RELEASE OF SILVER NANOPARTICLES FROM POLYSACCHARIDE FILMS BASED ON METHYLCELLULOSE

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Abstract

The present work is focused on preparation and characterization polysaccharide films based on methylcellulose. Films were doped with silver nanoparticles (AgNPs). AgNPs were prepared and stabilized by reduction of silver nitrate. Polyethylene glycol and glycerol were used as additives for better material properties of methylcellulose films. Properties of these films were analyzed with a number of analytical techniques. Wettability and water absorption of films were evaluated. Concentration of the AgNPs released into the solution during dissolution was studied by atomic absorption spectroscopy. The presence of AgNPs in solutions and solid films was monitored by the ultraviolet-visible spectroscopy. Solid films were dissolved at different temperatures and release of AgNPs from the film was observed during the dissolution time by the ultraviolet-visible spectroscopy. The presence of AgNPs was confirmed both in the solid films and in the solutions by the above mentioned methods. It was found that additives changed materials properties. Our research was aiming on use of these films in medicine as a new type of wound dressing with antibacterial properties or as a drug delivery system.

Keywords: Polysaccharides films, silver nanoparticles, methylcellulose

1. INTRODUCTION

Cellulose (β-1,4-glucopyranose) is the most abundant polysaccharides on the Earth. It belongs among a wide group of natural polysaccharides with excelent biological properties. Natural polysaccharides have excellent biological properties, such as non-toxicity, biocompatibility and biodegradability [1,2]. Their main advantages are good mechanical properties, easy preparation and low cost. Biological properties could be changed by the chemical or physical modification of their surface. Surface properties of the materials are inevitably bonded with tissue engineering, especially for polymers when improvement of the cell adhesion to the surface, the cell growth and uniformity are studied [3].

Cellulose is commonly used in health care like wound dressing or as a pharmaceutical excipients. Nowadays i tis also used as a laxative.[4]. Cellulose is further used in the paper, textile, cosmetic, food and chemical industries. Nowadays, cellulose has a lot of derivatives e.g. organic esters - celulose acetate or propionate, inorganic esters - nitrocelulose, celulose ethers - methylcellulose, hydroxypropylmethyl celulose, carboxymethyl celulose, etc. Every derivatives have special properties like solubility. This work is focused on methylcellulose. It is hydrophilic white powder which dissolves only in cold water. Dissolved powder makes a clear viscous solution or gel [5,6,7].

This work is focused on the preparation of polysaccharide films based on methylcellulose. The prepared films were doped with silver nitrate yielding AgNPs embedded in the polysaccharide matrix [8,9]. The influence of addition of glycerol or polyethylene glycol on the material properties was studied. Wettability and water absorption of the films were evaluated. The UV-Vis absorption of prepared solution and dissolved films was measured. Release of AgNPs was studied by UV-Vis, too.

2. EXPERIMANTAL

2.1. Material

Methylcellulose (MC) and silver nitrate ($AgNO_3$) were obtained from Sigma-Aldrich. Sodium citrate was purchased from Penta. Polyethylene glycol 400 (PEG 400) was obtained from Fluka Analytical and glycerol was purchased from Lach-Ner and distilled water. PEG 400 and glycerol were used plasticizers.

2.2. Preparation of polysaccharide films

Polysaccharide films were prepared via process shown in **Figure 1**. Chronologically: methylcellulose (2 g) was stirred in 200 mL distilled water. The solution was constantly stirred and heated at 80 °C [5,6]. After 45 min, suspension of MC removed from stirring and heating device. Suspension was cooled down for 20 min. The cooled-down suspension of MC was then placed in an ice bath. During the cooling down, 10 mL of sodium citrate (0.085 g of sodium citrate was dissolved in 10 mL of water) was slowly dropped to the suspension a then 10 mL of $AgNO_3$ was added (0.085 g of $AgNO_3$ was dissolved in 10 mL of water), too. This mixture was stirred for 30 min. After that, 4 mL of PEG 400 (or glycerol) were dropped to suspension. Suspension was still stirred. Then the solution was cooled down to the laboratory temperature and aliquots of 10 mL were poured into round silicone molds, 5 cm in diameter. The samples were dried for 17 h at 60 °C. Finally, we got round homogenous polysaccharide films. The rest of solutions was used to measurements as well. The other films were prepared by the same method under the condition of no PEG 400 or glycerol. These solutions and films were used to as control samples.

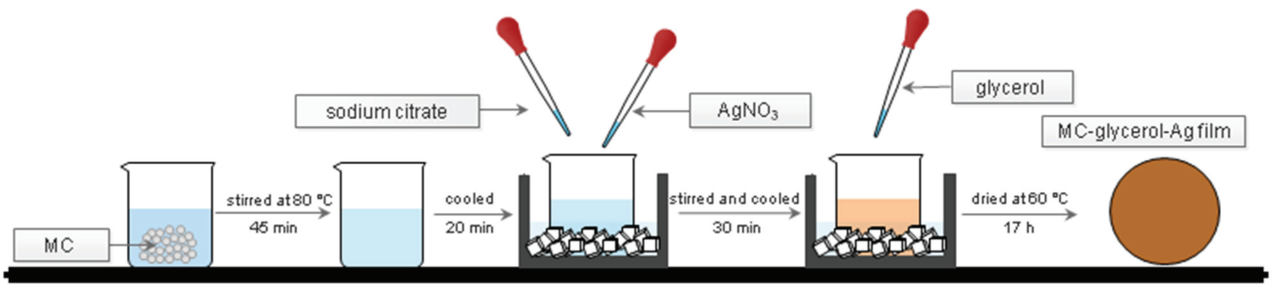

Figure 1 Schema of the preparation of polysaccharide films with AgNPs

2.3. Characterization methods

The presence and concentration of AgNPs in solutions and on the surface of the prepared films were studied by Ultraviolet-visible spectroscopy (UV-Vis, LAMBDA 25, PerkinElmer, USA). Wettability of the prepared films was evaluated by Surface Energy Evalution System Advex Instruments, Brno). Water absorption of the films was evaluated gravimetrically (RADWAG MAX 60, Poland). The release of AgNPs was observed at 2 different temperatures. Solid films were dissolved in ice bath 4°C and heated at 37°C. These solutions with release AgNPs were measured by UV-Vis. Concentration of release AgNPs from films was determined by atomic absorption spectroscopy (AAS).

3. RESULTS AND DISCUSSION

Three types of polysaccharide films based on methylcellulose were prepared. All these films contained AgNPs (**Figure 2**). First type of film was pristine, hereby referred as **MC-Ag**, consisting only of methylcellulose and AgNPs. The second type of film is here referred as **MC-glycerol-Ag**, consisting of metylcellulose film which was modified by plasiticizer glycerol during the preparation and also AgNPs. The third type is here referred as **MC-PEG 400-Ag** and it is aslo methylcellulose film which was modified by plasiticizer PEG 400 during the preparation. Then films with plasticizers and AgNPs were prepared, too. Films that contain AgNPs have orange-brown of gray-green colour in solid state. The colour change indicates the presence of AgNPs, on the other hand polysaccharide films without AgNPs are pure /citace/.

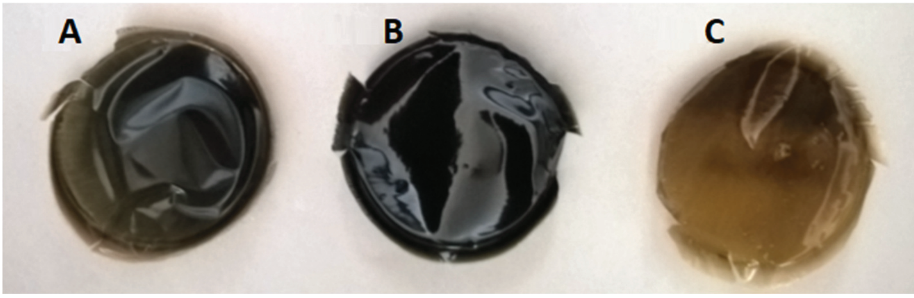

Figure 2 Prepared films: A - MC-Ag, B - MC-glycerol-Ag, C - MC-PEG 400-Ag

3.1. Ultraviolet-visible spectroscopy (UV-Vis) of solution

AgNPs were confirmed by UV-Vis spectroscopy in all three solutions that contained AgNPs. AgNPs have characteristic peak at wavelength around 400 nm [8]. **Figure 3** shows that the highest absorbance had solution **MC-Ag** that was used to prepare **MC-Ag** film. Very similar peak with a little bit lower absorbance was observed for the solution **MC-glycerol-Ag** film. The lowest absorbance had solution **MC-PEG 400-Ag**.

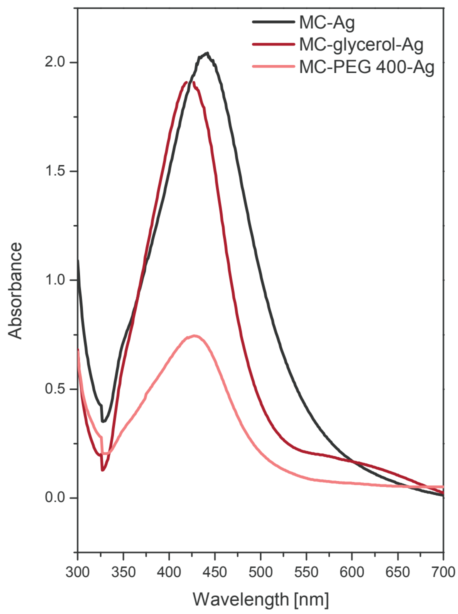

Figure 3 UV-Vis spectra of solutions for preparation MC films: A - MC-Ag, B - MC-glycerol-Ag, C - MC-PEG 400-Ag

3.1. Characterization of solid films

3.1.1. Wettability and water absorption

Wettability and water absorption are very important properties of materials which could be as a wound cover. The values of the contact angle and water absorption determined wettability of the films. It can subsequently be used as an indicator of the ability to absorb exudate from injury. These properties are necessary to design wound healing material. The measurements of wettability and water absorption were done only with films that contained AgNPs. From **Figure 4** is apparent that contact angles decreased with addition of plasticizers. The lowest wettability value and the highest contact angle value had film **MC-Ag**. On the other hand the lowest contact angle was measured at film **MC-PEG 400-Ag**. The film **MC-Ag,** which had the highest value of contact angle, had also the highest value of water absorption. The lowest value of water absorption had film **MC-glycerol-Ag**. We found out that the addition of plasticizers significantly reduced the wettability and water absorption. Plasticizers also change material properties like elasticity. The films which only based on MC were stroger than the others film with additives.

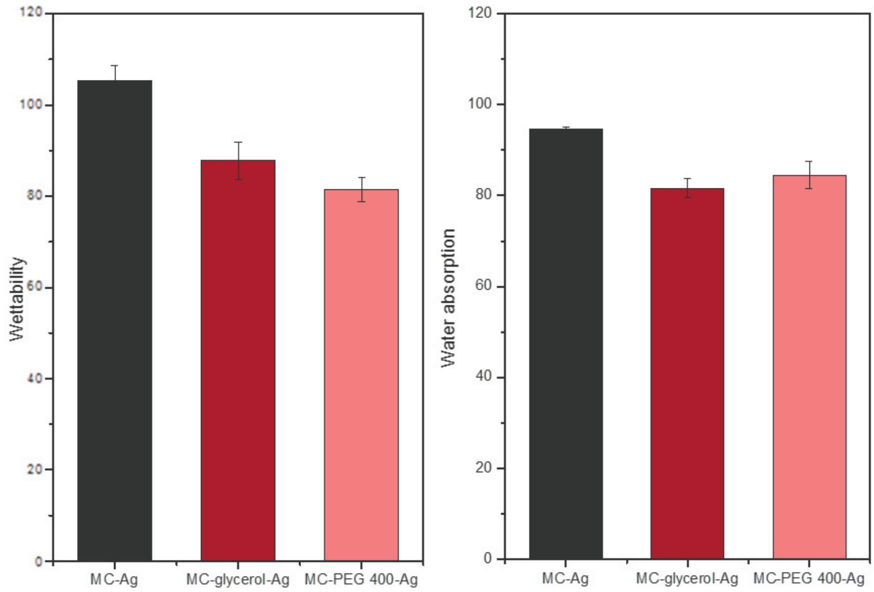

Figure 4 Wettability and water absorption of the prepared films

3.2. Characteristics of dissolved films

Due to the natural properties of methylcelullose, the solubility of prepared films and release of AgNPs were tested at distilled water. We chose two different temperatures: 4 and 37°C. The temperature of 4°C were chosen for termo was chosen due to the thermoreversible properties of the methylcellulose. And the temperature of 37°C as the temperature as the temperature simulating the warm human body. We dissolved a quarter of the prepared film in conditions and then ultraviolet-visible spectroscopy (UV-Vis) was measured. The concentration of AgNPs of the dissolved films was also determined by atomic absorption spectroscopy (AAS).

3.2.1. Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy was used to examine concentration of AgNPs that were released from the films in cold distilled water (4°C). During 3 days whole films were dissolved and all AgNPs were in the solution. **Table 1** shows that after 3 days the highest amount of AgNPs contained film **MC-Ag.** The lowest amount of AgNPs was measured at film **MC-PEG 400-Ag**. In this case, it is possible that between MC and PEG 400 or glycerol were created H bonds and thus did not completely reduce $AgNO_3$ to AgNPs as was the case with Mc-Ag. The concentration was measured with experimental error ±5 %.

Table 1 Concentration of released AgNPs studied by AAS

Sample	Ag (mg/L)
MC-Ag	99.3
MC-glycerol-Ag	88.1
MC-PEG 400-Ag	82.1

3.2.3. Release of AgNPs from polysaccharide films

The release of AgNPs from prepared films were studied by UV-Vis spectroscopy. Two different temperatures were used during the measurements. From **Figure 5** show that the AgNPs were most released from the film **MC-Ag**. It is possible that hydrogen bond between AgNPs and MC were weaker and AgNPs were easier released from the film. It was observed that temperature of solution influenced the released of AgNPs. AgNPs released from the films more and more rapidly at 37°C than at 4°C.

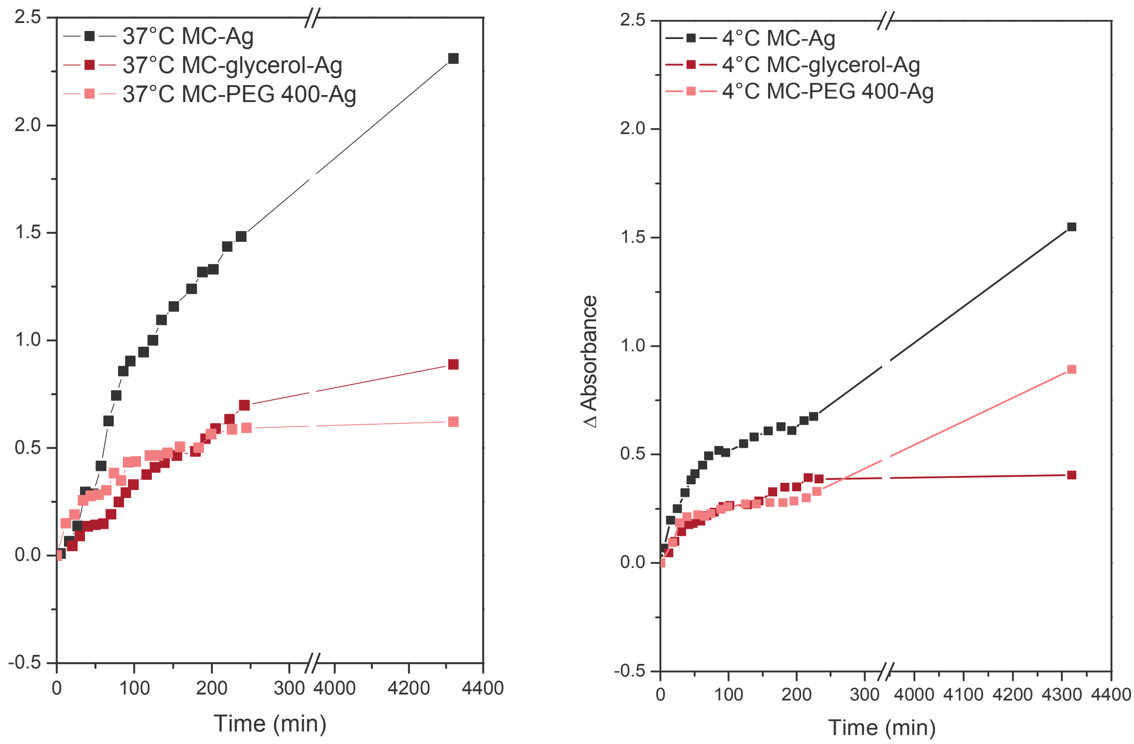

Figure 5 Differences in absorbance of released AgNPs from films: MC-Ag, MC-glycerol-Ag, MC-PEG 400-Ag

CONCLUSION

Three polysaccharide films based on methylcellulose were prepared. The presence of AgNPs was confirmed by UV-Vis and AAS. Prepared solutions were measured by UV-Vis before forming films. The highest concentration of AgNPs had **MC-Ag** films. It was found out that polysaccharides films containing plasticizers (glycerol, PEG 400) reduced wettability and water absorption. Release of AgNPs from polysacharide films were observed. It was found that the AgNPs were most released from the film **MC-Ag**. It was observed that temperature of solution influenced the released of AgNPs. AgNPs released from the films more and more rapidly at 37°C than at 4°C.

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