A simultaneous wet-spinning strategy for high-strength antimicrobial cellulose fibers embedded with silver nanoparticles

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Abstract

Developing a strategy to fabricate nanoparticle-embedded microfibers a single step has industrial and academic impact for a variety of functionally demanding textile applications. Here, we report a straightforward strategy for decorating the fiber surface with silver nanoparticles (AgNPs) while simultaneously carrying out the deacetylation of cellulose acetate (CA) into cellulose (CE) microfibers using sodium hydroxide (NaOH). We obtained antibacterial regenerated cellulose microfibers by successfully embedding silver nanoparticles and achieving a high level of tensile strength improvement at the same time. The physicochemical properties of regenerated cellulose microfibers embedded with AgNPs were compared with pure CA microfibers using various characterization techniques. Fiber thickness (270 vs 300 µm), mechanical properties (>5 vs <1 MPa Young's modulus), and antibacterial ability (50 vs 0 mm² zone of inhibition) of the fibers were also measured. The proposed method has been confirmed as a strategy that can greatly simplify the manufacturing process of CE@AgNPs microfibers with high strength and antibacterial properties, promising high applicability in fields requiring functional, antibacterial fibers.

1. Introduction

Cellulose is a polysaccharide that is easily found in nature and is widely regarded as a renewable and cost-effective material (Sharma, Thakur et al. 2019). Cellulose has traditionally been the most widely used natural source for the production of paper and textiles, and has also been used as construction materials (Moon, Lee et al. 2021). Cellulose microfibers possess both the structural advantages of microscale fibers as well as those of natural polymers (Praveen Kumar, Shreya Sai et al. 2019). In fact, cellulose meets various conditions required by modern industry and its use in various applications such as separators, energy storage, solar cells, sensors, electrical devices, and biomaterials is quickly becoming widespread (Zhou, Fuentes-Hernandez et al. 2013, Hickey and Pelling 2019, Li, Zhu et al. 2021, Wang, Lee et al. 2021, Suresh Khurd and Kandasubramanian 2022).

Wet spinning technology, along with melt electrospinning and extruding, is one of the preferred technologies for manufacturing continuous micro-diameter fibers (Kim, Kim et al. 2019). Various methods for direct production of cellulose fibers through wet spinning have been reported (Olsson and Westman 2013, Vehviläinen 2015, Kim, Kim et al. 2019, Araki and Miyayama 2020, Azimi, Maleki et al. 2022). However, for cellulose fibers manufactured in this way, a nanoparticle synthesis step must be added for functionalization using nanoparticles, which leads to a prolonged fiber manufacturing process. In order to solve this problem, various techniques that enable the synthesis of nanoparticles as well as production of polymer fibers are being studied.

Microfibers and nanoparticles are very attractive materials and are attracting attention in many fields (Liu, Bai et al. 2011, Xue, Niu et al. 2015, Shahzad, Zhang et al. 2019). In general, nanoparticles possess unique properties due to the quantum size effect, but the properties of particles can be controlled by varying the size during particle synthesis (de Dios, Barroso et al. 2005, Albanese, Tang et al. 2012).
Therefore, microfibers closely fused with nanoparticles can serve as a scaffold that possesses the functional properties of nanoparticles and fibers simultaneously, thereby expanding their application area. First, a uniform distribution of nanoparticles across the surface of the microfiber is possible. Second, it is easy to control the concentration of nanoparticles in the fiber manufacturing process. Third, functional properties can be imparted by the nanoparticles that are embedded in the fibers. Based on these facts, the fusion of microfibers and nanoparticles can improve the properties of each and at the same time realize enhanced performance.

Silver nanoparticles (AgNPs), which exist in the form of silver complexes or silver oxide (Ag₂O), have been widely used in various fields requiring antibacterial properties due to their excellent antibacterial properties (Siddiqi, Husen et al. 2018, Hamouda, Hussein et al. 2019, Rautela, Rani et al. 2019, Almatroudi 2020). However, the search for a manufacturing method that almost completely fuses cellulose fibers and silver nanoparticles to take advantage of those properties is ongoing. Here, NaOH is the key material for converting AgNO₃ to AgNPs. Since NaOH can also convert cellulose acetate into cellulose, we hypothesized that AgNPs could be formed simultaneously with the fabrication of cellulose fibers.

In this study, we report a novel, simple method by which the acquisition of cellulose microfibers and the synthesis of AgNPs can be performed simultaneously via wet spinning, a technique easily scaled up for the mass production of fibers in general, and of the proposed antibacterial microfibers. Concentrations and ratios of AgNO₃ and NaOH solvent systems were optimized for desired results. The morphology and physicochemical properties of the generated CE@AgNPs microfibers were evaluated by SEM (EDS-mapping), FT-IR, XRD, TGA, and UTM (universal tensile machine). In addition, to evaluate the antibacterial properties of the prepared scaffold, an antibacterial test using *E. coli* and *S. aureus* was performed. The method reported here can have a socioeconomical impact in the fields that regularly require the use of antibacterial membranes, such as wound dressings and air filters.

### 2. Experimental

#### 2.1. Materials

Cellulose acetate (CA; average Mn ~30,000) and silver nitrate (AgNO₃; Mw=169.87 g/mol) were purchased from Sigma-Aldrich (South Korea). Dimethyl sulfoxide (DMSO; Mw=78.13 g/mol) and sodium hydroxide (NaOH; Mw=40 g/mol) were purchased from Samchun (South Korea). Agar and LB powder for antibacterial experiments were purchased from Becton, Dickinson and Company (New Jersey, USA). All chemicals were used as received. *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were selected as gram-negative and gram-positive bacteria, respectively. All bacteria used in the experiment were sub-cultured once a week.

#### 2.2. Chemical reaction equations
The two central chemical equations in this study are based on NaOH. Formula (1) indicates that cellulose acetate is deacetylated by NaOH and converted to cellulose. Formula (2) indicates that AgNO₃ forms Ag₂O (AgNPs) by NaOH.

\[
\text{Cellulose acetate} + \text{NaOH} \rightarrow \text{Cellulose} + \text{NaNO}_3 + H_2O
\]

2.3. Preparation of CE@AgNPs microfibers

The fabrication of CE@AgNPs microfibers using the wet-spinning technique was carried out as follows: CA powder was mixed in DMSO solvent at a concentration of 20 wt% and completely dissolved by stirring for 24 hours using a magnetic stirrer. Then, AgNO₃ was added to the prepared CA solution and stirred for 24 hours in the same manner as in the previous method to obtain a solution for preparing CE@AgNPs. The solution for CE@AgNPs preparation was filled into a 12 mL plastic disposable syringe (NORMJECT®, Henke Sass Wolf, Germany) and placed in a syringe pump. The solution was discharged at a rate of 1 mL/h by a syringe pump (Model Fusion 710, Chemyx Inc., USA). A syringe, a plastic tube, and a 23-gauge tip (inner diameter \(\leq 330 \mu m\)) were connected to the syringe pump, and the solution flowed from the tip and spun into a coagulation bath of 0.1 M NaOH aqueous solution. The spun fibers were obtained after a certain deacetylation time, and were dried at room temperature after thorough washing with DI water. Wet spinning of CA microfibers was carried out in the same fashion, but into a DI water bath instead of a NaOH bath.

Sample preparation for optimization of deacetylation time was performed as follows. 20 wt% CA solution was prepared and spun in the same manner as in the previous method. Each CA fiber spun in DI water was obtained immediately after spinning, and dried at room temperature after washing. Fibers spun into 0.1 M NaOH aqueous solution and undergoing the conversion process from CA to CE were obtained after applying deacetylation times of 5, 15, 30, and 60 min, and were washed and dried at room temperature in the same manner as mentioned previously.

Sample preparation for optimization of AgNO₃ concentration for synthesis of AgNPs was performed as follows. A 20 wt% CA solution was prepared in the same manner as in the previous method. 0, 2, 20, 200, and 2000 mM AgNO₃ were mixed with the prepared CA solution and stirred for 48 hours until uniformly dissolved in the solution. The prepared solution was spun into a coagulation bath of 0.1 M NaOH, immersed for the optimal deacetylation time identified above, and dried at room temperature after washing.
2.4. Characterization

2.4.1. SEM and EDS-Mapping

We utilized variable pressure scanning electron microscopy (VP-SEM; SU3900, Hitachi, Japan) to compare the morphological properties of microfibers according to the difference in deacetylation time and the morphological characteristics of nanoparticles according to the AgNO$_3$ content. All samples used for the measurement were polymer-based and showed low electrical conductivity, requiring further processing. Platinum sputtering was performed for 60 s to increase the ease of measurement through improved electrical conductivity. In addition, EDS-Mapping technology was applied to the obtained SEM image to visually clarify the distribution of AgNPs.

2.4.2. X-ray diffraction

High resolution X-ray diffraction (HR-XRD; D8 ADVANCE, BRUKER, USA) was used to compare CA and CE by measuring the structure and crystallinity of materials and to measure the synthesis degree of AgNPs. The instrument was set to a Cu X-ray tube of 2.2 kW, maximum voltage of 40 kV, a scan speed of 5 °/min, and a diffraction angle of 2θ = (10–90)° were applied for measurement. We confirmed the formation of AgNPs on the fibers by XRD measurements, and confirmed that CA was successfully converted to CE.

2.4.3. Infrared spectrometry

Infrared spectroscopy (FT-IR; Frontier, Perkin Elmer, USA) was performed under the wavelength range (4,000–500) cm$^{-1}$ condition for all samples. Chemical structure analysis using infrared spectroscopy confirmed the degree of conversion of CA to CE under conditions. The purpose of this analysis is to confirm the assumption that the acetyl group of the polymer chain constituting CA is removed and converted through deacetylation in an aqueous NaOH environment and converted to CE. According to the assumption, depending on the degree to which deacetylation proceeds, it is expected that there will be no acetyl groups in the CE polymer chains constituting the microfibers.

2.4.4. TGA/DSC

TGA (Q600, TA Instruments Ltd., USA)/DSC (Q20, TA Instruments Ltd., USA) was utilized to analyze the thermal decomposition characteristics of the samples. Measurements were conducted over a temperature range from room temperature to 700 °C in a nitrogen gas environment.

2.4.5. Contact angle measurements

The contact angle of each sample (n = 5) was measured using a contact angle analyzer (UNI-CAM/M, GITSOFT, Republic of Korea). In order to measure the water contact angle as accurately as possible, a drop of DI water was dropped on the sample and an image was taken after 60 seconds. The captured images were used to measure the contact angle precisely using ImageJ software.
2.4.6. Swelling ratio test

A swelling ratio test was conducted to confirm the difference in swelling ratio according to the amount of AgNO$_3$ added to each sample. The swelling properties of CA, CE and CE@AgNPs prepared with various concentrations (2, 20, 200, 2000 mM) of AgNO$_3$ were all observed ($n = 5$) using deionized water as the swelling medium.

2.4.7. Mechanical strength

To characterize the mechanical properties of the microfibers according to the manufactured conditions, the tensile strength was measured using a universal tensile machine (UTM; UT020-E, MTDI, Korea) equipped with a 1 kN load cell. The environment at the time of measurement was maintained at 25 °C, 60% relative humidity. For measurement, all samples were prepared with a length of 9.53 mm, and the thickness was measured immediately before the measurement and reflected. All sample groups were remeasured 5 times under the same conditions to derive an average value.

2.5. Antibacterial test

We hypothesized that the AgNPs of CE@AgNPs microfibers developed by the novel method would have antibacterial properties, and we conducted an antibacterial test to evaluate them. The bacteria used in this test were *Staphylococcus aureus* (*S. aureus*), a representative gram-positive group, and *Escherichia coli* (*E. coli*), a gram-negative group. First, an agar solution and Luria-Bertani (LB) solution were prepared. To make agar, 40 g of agar powder was added to 1000 mL of DI water, and for LB solution, 12.5 g of LB powder was added to 500 mL of DI water. Both solutions were stirred for 10 minutes and then autoclaved at 120 °C for 90 min. After, 8 mL of the prepared agar solution was poured into a 90 mm × 15 mm petri dish to make an antibacterial plate. In addition, *S. aureus* and *E. coli* were added to the prepared LB solution at a ratio of 9:1 (LB:bacteria), and cultured in a shaking incubator for 24 hours. The two types of cultured bacteria were inoculated on the prepared agar plate and then spread. After that, each sample was prepared in lengths of 5 mm and attached to the plates. The plates were incubated in an incubator at 37 °C for 24 hours, at which time the zones of inhibition were measured to confirm the antibacterial effect of the microfibers.

2.6. Statistical analysis

Statistical analysis was conducted using Origin Pro 9 and ImageJ. All experimental data were calculated as the mean ± standard deviation of at least five independent samples with a significant difference indicated when $p < 0.05$.

3. Results And Discussion

3.1. Fabrication of CE@AgNPs microfiber
CE@AgNPs microfibers were produced using traditional wet spinning techniques. Methods were based on previous literature (Ozipek and Karakas 2014, Puppi and Chiellini 2017, Nechyporchuk, Yang Nilsson et al. 2020), and the wet spinning process used for this was adjusted to simultaneously form CE microfibers and synthesize AgNPs on the fiber surface.

After complete dissolution by adding 2-2000 mM AgNO₃ to the CA solution prepared at 20 wt% in DMSO, CE@AgNPs microfibers were produced by wet spinning. In this process, the coagulation bath was composed of an aqueous NaOH solution titrated to 0.1 M which played a key role in allowing reactions (1) and (2) to occur simultaneously. Reaction (1) shows the deacetylation of CA by NaOH, where the acetyl group of the CA polymer chain is converted to a hydroxyl group. Reaction (2) shows the formation of AgNPs by the reaction of NaOH and AgNO₃, where the AgNO₃ dispersed in the solution is converted into AgNPs that are embedded in the fiber surface. The whole aforementioned process is graphically summarized in Fig. 1.

All CA solutions for wet spinning were prepared at a concentration of 20 wt%. Pure CA was wet-spun into a coagulation bath filled with DI water, while the composite samples were spun into a coagulation bath of 0.1M NaOH. The spun fibers were collected in a bath after a reaction time of 60 minutes and dried for 24 hours. Figure 2 (top) is a digital image showing each sample. The CA and CE and CE@AgNO₃ with concentrations of 2-200 mM AgNO₃ all appear to show a similar level of fiber morphology. However, when the AgNO₃ content is increased to 2000 mM, the fiber shape was irregular and some of the AgNP coating was peeled off. This phenomenon appears to happen because AgNO₃ reacts preferentially with NaOH to form a coating layer and when a solution containing excessive AgNO₃ is spun, the synthesis of fibers is inhibited, thus reducing the bonding strength between the fibers and AgNPs. Figure 2A-F shows the SEM images taken after completely drying the microfibers fabricated under each condition. The different amounts of AgNO₃ that is added and the type of coagulation bath leads to varying diameters of the fibers. Figure 2A and B show CA and CE fibers deacetylated from CA, respectively. Upon comparing the two, we observed that CA had a diameter of 300 micrometers and CE had a diameter of 209 micrometers. This decrease in fiber diameter is seen as a direct effect of CA deacetylation by NaOH, whether it be because of the physical differences in molecular structure or because of the nature of the different baths and how they react with the CA solution. However, as can be seen in Fig. 2C-E, as the content of AgNO₃ increased from 2 mM to 200 mM, the diameter of the fiber gradually increased compared to that of the CE fiber. Furthermore, the diameter of the fiber when AgNO₃ content is increased to 2000 mM is completely irregular, as seen in Fig. 2F. These results are identical to the results previously analyzed through digital images, suggesting that the diameter when converting CA to CE can be adjusted depending on the presence and content of AgNO₃.

When CA solution mixed with AgNO₃ is wet-spun in NaOH solution, CA and AgNO₃ are converted into CE and AgNPs through deacetylation or chemical reaction with NaOH, as in reactions (1) and (2), and visualized in Fig. 3. The factors for the change in fiber diameter with increasing AgNO₃ content mentioned in Fig. 2 can be found here. Figure 3A and 3B depict the surfaces of CA and CE respectively,
which are smooth due to the absence of AgNO\textsubscript{3}. However, as can be seen in Fig. 3C-F, as the content of AgNO\textsubscript{3} increased, the particles were confirmed on both the fiber surface and embedded inside. We used EDS-mapping to identify the particles formed on the fiber, and as shown in Fig. 3J, the particles were indeed AgNPs. As a result, as the content of AgNO\textsubscript{3} increases, the AgNPs crystals present inside and on the fiber surface increase, which physically prevents the fiber from shrinking after conversion to CE and gradually covers the fiber. Accordingly, it is possible to control the uniformity of AgNPs decorating the fiber surface by varying the AgNO\textsubscript{3} content. However, the addition of excessive AgNO\textsubscript{3} adversely affects the preparation of CE@AgNPs. As can be seen in Fig. 2F and Fig. 3F, in the fiber to which 2000 mM AgNO\textsubscript{3} is added, an excessive number of AgNPs are formed due to the reaction of a large amount of AgNO\textsubscript{3} and NaOH, which causes physicochemical aggregation, causing a film to form on the fiber surface. Also, we found that the fibers became partially molted, exhibiting an irregular fibrous shape with the addition of some AgNO\textsubscript{3}. This suggests that the addition of excessive AgNO\textsubscript{3} adversely affects the uniform distribution of AgNPs on the fiber surface, resulting in non-uniform fiber diameters. Therefore, we determined that the addition of 20–200 mM AgNO\textsubscript{3} was suitable for the uniform diameter of the fibers and the uniform distribution of AgNPs formed on the fiber surface.

We also confirmed the distribution and size of silver nanoparticles present on the fiber surface. As shown in Fig. 4A, the crystal phase of silver nanoparticles was clearly confirmed on the surface of the CE@AgNPs microfiber. The confirmed crystalline phase was in the form of a tetrahedron and showed the same shape as that confirmed in several studies on silver nanoparticles performed previously. In addition, the particles showed an average size of 357.51 ± 3.82 nm, as shown in Fig. 4B. Judging from these results, it can be concluded that the CE@AgNPs microfiber fabrication method carried out in this study is effective in converting CA to CE, while simultaneously successfully synthesizing AgNPs.

### 3.2. Physicochemical characteristics of the CE@AgNPs microfiber

We compared the chemical structure changes according to the difference in the synthesis conditions of CA, CE, and CE@AgNPs by using FT-IR. In Fig. 5A, pure CA exhibited absorption peaks at 1228 (R-O stretching), 1370 (-CH\textsubscript{3} bending), and 1740 (-C=O-stretching) cm\textsuperscript{-1}. The rest of the data in Fig. 5A shows the results for CE versus time treated with 0.1 M NaOH (CE n, n = # min treated). In contrast to the FT-IR results of pure CA, the characteristic 1228, 1370, and 1740 cm\textsuperscript{-1} peaks observed in CA gradually disappeared as the NaOH treatment time increased and more deacetylation occurred. In addition, the -OH peak unique to CE gradually became more prominent in the 3000–3700 cm\textsuperscript{-1} wavelength. Based on these results, we found that it is possible to control the level of CA deacetylation by controlling the time of treatment with NaOH solution. In addition, it was confirmed that in order to derive CE from CA, a treatment time of at least 30 minutes is required for complete deacetylation, as verified by FTIR. Figure 5B shows the FT-IR spectra of CA, CE, and CE@AgNPs. In the corresponding results, CE@AgNPs have 1383, 1631,
and 2927 cm\(^{-1}\) peaks that do not overlap with CA or CE (Hu, Wu et al. 2019). All corresponding peaks are absorption peaks of Ag, and through these results, we confirmed that AgNP synthesis was successful.

Figure 5C shows the XRD results of CA and CE after deacetylation of CA. From these results, it can be verified that deacetylation of CA is complete and converted into CE; the XRD pattern of CA microfibers showed the amorphous nature of CA, whereas in the case of CE after deacetylation, peaks corresponding to (1 0 1) were shown at 12, 20, and 22°. The (1 0 1) peak is one of the (1 0 1) and (0 0 2) peaks, which are characteristic peaks of cellulose II indicating successful CE formation following deacetylation of CA with NaOH.

Figure 5D shows the results of CE@AgNPs analysis by concentration according to AgNO\(_3\) content. In the absence of AgNO\(_3\), it can be seen that CE derived from CA through wet-spinning and deacetylation sequentially does not have a characteristic peak for AgNPs. However, CE@AgNPs prepared in the same manner as the above with concentrations of 2, 20, 200, and 2000 mM AgNO\(_3\), show characteristic peaks of Ag at 38.23° (1 1 1), 44.42° (2 0 0), and 64.44° (2 2 0). We see that because of the prominence of AgNPs on the surface of the fibers, the characteristic peaks for AgNPs became stronger, flattening the other peaks. When AgNPs cover the surface of the fiber, the AgNPs on the surface interfere with the X-ray used for XRD measurement to measure CE inside the fiber, and as a result, the CE peak is weakly confirmed.

Figure 5E depicts the TGA-DSC graph for CE@AgNPs prepared by adding CA, CE, and CE@AgNO\(_3\). The TGA curve of CA showed a minimal weight loss around 20–50°C due to evaporation of water and volatile compounds bound to CA chains. CE and CE@AgNO\(_3\) experienced the same weight loss, but up to 250°C instead. CA experienced a significant weight loss around 320–400°C due to CA chain degradation and breakdown of bonds. This thermal decomposition is experienced at around 220–320°C and 270–380°C for CE and CE@AgNP\(_3\) respectively. Finally, the final stage of mass loss due to carbonization occurred around 400°C for all three samples, with the least amount of mass loss occurring for the samples containing silver nanoparticles. CE@AgNPs prepared with the addition of different concentrations (2, 20, 200, 2000 mM) of AgNO\(_3\) were compared as shown in Fig. 5F. As mentioned previously, each curve showed similar thermal decomposition behavior regardless of the amount of AgNO\(_3\), but the concentration did have an effect on the final amount of mass, with higher concentrations of AgNO\(_3\) corresponding to lower final mass loss.

3.3. Physical properties of CE@AgNPs microfibers

Figure 6A and B are the results of water contact angle measurements performed to confirm the difference in hydrophilicity of CE@AgNPs prepared with different concentrations of AgNO\(_3\). The digital images of Fig. 6A and the graph of Fig. 6B revealed that CA showed a water contact angle of about 70°, confirming its relatively low hydrophilicity, and CE showed a water contact angle of about 26°, confirming its relatively high hydrophilicity. In addition, as the amount of AgNO\(_3\) added to CE@AgNPs increased from 2
mM to 200 mM, the water contact angle for the sample increased, meaning that the addition of more Ag results in higher hydrophobicity. This result indicates that as the amount of AgNO$_3$ added to CE@AgNPs increases, the amount of AgNPs synthesized on the fiber surface increases and, naturally, the hydrophobicity of the fiber increases due to the AgNPs formed on the fiber surface. In general, the hydrophobicity of the samples went from CE@AgNPs (high concentrations) > CA > CE@AgNPs (low concentrations) > CE, with CE being very hydrophilic.

In addition to these changes in hydrophilicity, changes in the content of AgNPs also affect the swelling ratio of fibers. As is exhibited in Fig. 6C, the swelling ratio of CE was 112%, which was once again confirmed to have a higher hydrophilicity than that of CA (36%). The swelling ratio of CE@AgNPs gradually decreased as the AgNO$_3$ content increased and sharply decreased from 200 mM AgNO$_3$ onwards. The sudden drop in swelling ratio for the samples with greater than 200 mM AgNO$_3$ can possibly be explained by the excess AgNPs that are formed when in the solvent bath: the excessive amount of AgNPs can immobilize the CE fibers, hindering their expansion when met with water. As a result, we confirmed that a concentration of 2–20 mM AgNO$_3$ is most appropriate for the preparation of CE@AgNPs for a sufficient level of hydrophilicity as well as high swelling ratio.

Figure 7A shows the mechanical properties of CA and CE derived from CA. The tensile strength of CE was 45.53 MPa, which was higher than that of CA (~12.20 MPa), an occurrence that is well reported in the literature. The trade-off of that high tensile strength is the elongation; the elongation of CE (7.42%) is significantly lower than that of CA (53.85%). The aforementioned tensile strength and elongation results for CA and CE are caused by the conversion of acetyl groups to hydroxyl groups upon deacetylation of CA. CA, in which acetyl groups are dominant in the molecular structure, shows high elongation and low tensile strength due to acetyl groups, whereas CE, in which hydroxyl groups are dominant, shows low elongation and high tensile strength due to molecular structure and bonding.

The mechanical properties of CE@AgNPs prepared according to AgNO$_3$ content (0-2000 mM) is shown in Fig. 7B, and the Young's modulus (MPa), ultimate tensile strength (UTS, MPa), and elongation (%) values for all samples is exhibited in Fig. 7C. Interestingly, specific changes in tensile strength and elongation were observed with varying AgNO$_3$ content. Fibers containing 2-200 mM AgNO$_3$ showed tensile strengths comparable to or lower than CE. This phenomenon is attributed to the AgNPs inside the fibers formed during the transformation process; AgNPs inside the fibers physically interfere with the bonding between the CEs constituting the fibers, and at the same time have the potential to become the initiation point of cracks that can cause physical failure when the fibers are subjected to tensile force. Accordingly, the more AgNPs that are present in the fiber, the lower the tensile strength of the fiber, up until a certain point. The presence of AgNPs also affect elongation. Unlike pure CE, CE@AgNPs containing AgNPs show a somewhat high level of elongation due to binding interference by particles in the fiber, but the level decreases rapidly as the number of particles in the fiber increases. However, contrary to the trends shown by CE@AgNPs from 2-200 mM, CE@AgNPs fibers containing 2000 mM AgNO$_3$ have significantly higher tensile strength and elongation than other fibers. This result appears to occur because the excessive
amount of AgNO₃ in the fiber completely covers the surface of the fiber during the conversion to AgNPs, forming a layer on the outside of the fiber, resulting in higher tensile strength than before, and physically inhibits the deacetylation of CA, resulting in a relatively higher elongation than other CE and CE@AgNPs.

3.4. Antibacterial property of CE@AgNPs microfiber

We performed an antibacterial test to confirm the antimicrobial activity of fibers containing AgNPs. Figure 8 shows the results of the antibacterial experiment performed against both gram-positive (S. aureus) and gram-negative (E. coli) bacteria for each sample. As expected, CA and CE without AgNO₃ were found to have no antibacterial activity. In contrast, CE@AgNPs prepared by adding 2–2000 mM AgNO₃ exhibited zones of inhibition that measured 36.50 to 68.44 mm² against the gram-positive and 32.23 to 82.01 mm² against the gram-negative. These results show that AgNO₃ added during the manufacturing process of CE@AgNPs is converted into AgNPs by NaOH, and it was confirmed that the amount of AgNPs formed in the fibers increased as the AgNO₃ content increased.

4. Conclusion

Here, a treatment method capable of simultaneously performing two processes is presented: the formation of silver nanoparticles and the collection of cellulose fibers through the deacetylation of cellulose acetate. Through the results of this study, it is possible to obtain cellulose microfibers embedded with silver nanoparticles faster than ever before; the procedure presented here also promises scalability, although this was not directly tested in this study. In addition, the content of AgNO₃ added has a direct causal relationship with the amount of AgNPs formed on the surface of microfibers. CE@AgNPs microfibers showed the greatest balance of antibacterial and mechanical properties at 20 mM. The results show that the amount of AgNPs present in the fiber has an affect on the antibacterial activity and mechanical properties of the scaffold, such as hydrophilicity and tensile strength. The treatment process reported here is highly promising in fields that can utilize microfibers containing AgNPs, such as water treatment filters and antibacterial artificial ligament materials.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors whose names appear on the submission made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content; approved the version to be published; and agree to be
accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

**Availability of data and materials**

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

**Competing interests**

The authors have no competing interests to declare that are relevant to the content of this article.

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**Authors' Contributions**

All authors contributed to the study conception and design. Conceptualization, formal analysis, investigation, visualization, writing – original draft and funding acquisition were performed by Joon Yeon Moon. Formal analysis, investigation, writing – review & editing, visualization, validation and funding acquisition were performed by Joshua Lee. Visualization, validation, supervision and project administration were performed by Chan Hee Park. Validation, project administration and funding acquisition were performed by Cheol Sang Kim. All authors read and approved the final manuscript.

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References


Figure 1

Schematic of the preparation of the CE@AgNPs microfiber using the simultaneous method. The CA microfiber is changed to CE by reaction with NaOH. At the same time, AgNO₃ and NaOH react with each other to form AgNPs on the surface of the CE fiber. (White scale bar: 500 μm, yellow scale bar: 10 μm)
Figure 2

(Top) Digital photo of CA, CE, 2, 20, 200, 2000 mM AgNO$_3$-reacted CE@AgNPs. SEM images of (A) CA, (B) CE, (C) 2 mM AgNO$_3$, (D) 20 mM AgNO$_3$, (E) 200 mM AgNO$_3$, (F) 2000 mM AgNO$_3$. (White scale bar: 500 μm)
Figure 3

(Top) CA-based CE@AgNPs transformation schematics. SEM images of (A) CA, (B) CE, (C) 2 mM AgNO₃, (D) 20 mM AgNO₃, (E) 200 mM AgNO₃, (F) 2000 mM AgNO₃. (G)-(K) EDS mapping results of the CE@AgNPs. SEM image of (G) CE@AgNPs microfiber, and EDS results of (H) the combined elements, (I) carbon, (J) silver, and (K) oxygen. (White & yellow scale bar: 50 μm)
Figure 4

(A) SEM image of silver nanoparticles (Scale bar: 10 μm) and (B) size distribution graph of silver nanoparticles.
Figure 5

(A, B) FT-IR and (C, D) XRD and (E, F) TGA curves results of the wet-spun fibers. (A) IR spectra of CA and CE by treatment time (CE n, n = deacetylation time in min), and (B) CA, CE, CE@AgNPs. (C) XRD data of CA and CE, and (D) CE@AgNPs by AgNO₃ contents. (E) TGA curves of CA, CE and CE@AgNPs fibers, and (F) CE@AgNPs fibers by AgNO₃ concentration (2, 20, 200, 2000 mM).
Figure 6

(A) Digital images of water contact angle results of CA, CE and CE@AgNPs microfibers. (B) Bar charts of hydrophilicity test results and (C) swelling ratio test results of CA, CE, (2, 20, 200, 2000) mM CE@AgNPs.
Figure 7

(A) Stress-strain curves of CA and CE wet-spun fibers. (B) Stress-strain curves of CE and CE@AgNPs prepared according to AgNO₃ content (0-2000 mM). (C) Graphs of the Young’s modulus (MPa), UTS (MPa) and elongation (%) of samples.
Figure 8

(A, C) Images of the antibacterial test of CA, CE, CE@AgNPs, and CE@AgNPs prepared according to AgNO₃ content (0-2000 mM). (B, D) Graphs depicting the area of the inhibition zones of the prepared samples.