiber composites by in situ conventional heating

Viscose fibers (0.2 g) were soaked for 1 h in 25 mL $AgNO_3$ (1 mM, 10 mM, 50 mM and 75 mM). This suspension was added to a solution containing S-Chi (36 mg, 0.15 mmol) dissolved in water (40 mL) and the mixture was heated to 80 °C (120 min) using an oil bath under exclusion of light and *air*.

2.4. Silver NP cellulose fiber composites by in situ microwave heating

Viscose fibers (0.1 g) were soaked for 1 h in 12.5 mL $AgNO_3$ (1 mM, 10 mM, 50 mM and 75 mM). This suspension was added to a solution containing S-Chi (18 mg, 0.08 mmol) dissolved in water (20 mL) and the mixture was heated to 80 °C (4 min, stirring speed 600 rpm, 30 mL vessel) using sealed vessel microwave irradiation (Monowave 300) under exclusion of light and air.

2.5. Synthesis of silver NPs under microwave heating condition

2 mL of a S-Chi (2 mg/mL) solution and 1 mL of a 50 mM solution of silver nitrate were mixed in a 10 mL glass microwave vial equipped with a stir bar. The vessel was subsequently sealed with a septum. The resulting mixture was heated to the reaction temperature using the “as fast as possible” mode (ramp time = 25 s, Monowave 300). The mixture was heated for 5 min at 80 °C, and was subsequently cooled by compressed air to 55 °C. The solution was subjected to further characterizations without any work-up procedure.

2.6. Comparison study microwave vs. conventional heating at 80 °c in a sealed vessel

Comparison experiments were carried out using 2 mL of S-Chi (2 mg/mL) solution and 1 mL of a 50 mM solution of silver nitrate in a Pyrex 10 mL reaction vessel equipped with a stir bar. The vessels were sealed with a septum and the reaction mixtures were exposed to microwave irradiation (Monowave 300) for 5 min or immersed in a preheated oil bath at 80 °C for 5 min. In both cases the same ramp time and cooling time was applied as confirmed by internal fiber-optic temperature probes.

2.7. Comparison study under reflux condition (100 °C)

Comparison experiments were done using 13.33 mL of S-Chi (2 mg/mL) solution and 6.66 mL of a 50 mM solution of silver nitrate in a 50 mL round bottom flask under open vessel conditions at 100 °C (reflux condition) for 5 min. The reaction in the oil bath was performed using a 200 °C preheated oil bath (stirring rate: 400 rpm) and this reaction was repeated in a CEM Discover single-mode microwave reactor (stirring level: medium) with the same temperature profile. After cooling, the reaction mixtures were used directly for further characterization.

2.8. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The sample holders were sputtered with gold/platinum using an ion sputter (Jeol JFC-1100 E) which was operated at D = 10 mA. The thickness of gold was about 150 Å. A Carl Zeiss FE-SEM SUPRA 35 VP electron microscope was used for the measurements. The images were recorded with an acceleration voltage of 10 kV. The TEM measurements were performed using TITAN from FEI with a high-brightness electron gun (X-FEG). The images were made at an accelerating voltage of 300 kV. The images are zero-loss filtered with the energy-filter quantum from GATAN.

2.9. Dynamic and electrophoretic light scattering

The nanoparticles’ mean hydrodynamic diameter and polydispersity indices (PDI) were determined by dynamic light scattering (DLS) using a Brookhaven Instruments ZetaPlus zeta-potential Analyzer (wavelength: 674 nm, scattering angle: 90°). Mean particle diameters were approximated as the effective (z-average) diameters. The width of the distribution and the PDI were obtained by cumulant fitting, presuming spherical particle shape and log-normal size distribution. The measurements were repeated three times for each sample.

2.10. Atomic absorption spectroscopy (AAS)

An atomic absorption spectrometer (Perkin-Elmer A Analyst 600) equipped with an air-acetylene burner and silver hollow cathode lamp operating at 5 mA was used for determining silver without background correction. The operating conditions were as follows: wavelength: 328.1 nm, band pass: 0.7 nm, flow rate of acetylene: 2.5 L/min, and the flow-rate of air: 8 L/min. For a quantification of the amount of silver on the fibers, a calibration was performed using a stock solution of $AgNO_3$ in diluted aqueous HNO_3 [1% (v/v) $AgNO_3$ in HNO_3 (13%, v/v)]. For each silver determination, approximately 0.2 g of viscose fibers were used and digested in 20 mL of HNO_3 (65%, v/v) by refluxing for 2 h. The solution was cooled, quantitatively transferred into a volumetric flask and diluted to volume 100 mL with deionized water. All analyses were performed in 3 parallels.

2.11. UV–vis spectroscopy

The UV–vis measurements of silver NP aqueous solutions were performed on a UV-2101 PC Shimadzu UV–vis scanning spectrophotometer.

2.12. Tensile strength of the fibers

Stress-strain curves were recorded using the software-controlled Vibrodyn 400 dynamometer (Lenzing Instruments) according to standard ISO 5079:1995 (determination of breaking force and elongation at break of individual fibers). Clamped fiber samples were stretched to rupture, while computer software automatically records breaking force, tenacity values and the elongation at break. Fifty measurements were performed for each sample under standard conditions (20 ± 2° C, 65 ± 2% RH). The used testing conditions were: gauge length – 10 mm, clamping with pretension – 70 cN and rate of extension – 20 mm/min. Before determination of tensile properties was carried out, linear density of fibers was determined on the Vibroskop 400 (Lenzing Instruments), according to ISO 1973:1995 (determination of linear density – gravimetric method and vibroscope method).

2.13. Washing test of the fibers

Leaching of silver from fiber samples or stability of silver coatings to washing was tested with a washing procedure, adapted from a standard test method for color fastness to washing ISO 105-C03. Washing of the samples was done in a laboratory dyeing apparatus Labomat Mathis (Switzerland), with metal cuvettes in which the fiber samples were weighed and the standard soap solution with a concentration of 5 g/L, (pre-heated to 60 °C) was added, considering the bath ratio of 1:50. One washing cycle was carried out for 30 min at 60 °C and the frequency of rotation of the cuvettes was 40 min^{-1}. The washing procedure was repeated 20 times for each sample. Fiber samples were dried at room temperature after the washing in the absence of light and stored for further testing in an air conditioned room with standard conditions of 20 ± 2 °C and 65 ± 2% RH.

2.14. X-ray photoelectron spectroscopy (XPS)

XPS spectra were performed with a monochromatic K-Alpha spectrometer equipped with an Al X-ray source (1486.6 eV) operating with a base pressure in the range of 10^{-8} to 10^{-10} mbar. Survey scans were acquired with a pass energy of 100 eV and a step size of 1.0 eV. All spectra have been normalized to the Au 4f7/2 peak. Charge compensation was performed with an argon flood gun. The average chemical composition was calculated from wide scan spectra in two different locations on each surface. The peaks were fitted using a Gaussian/Lorenzian mixed function employing Shirley background correction. All analyses were performed at room temperature.

2.15. Cultivation procedure and antimicrobial testing

All experiments were performed under sterile conditions in three repetitions. All buffer, media, and *Escherichia coli MG 1655* [R1-16] cultures were prepared according to published procedures (Miller, 1977; Wagner, Zahrl, Rieser, & Koraimann, 2009; Zahrl, Wagner, Bischof, & Koraimann, 2006). The test fibers were sterilized using ethanol (Roth Karlsruhe, Germany), and fixed at the bottom of 12-well plates. 2 mL of bacterial culture (*E. coli MG 1655* [R1-16] cultivated in M9 medium) were added (OD_{600} was set to 0.03) to each sample, and the plates were incubated for 12 h (37 °C, shaking with 180 rpm). Then, the bacterial suspension was removed, and the samples were rinsed extensively with PBS buffer (150 mM sodium chloride and 150 mM sodium hydrogen phosphate, pH 7.4, salts purchased from Roth Karlsruhe, Germany) in order to remove loosely attached bacteria. In order to cultivate bacteria attached to the sample surface, 2 mL fresh medium was added to each sample, followed by incubating for 12 h at 37 °C. Finally, the samples were extensively rinsed with buffer as described above, and analyzed according to their OD_{600}.

3. Results and discussion

3.1. Microwave synthesis of silver NPs

We initially investigated the effects of different parameters on the hydrothermal synthesis of silver NPs under microwave dielectric heating. The synthesis of silver NPs was performed using silver nitrate as silver source and S-Chi as reducing and stabilizing agent. The influence of the following three parameters: reaction temperature, precursor ratios and reaction time on the particle size was carefully investigated. During this study, the size of the resulting silver NPs was monitored by DLS. For these experiments a dedicated single-mode microwave reactor (Monowave 300) with an internal fiber-optic temperature probe was employed, allowing sealed vessel processing up to 300 °C and 30 bar of pressure in combination with an efficient magnetic stirring system (Gutmann et al., 2010; Obermayer, Gutmann, & Kappe, 2009).

In order to investigate the influence of the reaction temperature in the synthesis of silver NPs, the formation of silver NPs was monitored at reaction temperatures of 80 °C, 100 °C, 120 °C, and 130 °C. The syntheses were performed for 5 min hold time and a solution of $AgNO_3$:S-Chi (1:2) was applied as precursor. The reaction at a certain temperature was repeated three times and the particle size presented in Table 1 is the average size of particles obtained in three experiments. The UV–vis spectra of synthetic silver NPs at different temperatures are shown in Fig. 1. The results indicate that temperature has an almost negligible influence on the particle size with higher temperatures leading to a slightly smaller mean particle size (Table 1). On the other hand, using higher reaction temperatures increased the number of silver NPs generated (Fig. 1). Since for the in situ preparation of silver NPs on cellulosic fibers our aim was to generate silver NPs with a particle size of ∼50 nm it was decided to run all subsequent experiments at the 80 °C. Attempts to generate silver NP under our general conditions at ≤80 °C resulted in very low numbers of particles.

Similar experiments were performed to study the effect of molar ratio of silver precursor to S-Chi (Table 2) and reaction time (Table 3). The results in Table 2 highlight that varying the amount of S-Chi does not have a significant influence on particle size. Further experiments on the influence of reaction time led to similar conclusions (Table 3). In other words, by prolonging the reaction time from 1 min up to 1 h only a comparatively small difference in particle size could be observed. These results clearly demonstrate that the size of the desired silver NPs is only slightly affected by parameters such as reaction time, reaction temperature and precursor ratios. The protocol can therefore be considered as rather robust,

Table 1
Effective diameter and polydispersity index (PDI) of the silver NPs.[a]

T (°C)	Effective diameter (nm)	PDI
80	44	0.28
100	42	0.30
120	35	0.22
130	33	0.22

[a] Reaction time = 5 min and $AgNO_3$:S-Chi ratio = 1:2. The reactions were repeated three times.

Table 2
The effective diameter and polydispersity index (PDI) of silver NPs synthesized using different silver/precursor ratios.[a]

$AgNO_3$:S-Chi	Effective diameter (nm)	PDI
1:1	33	0.26
1:2	44	0.29
1:4	32	0.25
1:6	30	0.21
1:8	44	0.26

[a] Reaction time = 5 min and reaction temperature = 80 °C. Average values of three repetitions.

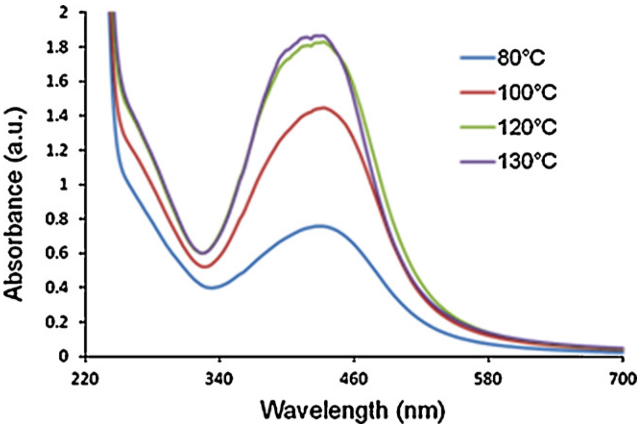

Fig. 1. The absorption spectrum of the silver NPs synthesized at different temperatures. Reaction time = 5 min and $AgNO_3$:S-Chi ratio = 1:2.

Table 3
The effective diameter and polydispersity index (PDI) of silver NPs synthesized using different reaction times.[a]

Time (min)	Effective diameter (nm)	PDI
1	40	0.27
2	38	0.25
5	39	0.32
10	35	0.28
60	40	0.29

[a] $AgNO_3$:S-Chi ratio = 1:2 and reaction temperature = 80 °C. Average values of three repetitions.

ideally suited for practical applications such as the generation of silver cellulose nanocomposites.

3.2. *In situ synthesis of silver NPs on viscose fibers*

The synthesis of the silver nanocomposites on the fibers follows a very easy procedure which is performed in an atmosphere of nitrogen and exclusion of light. Prior to heating (either by oil bath or microwave, see below), the fibers are subjected to swelling in aqueous solutions containing different concentrations of silver. In a second step, the fibers are added to an aqueous solution which contains the reducing and stabilizing agent, 6-O chitosan sulfate (S-Chi, Fig. 2).

Subsequently, the suspensions are heated to 80 °C using an oil bath (CH, for 120 min) or, alternatively, using a microwave reactor (MW, for 5 min). From previous studies, we know that S-Chi is a reductive polysaccharide bearing an aldehyde group at the reducing end which is capable to reduce silver (I) to silver (0) (Breitwieser et al., in press). Additionally, S-Chi acts as a stabilizing agent due to its high negative charge over a wide pH range (−30 mV at pH 7) and therefore the formed particles are surrounded by a sulfated chitosan shell which stabilizes the particles via electrostatic repulsion. The formed core–shell particles are already in close spatial proximity to cellulose fibers and adsorb on these. While adsorption by electrostatic interactions is highly unlikely due to the slightly negative charge of cellulosic surfaces at pH 7 (−5 to −10 mV) (Stana-Kleinschek, Kreze, Ribitsch, & Strnad, 2001), an interaction via structural similarity probably takes place. This behavior is known for several systems involving cellulose and other negatively charged polysaccharides like carboxymethyl cellulose cationic cellulose and xyloglucans (Kargl et al., 2012; Kontturi, Tammelin, Johansson, & Stenius, 2008; Mishima, Hisamatsu, York, Teranishi, & Yamada, 1998; Orelma, Filpponen, Johansson, Laine, & Rojas, 2011; Mohan et al., 2013). The amount of adsorbed particles on the fibers is proportional to the initial concentration of the silver nitrate solution and can be easily followed by the coloration of the fibers due to the plasmon resonance of the synthesized silver nanoparticles at λ_{max} = 430 nm. In addition to an apparent change in the color of the fibers, which can be seen by the naked eye (Fig. 3), the samples were subjected to further analysis. Scanning electron microscopy (SEM) clearly reveals the presence of particles on the fiber surface. The surface coverage of the fibers with the particles strongly depends on the initial silver nitrate concentration and increases with increasing silver concentration. However, there seems to be a slight difference between the heating methods and reaction time concerning the shape of the particles. While conventional heating for 2 h leads to more or less spherical aggregates, microwave heating for 5 min at the same temperature of 80 °C yields slightly elongated particles (Fig. 4). The origin of these differences will be investigated comprehensively in the next section of this paper.

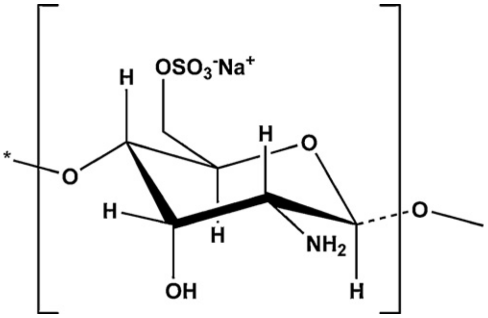

Fig. 2. Molecular structure of 6-O-chitosan sulfate.

A quantification of the results using atomic absorption spectroscopy (AAS) revealed similar results for all samples. In all cases, the silver content is in a range between 0.1 and 0.6 mg/g fiber (Fig. 5).

While for the oil-bath heating the silver content on the fibers increases with an increase in the initial silver nitrate solution, for the MW assisted synthesis, such a clear trend cannot be followed; all samples exhibit the same amount of silver on the fibers (within the standard deviation). AAS is a highly sensitive method for the detection of elements, but the appearance of the samples makes precise and accurate analyses difficult. The major problem in the determination of the silver content on the fibers is the uneven distribution of silver on the fibers (see also Fig. 4). Therefore, potentially large experimental errors between single fibers are observed leading to rather high standard deviations. In order to get additional information on the silver content of the fibers, X-ray photoelectron spectroscopy was employed. This technique enables a qualitative and quantitative analysis of elements (except hydrogen) on surfaces as well as their chemical environment. The analysis by XPS clearly proves the presence of silver in its elemental oxidation state on the fibers (Fig. 6).

The characteristic Ag3d binding energies are split into a $Ag3d_{5/2}$ component at 368.03 (CH)/368.40 (MW) eV and a $Ag3d_{3/2}$

Fig. 3. Comparison of photographs showing fibers equipped with AgNPs by conventional heating (CH) using different $AgNO_3$ precursor concentrations.

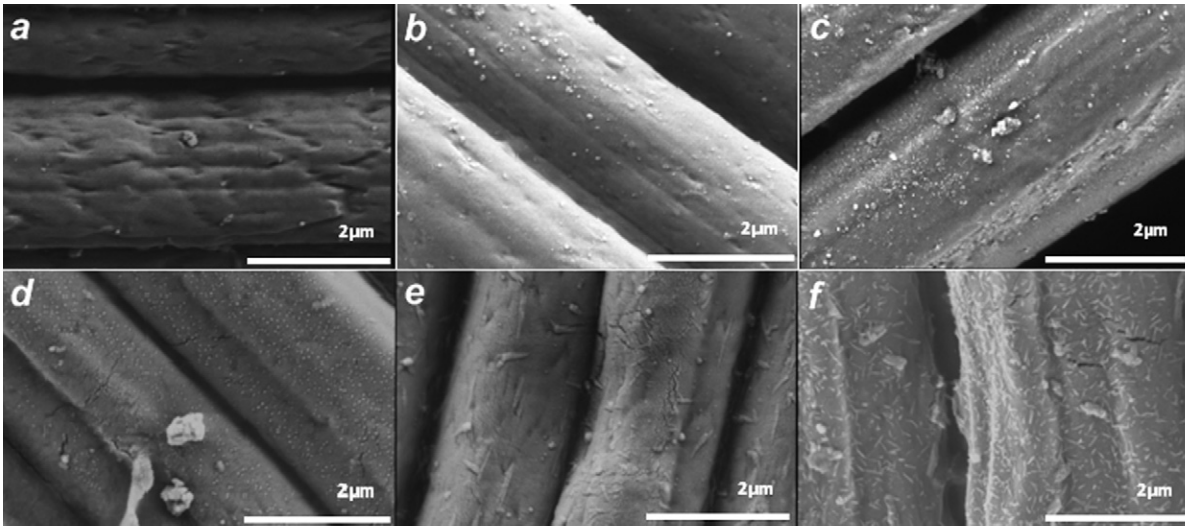

Fig. 4. SEM images of silver NPs on cellulosic fibers using different $AgNO_3$ precursor concentrations (10, 50 and 75 mM, respectively), magnification 20,000, *a–c*: using conventional heating and *d–f*: using microwave heating.

component at 374.04 (CH)/374.41 (MW) eV which are close to the binding energies for reported Ag3d of elemental silver (368.24 and 374.25 eV) (Crist, 1999). In contrast, the binding energies for Ag3d in Ag_2O have been reported 367.67 and 373.62 eV respectively (Crist, 1999). As depicted in Fig. 5, the silver content on the fibers showed distinct differences between the microwave and the conventional method for the 75 mM initial silver concentration. While for MW assisted heating a total amount of 1.1 at.% silver content has been determined, samples obtained from conventional heating revealed 0.6 at.% of silver on the fibers. On flat substrates such differences are significant; however, on fibers the experimental error of this technique is much higher due to diffuse scattering of the electrons after they have ejected from the surface. While the silver could be identified unambiguously, the situation for nitrogen and sulfur is rather different. These elements should be present in the sulfated chitosan shell around the silver core which is several nanometers thick. It is known that sulfur can be detected by XPS only in larger amounts in even flat samples; therefore it is not surprising that we cannot detect sulfur with a satisfying signal-to-noise ratio for both samples. Only for the microwave sample peak corresponding to $S2p_{3/2}$ (169.1 eV, typical for S(VI)) can be quantified with an area of 0.8 at%. For nitrogen, also poor signal-to-noise ratios have been obtained yielding 1.0 and 0.4 at% nitrogen in the samples at the N1s peak (399.9 eV). Considering the variability of the silver contents between the single fibers, these findings fit well to the ones of the AAS at least within the error limits, and obtained silver contents are in a similar range.

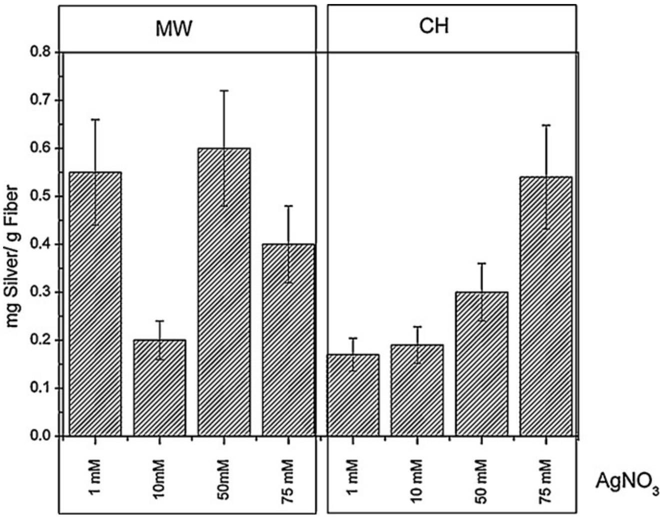

Fig. 5. Comparison of the silver content of the modified fibers in dependence of the initial $AgNO_3$ concentration obtained by microwave (MW, 80 °C, 5 min) and conventional heating (CH, 80 °C, 2 h) as determined by AAS.

Especially for textile applications, it is crucial to know the stability and durability of the nanoparticles on the fibers. For this purpose, a standardized washing test according to ISO 105-C03 has been employed. In the course of this test setup, the coated fibers are washed in a similar manner than in a commercially available washing machine with a specified amount of soap and different agitation speeds. Both, the microwave and conventionally treated samples show a very similar behavior. In all cases, 2/3 of the silver are removed from the fibers after three washing cycles which is an average value for many commercially available silver containing textiles (Pivec et al., 2012; Ravindra et al., 2010) After five cycles, a tenth of the initial silver content is still available and after 20 washing cycles only 1/400 of the initial silver content is present on the fibers. On the other hand, the influence of the coating with the nanoparticles on the mechanical stability is of great importance in respect to a manufacturing of such fibers to fabrics and textiles. In principle, each modification step exposes the fibers to mechanical stress and their microfibrillar structure is successively weakened. In our modification procedures, mechanical stress was introduced by stirring and swelling. According to ISO 5079:1995 the tensile strength of the fibers was determined. The tensile strength of the fibers remains close to the original levels (24.5 ± 1.2 cN/tex, viscose fiber) with lowest values of 20.0 ± 2.1 cN/tex (MW, 75 mM) up to (23.0 ± 1.3 cN/tex (CH, 75 mM). All samples show a similar mechanical behavior regardless of the heating method and a significant reduction in mechanical strength cannot be observed upon nanoparticle loading.

In recent years, a wide variety of sportswear has been brought to the market which is equipped with silver to avoid bad odors stemming from bacterial growth. The mechanisms of action of silver toward pathogens are manifold and therefore silver based materials are classified as unspecific antimicrobials. The most important interactions of silver with pathogens include a rupture of bacteria membranes, concomitant with an inhibition and damage of enzyme systems responsible for growth and viability of the pathogens (Lara, Garza-Treviño, Ixtepan-Turrent, & Singh, 2011).

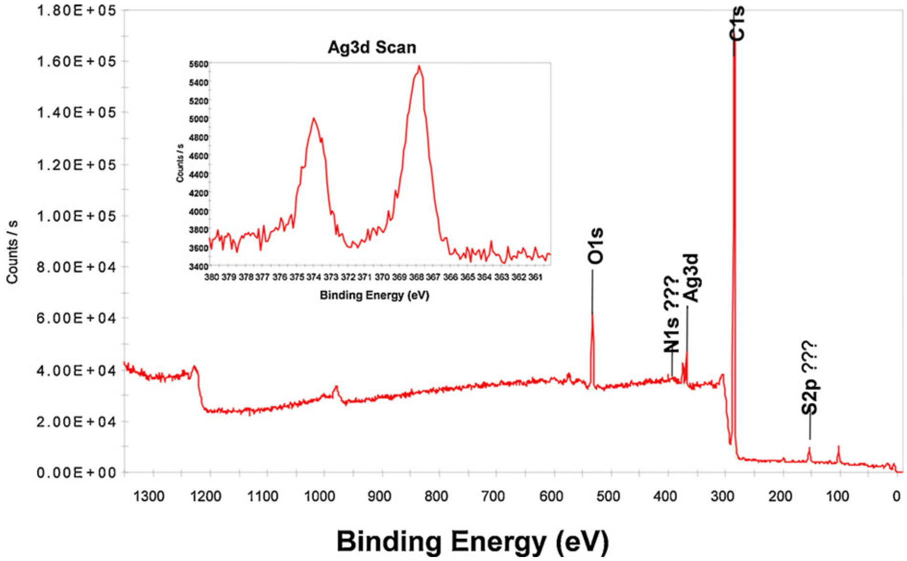

Fig. 6. XPS spectra of the AgNP coated fibers using 75 mM $AgNO_3$ precursor concentration by microwave synthesis (5 min, 80 °C). The question marks indicate low confidentiality assignments. Additional data can be found in the supporting information.

Consequently, the modified fibers were subjected to antimicrobial testing toward *E. coli MG 1655 [R1-16]* which served as a test organism in this study. The test setup is designed in a way that in a first step bacteria are cultivated overnight in the presence of fibers coated with silver nanoparticles followed by a rinsing step to remove loosely attached bacteria and a second cultivation overnight. Afterwards, the OD_{600} (optical density at 600 nm) is determined which is a measure for the amount of bacteria present on the surfaces. In case of the uncoated fibers and the blank, an OD_{600} of 0.4 is determined (corresponds to 4×10^4 cells/mL) after the second overnight cultivation. The identical OD_{600} values for cellulose and the blank are not surprising since cellulose is known to be inactive against microorganisms. In contrast, the silver nanoparticle coated fibers exhibit a significant reduction. All samples exhibited an OD_{600} smaller than 0.03 (corresponding to ca. 3×10^3 cells/mL suspension) which is the proportionality limit for this method. A difference in the antimicrobial activity cannot be observed for any samples. After a further ONC, the OD_{600} could not be detected which is a strong evidence for lyzed cells. These results are in line with previous observations where silver modified viscose fibers using a sol-gel process were investigated. It was shown that concentrations down to 0.06 mg/g fiber are sufficient for antimicrobial activity toward *E. coli* bacteria (Pivec et al., 2012; Ristic et al., 2011).

3.3. *Colloidal silver NPs formation: microwave vs. conventional heating*

An analysis of the above results involving the generation of silver nanocomposites may imply the existence of some sort of “microwave effect” in the preparation of these materials, since the obtained materials differ somewhat in their properties. Notably, in the synthesis of silver NPs discrepancies between microwave and conventionally heated reaction mixtures have frequently been reported (Baruwati et al., 2009; Horikoshi et al., 2010; Nishioka et al., 2011a, 2011b; Silva & Unali, 2011; Tsukahara et al., 2006; Wada et al., 2007; Xia et al., 2008). However, in most of these investigations – as in the fiber study described above – a fair comparison using the exact same reaction conditions was not performed. Since it is well-established that the geometry of the reaction vessel, the reaction volume, the heating and cooling ramps, and the stirring speed can sometimes have a significant influence in chemical reactions (Baghbanzadeh et al., 2011; Bilecka & Niederberger, 2010; Obermayer & Kappe, 2010; Tsuji et al., 2005), a series of carefully executed control experiments was designed to minimize these effects. For nanomaterials' chemistry, the above mentioned factors may additionally influence reduction processes, surfactant adsorption/desorption, and complexing stability, the formation and growth rate, and hence the shape, size, and size distributions of the generated nanoparticles (Jiang, Chen, Chen, Xiong, & Yu, 2011).

To establish the specific role of microwave irradiation in the preparation of silver NPs, it is therefore important to heat both samples either conventionally or under microwave heating applying completely identical conditions. For the synthesis of the cellulosic fibers loaded with silver NPs this cannot easily be achieved mainly because of the heterogeneous nature of the reaction mixture and the therefore ensuing difficulties in achieving efficient agitation and mass transfer. Thus, to evaluate the specific role of microwave irradiation in these processes, we have focused on the preparation of colloidal silver NPs as described above. For this purpose, the synthesis of colloidal silver NPs was initially performed in a preheated oil bath at a bath temperature of 80 °C using 3 mL of reaction mixture in a 10 mL microwave vessel (5 min at 80 °C). Then the synthesis was repeated in the same vessel under microwave dielectric heating by defining the ramp time identical to oil bath process to achieve the same heating profile (Fig. 7a). Internal temperature control using fiber-optic technology was used for both microwave and conventionally heated runs since there is overwhelming evidence that monitoring reaction temperatures by conventional infrared sensors on the outside of the reaction vessel wall is not a suitable technique if an accurate temperature profile for comparison studies needs to be obtained (Bilecka & Niederberger, 2010; Hosseini et al., 2007; Kremsner & Kappe, 2006; Tsuji et al., 2005).

The outcome of these experiments is summarized in Fig. 7b and Table 4. The UV–vis spectra shown in Fig. 7b demonstrate that NPs with the same size and concentration were obtained. The results clearly highlight that the NP products obtained under conventional heating did not appreciably differ from those obtained under microwave irradiation as long as the reaction temperature was identical. By evaluating the DLS data (Table 4) again no appreciable differences in NP particle size between microwave and conventionally synthesized materials were seen. Notably, under conventional heating no precipitation of silver NPs on the wall of reaction vessel was observed. These results demonstrate that under completely

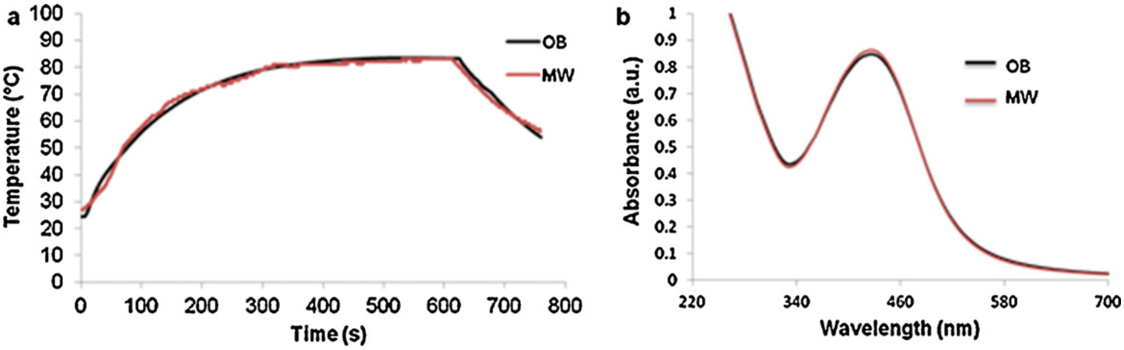

Fig. 7. (a) Temperature profile of the reaction mixture at 80 °C oil bath (OB) and microwave (MW); ramp time = 5 min, hold time = 5 min. (b) The absorbance UV–vis spectra of the silver NPs synthesized in oil bath (OB) and microwave (MW) at 80 °C, 5 min reaction time and 1:2 ratio of $AgNO_3$:S-Chi.

Table 4
The effective diameter and polydispersity index (PDI) of the silver NPs synthesized under different conditions.[a]

Heating source	Effective diameter (nm)	PDI
Microwave	29	0.22
Oil-bath	31	0.26

[a] Reaction condition: 80 °C, 5 min reaction time, $AgNO_3$:S-Chi-1:2. Average values of three repetitions.

identical conditions the size and number of silver NPs are independent of heating source.

Of particular interest to us in the context of the preparation of silver NPs was the evaluation of wall effects. It should be emphasized that microwave irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling of microwave energy with the molecules (solvents, precursors, nanoparticles, etc.) that are present in the reaction mixture. Microwave irradiation therefore raises the temperature of the whole volume simultaneously (bulk heating) whereas in the conventionally heated vessel, the reaction mixture in contact with the vessel wall is heated first. The elimination of a hot vessel surface has often been stated as being one of the key advantages of using microwave technology in synthesis of NPs (Horikoshi et al., 2010; Nishioka et al., 2011b; Tsukahara et al., 2006; Zhu, Zhang, Li, & Wang, 2010). An intriguing example of the wall-effect phenomenon was observed in the preparation of silver NPs from $Ag(NH_3)^{2+}$ and CMC as reducing agent in a water based environment under reflux condition (Horikoshi et al., 2010). It was shown that performing the synthesis in a preheated oil-bath led to the formation of a thin silver film at the inner reactor walls (silver mirror) as the NPs grew and accumulated preferentially at these locations, while such kind of mirror was not observed under microwave conditions (Horikoshi et al., 2010). In the context of the work described above we therefore additionally conducted a study comparing the generation of silver NPs using reflux conditions applying either microwave or oil bath heating, paying particular attention to the formation of silver mirrors and wall effects.

For these investigations, we have utilized a CEM Discover single-mode microwave reactor equipped with a fiber-optic probe provided by the instrument manufacturer for directly monitoring the internal reaction temperature (Hosseini et al., 2007). This setup can be either immersed into the cavity of the microwave reactor or into a preheated and temperature-equilibrated oil bath placed on a magnetic stirrer/hotplate. In both cases, the software of the microwave instrument is recording the internal temperature. This system has the advantage that the same reaction vessel/flask and the same method of temperature measurement are used. In this way, all parameters apart from the mode of heating are identical, and therefore, a fair comparison between microwave heating and thermal heating can generally be made.

In this synthesis a 50 mL round bottom flask containing a 20 mL aqueous solution of $AgNO_3$:S-Chi (1:2) was used. For the oil bath experiment the round bottom flask was equipped with a stir bar and

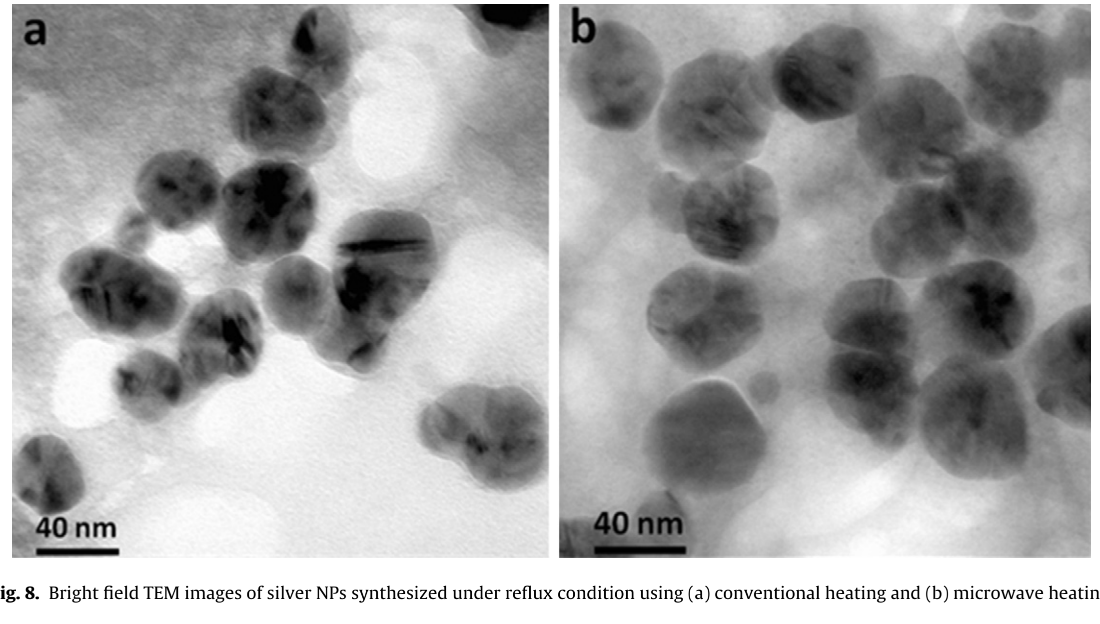

Fig. 8. Bright field TEM images of silver NPs synthesized under reflux condition using (a) conventional heating and (b) microwave heating.

Table 5
The effective diameter and polydispersity index of the silver NPs synthesized under microwave and oil bath reflux conditions (100 °C).

Entry	Condition	Effective diameter (nm)	PDI
1	Oil bath[a]	75	0.29
2	Microwave	65	0.30
3	Oil bath[b]	76	0.31

[a] Reaction condition: reaction temperature 100 °C, reaction time 5 min, 1:2 ratio of $AgNO_3$:S-Chi, magnetic stirring. Average values of three repetitions.
[b] Reaction was done without stirring.

connected to reflux condenser and was subsequently immersed into a preheated oil bath. Particular attention was paid to the fact that the flask was immersed into the bath fluid in such a way that the hot bath fluid would not cover the surface of the round bottom flask above the meniscus of the reaction mixture. A 200 °C preheated oil bath was used to heat the reaction mixture as fast as possible and to amplify any possible wall effect due to the very hot surface of the reaction flask. For the microwave synthesis the same experimental set-up was placed in the cavity of a CEM Discover microwave system. By adjusting the power of the instrument the same temperature profile was applied under microwave irradiation to heat the reaction mixture as similar as possible to the conventionally heated mixture (Fig. S1a in the supporting information). The UV–vis spectra of the silver NPs synthesized under microwave and oil bath conditions (5 min, 100 °C) are presented in Fig. S1b. As can be seen, the number of particles and the size of the particles were not influenced by the heating source. More importantly, in contrast to a previously described protocol (Horikoshi et al., 2010), no precipitation of silver (silver mirror) on the reaction container wall could be observed in the oil-bath synthesis (Fig. S2). Analysis of the particle size with both DLS (Table 5, entries 1 and 2) and by TEM (Fig. 8) exhibited only a slight difference between samples prepared under conventional and microwave heating. It is worth to mention that even running the synthesis in an oil-bath under non-stirring conditions did not lead to mirror formation (Table 5, entry 3, and Fig. S2c). The often claimed advantages of using microwave dielectric heating in order to eliminate wall effects could therefore not be confirmed (Dallinger, Irfan, Suljanovic, & Kappe, 2010).

4. Conclusion

In this paper, we present an environmentally friendly synthesis of silver nanocomposite cellulose fibers using conventional and microwave assisted heating. The nanocomposite fibers are made by an in situ process where silver nanoparticles are generated by reduction of $AgNO_3$ in the presence of S-Chi in close spatial proximity to the fiber where adsorption takes place. All nanocomposites exhibit similar mechanical strength compared to the unmodified fibers and show excellent antimicrobial activity toward *E. coli* bacteria. The heating method has only a minor influence on the final properties of the materials, but slight differences in the shape of the particles can be observed in case of microwave heated samples. However, these differences do not originate from so-called microwave effects rather than by problems to ensure exactly the same reaction conditions (stirring, mass transfer, etc.) for fibers suspended in aqueous solution. Carefully conducted control experiments involving the generation of colloidal silver nanoparticles under microwave and conventional heating under otherwise identical reaction conditions demonstrate that no appreciable differences between particle size and morphology are found when comparing the two heating methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.01.077.

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