OBTAINING AND PROPERTIES GRAFT COPOLYMERS OF DIALDEHYDE CARBOXYMETHYLCELLULOSE/SERICINE

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Abstract.
In this article, research work on obtaining graft copolymers based on dialdehyde carboxymethylcellulose (DCMC) with a molecular weight of 141 kDa, oxidation degree of 82% and sericin with a molecular weight of 180 kDa and study their physics-chemical properties. The functional groups in the obtained DCMC/sericin graft copolymers were analyzed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy methods. It was observed that the sorption and physical-mechanical properties of DCMC-sericin graft copolymers increased compared to the initial samples. It was found that DCMC, sericin, DCMC-sericin graft copolymers absorbed water vapor in the amount of 8, 9, 13 mmol/g, respectively. Based on the sorption properties, the value of Gibbs energy was calculated to study the polymer-solvent effect.

Keywords: dialdehyde carboxymethyl cellulose, sericine, imin bond, graft copolymers, infrared and nuclear magnetic resonance spectroscopy, physics-chemical properties.

Introduction

Nowadays world health organization mentioned chronic diabetic disease has been increasing with high level day by day [1]. This is disease high level effect to the tissue condition and it is negative effect of regeneration of tissue engineering [2]. Therefore, studies have been conducted on the use of sericin-based biopolymer materials obtained from natural raw materials to treat diabetes and prevent its negative consequences [3]. Because sericin is highly hydrophilic and has the properties of easy association with other molecules, it is used in the field of biomedicine because it has the properties of cell adhesion and biological activity. In addition, sericin has antioxidant, anticoagulant, and skin cell regeneration properties [4]. Due to the presence of polar functional groups in sericin, it is widely used in the production of hydrogel and 3D composite materials with various polymers [5]. Due to hydroxyl, carboxyl and amino groups in sericin [6], it can be easily modified with various polymers. Today, research is being conducted on a number of medical biological materials based on sericin [7] in the form of sponges, films, and hydrogels [8]. In order to increase the possibilities of using sericin in medicine and other fields, its physicochemical properties were improved by modifying it with polysaccharides [9]. Especially, composites biomaterials are very important based on sodium carboxymethyl cellulose (Na-CMC) [10]. Due to the absence of harmful effects on the body and the high property of hydrogel formation, Na-CMC is used for various purposes in the pharmaceutical and medical fields. [11]. The hydrogel formed by Na-CMC has the properties of absorbing a large amount of water and being absorbed into the wound. [12]. In addition, the composites obtained on the basis of Na-CMC are flexible to skin cells and exhibit high biocompatibility properties [13]. Considering the highly biologically active properties of Na-CMC/sericine, their blood glucose control, skin tissue healing, use as an anti-inflammatory biologically active polymer, as well as fat peroxidation and antioxidant properties have been studied and thier properties confirmed to have highly effective [14]. However, literature indicates that copolymers linked through chemical bonds exhibit more complex interactions compared to composites. [15]. Considering the above, we aimed to graft copolymers based on oxidized carboxymethyl cellulose and sericine then study their physics-chemical properties.

Computational methods

Obtaining graft copolymers based on dialdehyde carboxymethyl cellulose/sericin

Firstly, DCMC solution preparated of 2%. Next, sericin solution (3.33%) was blended with each DCMC solution at 60 °C under stirring for 1 h. Finally, DCMC/sericine obtained look like films, sponge like, powder and gels.

IR-spectroscopy

IR spectroscopy was performed using an Inventio-S IR Fourier spectrometer (Bruker, Germany). The spectra were analyzed, specifically focusing on changes in the 0.085 cm^{-1} and 500-4000 cm^{-1} regions.

Nuclear Magnetic Resonance (NMR) spectroscopy

NMR spectra were recorded in NaOH, D_2O, on Unity 400 plus (Varian, USA) and JNM-ECZ400R spectrometers (JEOL, Japan) at operating frequency 400 MHz. TMS (0 ppm) was used as an internal standard in ^1H NMR spectra; solvent chemical shifts (NaOH, D_2O 10.00 ppm.), in ^{13}C NMR spectra.

Sorption properties

Sorption properties studied of DCMC, sericine, DCMC/sericine graft copolymers analyzed by Mac-Ben at high pressure. Amount of water vapor absorbed by polymer samples was calculated follow equation:

$$g_2=g_1-\frac{r_{\Delta h_0}}{1000} \quad (1),$$

Where g_2 is the polymer mass after sorption (g), g_1 is the polymer mass before sorption (g), r is the sensitivity of the spring (mm/ mg) and Δh_0 is the difference between catheter index before and after sorption.

To measure the vapor pressure of a solvent in a polymer solution, a graph draw based on the following relationship:

$$g_2=g_1-\frac{r_{\Delta h_0}}{1000} \quad (2),$$

Δg^m finds follow equation:

$$\Delta g^m=\Delta\mu_1\omega_1+\Delta\mu_2\omega_2 \quad (3),$$

Then graph draw depend on Δg^m and ω_2 after calculate Gibbs energy for all the samples:

$$\Delta g^m=f(\omega_2) \quad (4)$$

Results and Discussion

We can be obtain films, gels, powder and sponge like materials based on DCMC/sericine graft copolymers (Figure 1).

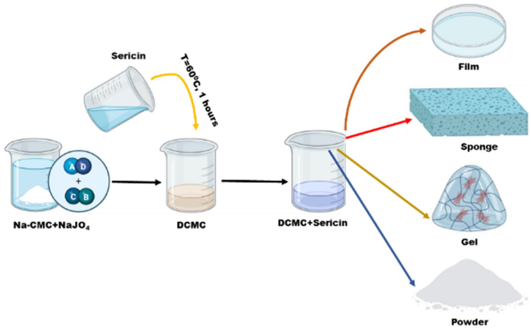

Figure 1. Obtaining scheme different materials based on DCMC and sericine.

We used oxidation degree 82% [16] and molecular weight of 141 kDa of DCMC samples also, molecular weight 180 kDa of sericine for DCMC/sericine graft copolymers. Chemical reaction was happened between aldehyde groups in DCMC and primary amino groups in sericine as a result imin bond was formed then it was determined by IR and NMR spectroscopy methods. Functional groups analyzed by IR-spectroscopy of DCMC/sericine graft copolymers (Figure 2).

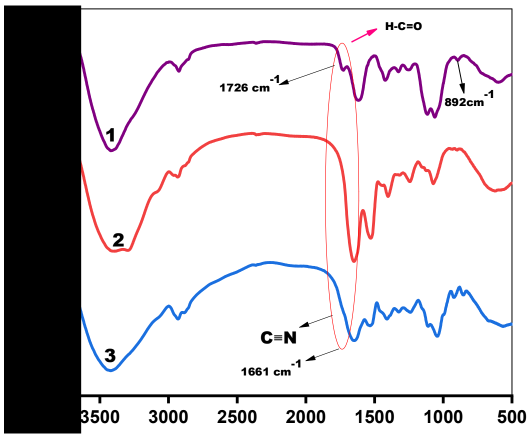

Figure 2. IR-spectroscopy analysis of 1-DCMC, 2-sericine, 3-DCMC/sericine graft copolymers.

The band at 1045 cm^{-1} and 1265 cm^{-1} are ascribed to the symmetrical and asymmetrical C-O-C stretching vibration, respectively. The bands at 1324 cm−1, 1418 cm^{-1} and 1597 cm^{-1} are attributed to -CH2 scissoring, -OH bending vibration and ring stretching of glucose, respectively. The peaks at 3300 cm^{-1} and 2900 cm^{-1} are assigned to -OH and -CH stretching vibrations, respectively.

Five bands at 3278, 3080, 1620, 1516 and 1240 cm^{-1} appeared in all FT-IR spectra, corresponding to the amide A, B, I, II and III of sericin, respectively. The band at 1060 cm^{-1} is as- signed to the C-OH stretching vibration. The amide I, II and III bands are commonly associated with C=O stretching vibration, the combination of C–N stretching and N-H bending vibration and the combination of N-H coupled to C-N stretching vibration. The amide A and B bands are assigned to N-H stretching vibration. The amide A band shifted to lower wavenumber with the increase of DCMC content, which may indicate the hydrogen bond interactions of DCMC and sericine. The band at 1661 cm^{-1} for C≡N (Schiff's base) vibration disappeared, which maybe masked by the amide I of sericine

Besides, functional groups studied NMR spectroscopy of DCMC/sericine graft copolymers (Figure 3).

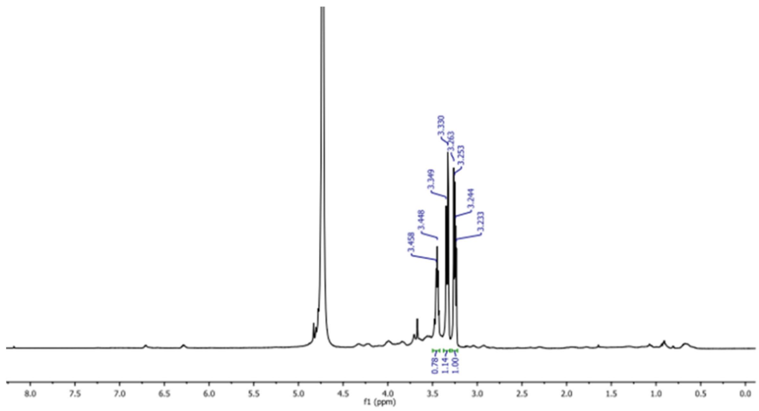

Figure 3. NMR spectroscopy analysis of DCMC/sericine graft copolymers.

It was observed that the intensities in the 9.72 area typical for aldehyde have completely disappeared. These changes in the composition of DKMS/sericine graft copolymers indicate that the aldehyde has completely reacted with the primary amino group in sericine.

The sorption properties of DCMC/sericin graft copolymers were studied (Figure 4).

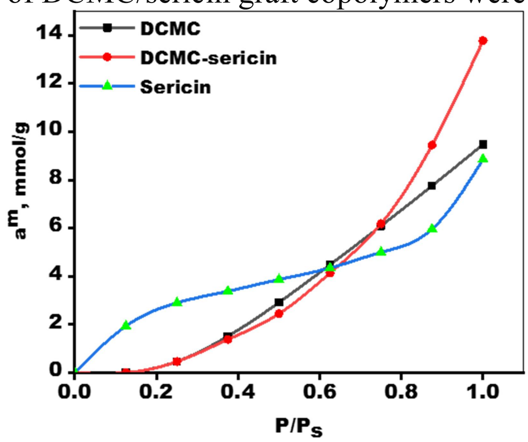

Figure 4. Sorption isotherm of DCMC, sericine and DCMC/sericine graft copolymers.

Sorption properties of DCMC/sericine graft copolymers was higher than initial DCMC and sericine samples. Due to this, the amount of polar functional groups in DCMC/sericine graft copolymers increases, and due to the increase in the size of the micro- and mesopores in the graft copolymers, the resulting graft copolymers absorbed more water vapor than the initial samples. DCMC, sericine and DCMC/sericine graft copolymers were absorbed 8, 9, 13 mmol/g water vapor respectively. Then studied capillary structure based on sorption isotherm of DCMC, sericine, DCMC/sericine graft copolymers (Table 1).

Table 1

Capillary-porous structure of DCMC, sericine and DCMC/sericine graft copolymers

№	Index	DCMC	Sericin	DCMC/Sericin
1	X/m, g/g	0,59	0,585	0,681138
2	S cm^2/g	41,65	65,09	83,65
4	r_k A°	81,9	59,3	113,7
5	W_{meso} cm^3/g	0,08	0,08	0,26
6	$W_{(mic)}$ cm^3/g	0,087	0,117	0,923
7	a^m mmol/g	0,641	0,661	1,00671
8	V_S cm^3/g	0,170	0,193	0,34822

High sorption values in DCMC-sericin copolymers are explained by the large amount of hydrophilic functional groups and the large size of pores of different sizes. Saturation value of DCMC/sericine graft copolymer is higher than initial DCMC and sericine.

Gibbs energy values for DCMC, sericin and DCMC/sericin graft copolymers were calculated (Figure 5).

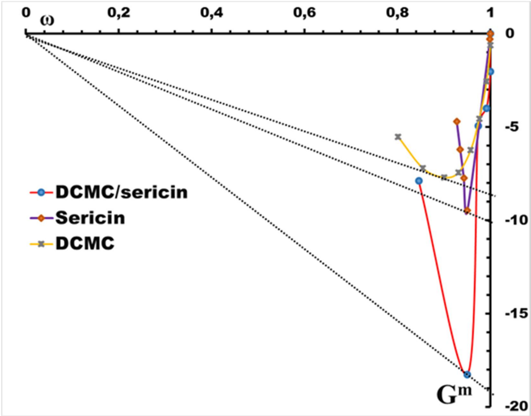

Figure 5. Gibbs energy of DCMC, sericine, DCMC/sericine graft copolymers.

As the value of the Gibbs energy decreases, the property of interaction between the solvent and the polymer increases. Gibbs energy values were found to be -7, -9, -19 for DCMC, sericine and DCMC/sericine graft copolymers, respectively.

Conclusions

Studies were conducted on obtaining graft copolymers based on DKMS and sericin and studying their properties. Functional groups in the composition of obtained graft copolymers were analyzed using IR and NMR spectroscopy methods, and it was confirmed that graft copolymers were obtained. The sorption properties of the obtained graft copolymers were studied, and it was found that DCMC, sericine, and DCMC/sericine graft copolymers absorbed 8, 9, and 13 mmol/g of water vapour, respectively. The high sorption property of graft copolymers is explained by the increased amount of hydrophilic functional groups and the large size of micro and meso pores. Gibbs energy was calculated to study polymer-solvent interaction based on sorption properties. Gibbs energy was found to be -7, -9, and -19 for DCMC, sericine, and DCMC/sericine graft copolymers, respectively.

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