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SYNTHESIS OF SILVER NANOPARTICLES IN A BIOPOLYMER MATRIX BASED ON DIALDEHYDE CARBOXYMETHYLCELLULOSE/SERICIN

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Abstract: In this study, the formation of silver nanoparticles (AgNPs) within a graft copolymer matrix based on dialdehyde carboxymethyl cellulose (DCMC) and silk sericin was investigated. The formation of Schiff bases between the aldehyde groups of DCMC and the amino groups of sericin resulted in the development of a stable biopolymer network, which enabled the simultaneous reduction and stabilization of nanoparticles. The mechanism of the photochemical reduction of silver ions into their metallic form and their interaction with the polymer matrix was comprehensively analyzed.

The structure and morphology of the obtained nanocomposites were characterized using Fourier-transform infrared (FTIR) and UV–Vis spectroscopy methods. According to the results, stable silver nanoparticles with spherical and needle-like morphologies, ranging in size from 30 to 90 nm, were uniformly distributed within the polymer matrix. The findings demonstrate that DCMC/sericin-based biopolymer systems possess significant potential for application as functional nanocomposites, particularly in the development of antimicrobial materials.

Keywords: dialdehyde carboxymethyl cellulose, sericin, graft copolymer, silver nanoparticles, Schiff bases, biopolymer matrix, nanocomposite, photochemical reduction, antimicrobial materials.

Introduction

In recent years, there has been a sharp increase in the demand for sustainable, biodegradable, and bio-based materials, significantly enhancing the interest in developing functional materials based on natural polymers, particularly polysaccharides and proteins [1–3]. Cellulose and its derivatives, including sodium carboxymethyl cellulose (Na-CMC), are widely used in various scientific and practical fields due to their high hydrophilicity, biocompatibility, and susceptibility to chemical modification [4-7]. Furthermore, functionalizing cellulose

derivatives to enhance their reactivity and create new composite systems is becoming increasingly viable [8-9].

Oxidizing Na-CMC to obtain dialdehyde carboxymethyl cellulose (DCMC) introduces highly reactive aldehyde groups into the cellulose chain [10–12]. This makes DCMC an efficient matrix for forming chemical bonds with proteins and biopolymers containing amino groups via Schiff bases [13–15]. In particular, hydrogels and composites based on DCMC have shown high mechanical stability, biocompatibility, and functional properties in numerous studies [16–17].

Nevertheless, the formation of silver nanoparticles in dialdehyde carboxymethyl cellulose and sericin-based graft copolymer matrices, as well as the factors affecting their formation mechanism, morphology, and stability, have not been adequately studied. In particular, there is limited data on the effect of the network structure formed through aldehyde-amine interactions on the size and distribution of nanoparticles.

Thus, the aim of this work is to synthesize a graft copolymer based on dialdehyde carboxymethyl cellulose and sericin and to study the process of silver nanoparticle formation in this biopolymer matrix. The mechanism of nanoparticle formation, their morphology, size, and stability were analyzed using spectroscopic and microscopic methods.

Experimental Part

Materials. In the study, the following materials were used: DCMC obtained from Na-CMC of Asdacell HV brand, produced by "Promxim Impex" LLC (Uzbekistan) with an oxidation degree of 82% and molecular weight of 141 kDa, sericin derived from silk industry fibrous waste, and silver nitrate ($AgNO_3$) salt (Sigma Aldrich).

2.1. Preparation of Dialdehyde Carboxymethyl Cellulose (DACMC)

1 g of Na-CMC is dissolved in 30 ml of water with the help of a mechanical stirrer. To the resulting solution, 10% $NaIO_4$ solution is added. The solution's pH is adjusted to 3.5 by adding 1 M HCl dropwise. The oxidation reaction is carried out under the effect of high-intensity (10%) ultraviolet (UV) light at 70 W for 10 minutes, with cooling every 2 minutes. The temperature of the oxidation reaction is maintained below 35°C. The obtained mass is precipitated in 300 ml of 94% ethanol. The mass is filtered and washed with 70% ethanol until neutral. The obtained mass is dried in a lyophilizer for 6-8 hours.

2.2. Extraction of Sericin from Natural Silk Fibers

Sericin is extracted from natural silk fibers by thermal hydrolysis. Ground natural silk fibers are soaked in water at a ratio of 1:10 and boiled in an autoclave at 110°C for 24 hours. The resulting mass is filtered, and the filtrate is dried in a lyophilizer for 8-10 hours.

2.3. Preparation of DCMC/Sericin Graft Copolymer

A 2% solution of DCMC is prepared and mixed with a 3% solution of sericin in a 1:1 mass ratio. The Schiff base formation reaction is carried out at 60°C for 1 hour. The resulting solution is dried in Petri dishes at 37°C.

2.4. Formation of Silver Nanoparticles in the DCMC/Sericin Graft Copolymer Matrix

For the formation of silver nanoparticles in the DCMC/sericin graft copolymer matrix, a 0.1 M aqueous solution of pure silver nitrate ($AgNO_3$) is used according to GOST 277-75 for analysis. A 2% aqueous solution of the copolymer is prepared, and 3-10 ml of a 0.1 M $AgNO_3$ solution (pH = 5.14) is added at 25°C. The solution is mechanically stirred at 1400 rpm for 30 minutes and treated in an ultrasonic disperser (UZDN-2, U-4.2, Russia) for 20 minutes. The resulting hydrogel and films based on them were analyzed using FTIR and UV–Vis spectroscopic methods.

2.5. FTIR Spectroscopy

FTIR spectroscopy was carried out using an Inventio-S IR Fourier (Bruker, Germany) device. Spectra were studied in the range of 500-4000 cm^{-1} with a resolution of 0.085 cm^{-1}.

2.6. UV-Vis Spectroscopy

The UV-Vis spectra of the samples were recorded using a "Specord M210" spectrophotometer in the range of 200-900 nm.

Results and Discussion

In our previous studies, the process of synthesizing high molecular weight and oxidized Na-CMC (with an oxidation degree of 82% and molecular weight of 141 kDa) via periodate oxidation reaction under the influence of ultra-high-frequency (UHF) radiation was investigated [10]. In this case, the oxidation reactions of Na-CMC samples under the influence of UHF radiation and in the presence of sodium periodate follow the equation:

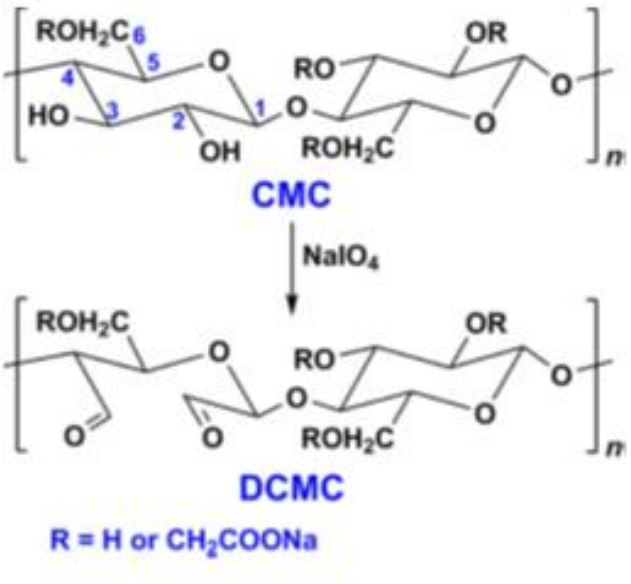

Figure 1. Oxidation reaction of Na-CMC in the presence of sodium periodate.

Additionally, under the influence of ultra-high-frequency (UHF) radiation, the conditions for obtaining sericin with high efficiency and effectiveness from silk industry fibrous waste have been determined [11]. The process of synthesizing the graft copolymer based on the obtained DCMC and sericin is shown in the following figure [Figure 2].

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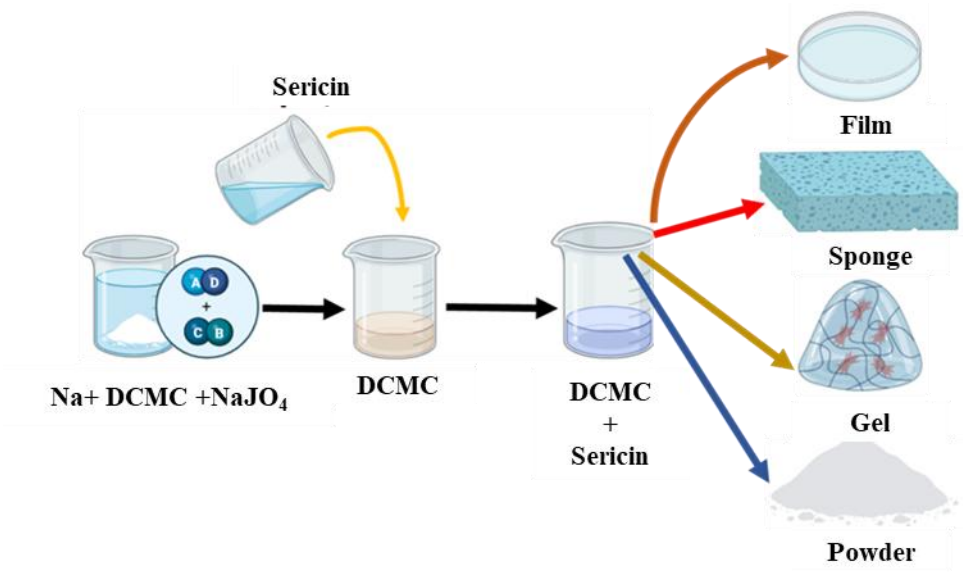

Figure 2. Synthesis of the DCMC/sericin graft copolymer.

In this process, the aldehyde groups react with the amino groups in a nucleophilic substitution reaction [10], forming Schiff bases and creating a graft copolymer via imine (carbinolamine) bonding [12]. The new absorption regions in the DCMC-sericin graft copolymer were studied using the FTIR spectroscopy method.

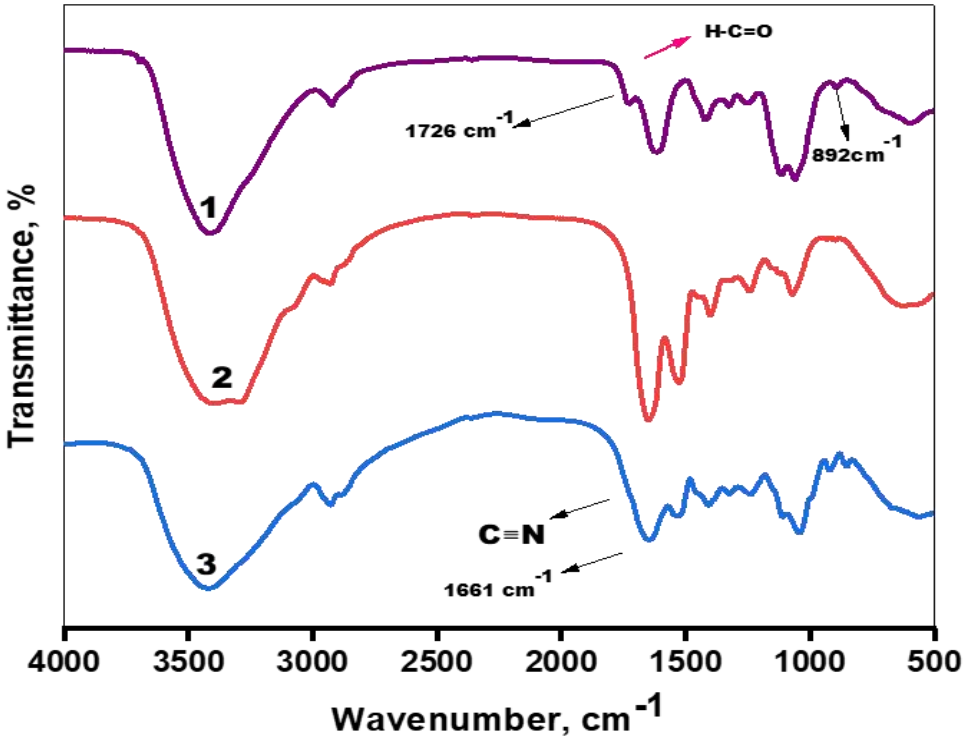

Figure 3. FTIR spectra of DCMC (1), sericin (2), and DCMC/sericin graft copolymer (3).

As shown in Figure 3, when the DCMC/sericin copolymer is formed, the absorption band characteristic of the carbonyl (-C=O) group of dialdehyde at 1726 cm^{-1} disappears. It was found that in the DCMC/sericin copolymer, absorption intensities characteristic of sericin's I, II, and

III bands were observed at 1620, 1516, and 1240 cm^{-1}, respectively [13]. Furthermore, new absorption intensities at 1661 cm^{-1}, which are characteristic of the imine (C≡N) linkage formed in the DCMC/sericin copolymer, were also observed.

The process of forming silver nanoparticles in the graft copolymer matrix was carried out according to the method described in [14]. The results of the UV-spectroscopic analysis of the silver nanoparticles formed in the graft copolymer matrix are shown in Figure 4.

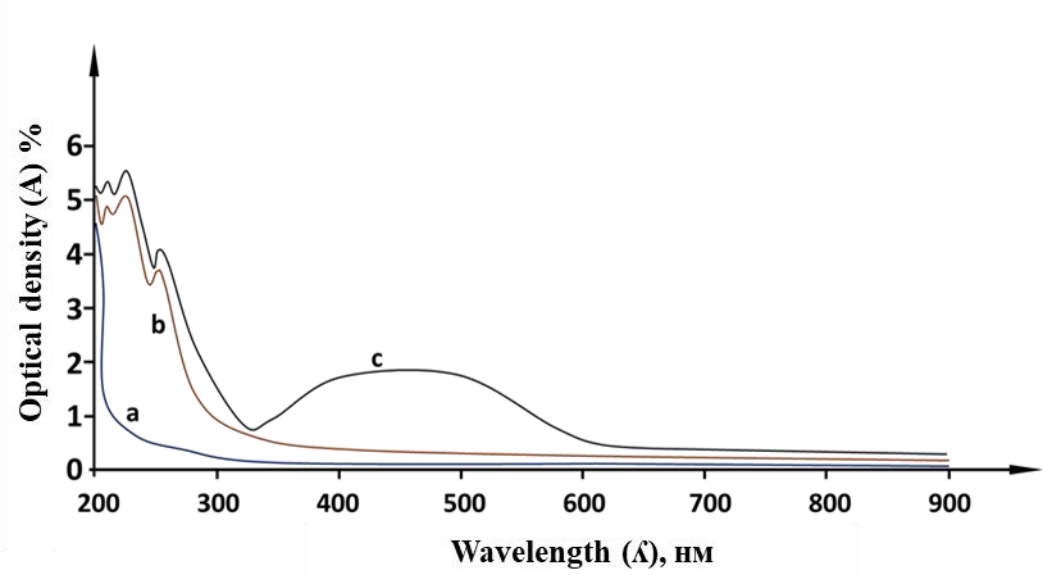

Figure 4. UV spectra of DCMC/sericin graft copolymer samples containing silver nanoparticles a) DCMC/sericin, b) Ag^{+}/DCMC/sericin, c) Ag^{0}/DCMC/sericin

The UV spectra of the DCMC/sericin graft copolymer and its modified samples containing silver ions and nanoparticles were analyzed in the 200–800 nm range (Figure 4). The obtained spectra revealed three distinct states: (a) the initial copolymer matrix, (b) the system complexed with Ag^{+} ions, and (c) the system containing Ag^{0} nanoparticles formed by photoreduction.

For the initial DCMC/sericin copolymer, a broad absorption band with low intensity was observed around 260–290 nm. This signal is related to n→π* and π→π* electronic transitions associated with aromatic amino acids (tyrosine, tryptophan) in the sericin, as well as carbonyl (C=O) and imine (C=N) groups [13,18]. This directly confirms the successful formation of Schiff bases in the copolymer network.

In the sample with added silver ions (Ag^{+}), an increase in absorption intensity and the widening of the spectral line in the 270–300 nm range was observed. This can be explained by the formation of coordination complexes between Ag^{+} ions and the functional groups (–CHO, $–COO^{-}$, $–NH_2$) in the polymer matrix. Moreover, the redistribution of electron density results in the enhancement of n→π* transitions. At this stage, metal nanoparticles have not yet formed, and ion–polymer interactions dominate in the system.

After photoreduction, the sample spectrum shows a distinct and intense absorption peak in the 400–450 nm range (λmax ≈ 420–430 nm). This peak is associated with the surface plasmon resonance (SPR) of silver nanoparticles, indicating the successful reduction of Ag^{+} to Ag^{0} [16,19]. The relatively broad and asymmetric shape of the SPR peak suggests that the nanoparticles are polydisperse and have different morphologies (spherical and partly needle-like).

Furthermore, the SPR peak located around 420 nm indicates that the nanoparticle size is approximately in the range of 20–80 nm. The shift of the peak toward longer wavelengths and the increase in intensity may be related to clustering in the polymer matrix and interparticle

interactions. This confirms that the DCMC/sericin matrix not only acts as a reducing agent but also as an effective stabilizer[20].

An important aspect is that the hydroxyl, carboxylate, and amine groups in the polymer matrix adsorb on the surface of the silver nanoparticles, limiting their aggregation and ensuring colloidal stability. As a result, the nanocomposite system forms a stable structure that maintains optical stability over time.

The particle size is approximately in the range of 30–90 nm, as visually estimated, which correlates well with the XRD and UV-Vis results. While some nanoparticles have formed aggregates, they are generally uniformly distributed throughout the polymer matrix. This demonstrates the high stabilizing efficiency of the DCMC/sericin matrix.

The density and distribution of nanoparticles on the surface are associated with the coordination and electrostatic interactions between silver ions and the functional groups (–OH, $–COO^-$, $–NH_2$, and –CHO) in the polymer matrix. These groups adsorb on the surface of the nanoparticles, limiting their aggregation and ensuring colloidal stability.

The clearer morphology of the nanoparticles in images (e–f) confirms that they are spherical and partially elongated. The presence of needle-like elements may be related to the rapid nucleation and subsequent growth stages in the photochemical reduction process.

Conclusion:

This study investigated the possibility of forming silver nanoparticles in a DCMC/sericin graft copolymer matrix. SEM analysis results revealed that the polymer matrix had an amorphous, lamellar, and micro-porous structure, and significant morphological changes occurred after the formation of silver nanoparticles. Specifically, nanoparticles in the range of 30–90 nm, mainly spherical and partially anisotropic, were observed. Their relatively even distribution within the matrix indicates the high stabilizing ability of the DCMC/sericin system. The physical-chemical analysis (SEM, XRD, UV-Vis) confirmed the crystalline nature and size of the nanoparticles. Furthermore, the presence of anisotropic morphology elements was linked to competitive kinetic mechanisms between nucleation and growth stages in the photochemical reduction process. Based on the conducted research, a stable silver nanoparticle-loaded DCMC/sericin copolymer was synthesized.

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