RHEOLOGICAL CHARACTERISTICS OF COMPOSITES BASED ON CARBOXYMETHYL CHITOSAN

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Abstract

Composite formation is a widely used method to modify polymer performance because such systems can combine the advantageous properties of each ingredient. This research evaluates the rheological properties and structure of biopolymer composites based on carboxymethyl chitosan (CMCS), with various additions of an aqueous dispersion of α -chitin (ChA) and glycerin (GLY). Composites containing carboxymethyl chitosan, α-chitin dispersion, and glycerin are designed for potential cosmetic and/or biomedical applications. The rheological properties of carboxymethyl chitosan, *a*-chitin aqueous dispersion, and their mixtures were determined using a ROTAVISC lo-vi Complete rotational viscometer in the temperature range of 25-40°C and under various shear rates (1.3-33 s⁻¹). The activation energy of the viscous flow and the rheological parameters from the power law were calculated and analyzed using Arrhenius plots and flow curves, respectively. As part of this investigation, composite films were prepared and characterized using infrared analysis. The studies conducted classified the prepared systems as non-Newtonian liquids that exhibit a shear-thinning effect (i.e. typical pseudoplastic fluids). The results revealed that the introduction of chitin whiskers as an aqueous dispersion into the CMCS matrix significantly altered the rheological properties of the tested composites. These changes were attributed to the mutual interactions between the polymer components and the low-molecularweight additives.

Keywords: carboxymethyl chitosan, α -chitin, composites, apparent viscosity

Introduction

In recent years, research on new materials has intensified, with a particular focus on polymer composites as a response to the demand for materials with precisely tailored properties [1,2]. The study of composites continues to grow, mainly due to their superior properties compared to polymers alone [3,4]. Natural polymers derived from the environment have gained significant attention for this purpose due to their beneficial properties [5]. They are nontoxic, biodegradable, and readily available, making them environmentally friendly [6].

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Copyright © 2025 by the authors. Some rights reserved. Except otherwise noted, this work is licensed under https://creativecommons.org/licenses/by/4.0 Among these, carboxymethyl chitosan (CMCS), a watersoluble derivative of chitosan, has emerged as a promising candidate due to its inherent biocompatibility, biodegradability, and versatility in applications [7-10].

Rheology, the study of material flow and deformation under external forces, plays a crucial role in understanding and optimizing polymer composites for various conditions. It provides essential insights into the processability, stability, and mechanical properties of composites. Rheological properties, such as apparent shear viscosity, shear stress, and activation energy of viscous flow, are key factors in determining the suitability of a material for specific applications [11,12]. Research on the rheology of polymer composites enables the development of materials with tailored functional and mechanical properties. For biopolymer-based systems, rheological characterization is crucial for predicting their behaviour in various applications, including biomedical engineering, the food industry, and pharmaceuticals.

Chitosan (CS) is a naturally occurring polysaccharide derived from chitin through alkaline deacetylation. It is valued for its biological and physicochemical properties and can be obtained from shells of marine organisms such as crabs, shrimp, and squid [13,14]. CS exhibits bacteriostatic, fungistatic, healing, and antioxidant properties, accelerates tissue regeneration, has hemostatic characteristics, and stimulates the immune system. These qualities make it widely used in biomedicine, biotechnology, and pharmaceuticals [15-19].

CS is biodegradable, biocompatible, and nontoxic to living organisms, while also being sensitive to pH changes [20,21]. However, its crystalline structure limits its solubility in neutral and alkaline solutions, as well as in most organic solvents, restricting its broader application [22,23]. To enhance its practical utility, researchers have modified its molecular structure to improve its properties. Chemical modifications of the amino and hydroxyl groups of chitosan have led to various water-soluble derivatives, the most notable being carboxymethyl chitosan (CMCS) [24]. Due to the presence of carboxymethyl groups, CMCS exhibits improved physicochemical and biophysical properties compared to native chitosan. It is more biodegradable, hydrophilic, and biocompatible with strong antibacterial activity. In addition, its excellent solubility across a wide pH range, which is acidic, alkaline, and neutral, greatly expands its potential applications beyond those of unmodified chitosan.

CMCS is classified into four types based on the attachment site of the carboxymethyl group: O-carboxymethylchitosan, N-carboxymethylchitosan, N,N-carboxymethylchitosan, and N,O-carboxymethylchitosan. The number and location of carboxymethyl groups in the polymer chain significantly influence its properties [25-27]. In a biopolymer composite, the biopolymer matrix primarily determines its structure, resistance to environmental factors, and durability, while the reinforcing fibre contributes to its stiffness and strength [28]. Chitin nanowhiskers, a product of chitin hydrolysis, serve as a reinforcement in many biologically derived polymer matrices [29]. Microfibrillated chitin can form a compact structure through hydrogen bonding, both between and within the fibres. This nanomicrofiber network organization significantly improves the stability of the matrix, reinforcing its structure and increasing its strength and stiffness [30-32]. Chitin, a natural, renewable, and biodegradable polysaccharide, is known for its mechanical stability, nontoxicity, and physiological neutrality [33].

This study aimed to evaluate the rheological properties and structure of biopolymer composites based on carboxymethyl chitosan (CMCS) with varying amounts of aqueous α -chitin dispersion and glycerin. These CMCS-based composites, containing α -chitin dispersion (ChA) and glycerine (GLY), are designed for potential cosmetic and biomedical applications.

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Materials

The CMCS sample was purchased from Chemat (Gdańsk, Poland) and had a viscosity average molecular weight of 250 kg/mol. ChA was obtained from PRIMEX (Siglufjordur, Iceland), while other reagents were sourced from Chempur (Piekary Śląskie, Poland). All chemicals used in this study were of analytical grade and were utilized as received without further treatment.

Preparation of solution and films

To prepare a 2% (w/w) CMCS solution, CMCS was dissolved in distilled water at room temperature using a magnetic stirrer. The solution was stirred continuously for 24 h until CMCS was fully dissolved.

The preparation of an aqueous dispersion of α -chitin (ChA) (chitin whiskers) using the hydrolysis method to remove the amorphous region of chitin was carried out according to previous reports [34,35]. Briefly, 5 g of chitin powder was mixed with 150 ml of 3M HCl solution in a round-bottom flask, fitted with a magnetic stirrer (set to 280 rpm), a hotplate, and a flask under reflux condenser for 3 h at 90°C.

After acid hydrolysis, the suspension was centrifuged at 5000 rpm for 10 min. This process was repeated three times, with the suspension diluted with distilled water (volume of suspension mass and volume of distilled water were taken in a 1:1 ratio) after each run. The chitin whisker slurry was then collected and transferred into a dialysis bag. The dispersion was dialyzed in distilled water for 48 h until a neutral pH was achieved. Finally, ChA was stored in a glass bottle at 8°C with a final concentration of 6.1% of chitin whiskers in the aqueous dispersion (FIG. 1). The concentration was determined using the gravimetric method.

CMCS/G and CMCS/G/ChA mixture solutions were prepared by blending aqueous solutions of CMCS, ChA and GLY in different weight proportions as detailed in TABLE 1. The mixtures were stirred with a magnetic stirrer for 24 h at room temperature. The resulting solutions were subsequently used to investigate their rheological properties.

Films were prepared using the solution casting technique. Specifically, 30 mL of the polymer solution was poured into square plastic Petri dishes (100×100×15 mm, FIG. 2) and left to dry at room temperature for 72 h. Once dried, the films were peeled off and used for further analysis. An example of as prepared CMCS film is shown in FIG. 2.



Steady shear measurements

Steady shear measurements were performed using a ROTAVISC lo-vi Complete rotational viscometer equipped with a concentric cylinder (IKA-Werke GmbH & Co. KG, Strufen, Germany). The shear rate was incrementally increased from 1.3 to 33 s⁻¹ across a temperature range of 25-40°C. The experimental data were analysed and fitted using the Ostwald-de Waele equation (power-law model) [36]:

τ = **k** γ ⁿ

τ – shear stress (Pa)

k – consistency index (Pa*s)ⁿ

n – non-Newtonian index (-)

 γ – shear rate (s⁻¹)

The impact of the temperature on the apparent viscosity (η_a) of the solution was calculated using the Arrhenius equation:

A – the preexponential parameter

 E_{a} – the activation energy of viscous flow (kJ/mol)

R – the gas constant (8.134 J/mol*K)

T – the absolute temperature (K)

TABLE 1. Composition of blended solutions used for rheological properties analysis and film preparation.

sample	CMCS (g)	GLY (g)	ChA (g)
CMCS	30	-	-
CMCS/GLY	30	0.3	-
CMCS/GLY/ChA1	30	0.3	0.5
CMCS/GLY/ChA2	30	0.3	1.0
CMCS/GLY/ChA3	30	0.3	1.5

Infrared spectroscopy

The infrared spectra of CMCS, ChA, CMCS/GLY, and CMCS/GLY/ChA films were recorded using a Nicolet iS10 spectrometer (Thermo Scientific, USA) operating in attenuated total reflectance mode with a diamond crystal. A total of 100 scans were performed at a resolution of 2 cm⁻¹. The measurements were recorded within the spectral range of 4000 cm⁻¹ to 400 cm⁻¹.



FIG. 2. An example of a film prepared from a CMCS solution.

Results and Discussions

In the steady shear studies, the values of apparent shear viscosity (η_a), the rheological parameters (n and k) from the Ostwald-de Waele equation (power-law model), and the activation energy of viscous flow (E_a) for the ChA dispersion and the CMCS solutions, with and without ChA and GLY at 25°C were obtained. The viscosity curves for the solutions of ChA and CMCS with various additions of other components are presented in FIG. 3 and FIG. 4. As observed, all investigated systems exhibited non-Newtonian behaviour with shear-thinning characteristics. Thus, apparent shear viscosity decreased with increasing shear rate, demonstrating a pseudoplastic nature. According to previous reports [36-39], the observed changes in viscosity values are related to the alignment of polymer molecules along the flow streamline.



FIG. 3. Viscosity curves of aqueous ChA dispersions before and after hydrolysis at 25°C.





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TABLE 2. Parameters of the Ostwald-de Waele equation for CMCS mixture solutions at 25°C, and E_a and R² values calculated using the Arrhenius equation from steady shear measurements.

sample	n	k (Pa*s) ⁿ	R ²	E _a (kJ/mol)	R ²
ChA	0.51	0.68	0.999	10	0.999
CMCS	0.86	0.18	0.999	32	0.990
CMCS/GLY	0.62	0.58	0.987	24	0.997
CMCS/GLY/ChA1	0.76	0.33	0.989	24	0.995
CMCS/GLY/ChA2	0.84	0.25	0.999	27	0.994
CMCS/GLY/ChA3	0.80	0.30	1.000	28	0.992

The ChA suspension before hydrolysis was characterized by very low apparent viscosity values, close to those of pure distilled water (FIG. 3). After modification, a considerable increase in viscosity was observed for the ChA dispersion, along with a more regular decrease in viscosity with an increase in shear rate, indicating a strong pseudoplastic effect. The chitin whisker dispersion remained stable without sedimentation. The stability and viscosity of the aqueous ChA dispersion are mainly attributed to its hydrophilicity and the electrostatic repulsion of positively charged acetyl groups [40].

For CMCS solutions (FIG. 4A), the influence of ageing over 28 days showed that storage time had little to no effect on apparent viscosity. It may be assumed that the apparent viscosity of this solution remains stable for at least 28 days. Moreover, the CMCS/G and CMCS/G/ChA solutions exhibited a higher apparent shear viscosity than that of pure CMCS solution (FIGs. 4B and C). This synergy can be attributed to electrostatic interactions and hydrogen bonding between CMCS molecules, ChA, and GLY in the mixture, resulting in increased apparent viscosity.

The dependence of apparent shear viscosity was analyzed using the Ostwald-de Waele equation [36]. The corresponding values of the rheological parameters are listed in TABLE 2. For all the investigated solutions, the power-law model provided a good fit to the experimental data over the applied shear rate range. The n parameter values were found to be less than 1, indicating typical pseudoplastic behaviour. Among the investigated solutions, ChA and CMCS/ GLY exhibited the lowest n values and the highest k values.

For the CMCS/G/ChA mixture solutions, the *n* parameter values were lower than those of the pure CMCS solution. The addition of ChA to the CMCS solution increased the consistency index (k) compared to CMCS solutions. This may be attributed to the formation of a temporary network or an increase in the number of entanglements of unfolded molecules. Hydrogen bonding and electrostatic interactions play key roles in determining the structure and properties of the mixture solutions. TABLE 2 also presents changes in the activation energy of the viscous flow of CMCS mixture solutions with different compositions.

The ChA dispersion is characterized by a lower E_a value than the CMCS solutions, both with and without ChA and GLY. The highest E_a value was observed for the pure CMCS solution. In contrast, the CMCS/GLY and CMCS/GLY/ChA solutions exhibited lower E_a values than the pure CMCS solution, indicating greater ease of molecular movement.

The intermolecular interaction between fillers and the polymer matrix is a critical factor in determining improvements in composite properties. The ATR-FTIR spectra of ChA, CMCS, CMCS/GLY, and CMCS/GLY/ChA are shown in FIG. 5.

For ChA, the region $3600-3000 \text{ cm}^{-1}$ corresponds to the characteristic absorption of O-H and N-H stretching vibrations, with the band at 3433 cm^{-1} attributed to the vibration of the intermolecular hydrogen bond O(3)H•••O(5) from the ring.

The N-H stretching vibrations are identified by bands at 3253 cm⁻¹ (intermolecular hydrogen bonding) and 3101 cm⁻¹ (intramolecularly bonded NH groups) [41-43]. The amide I bands are observed at 1656 cm⁻¹ and 1618 cm⁻¹, corresponding to single H-bonded and doubly H-bonded structures, respectively. The amide II band appears at 1558 cm⁻¹. Additional bands are found at 1308 cm⁻¹ (amide III) and at 1152, 1116, 1071, and 1011 cm⁻¹, which correspond to secondary and primary alcohols, as well as the vibration of the glycoside linkage C–O–C ring [41-44].

The spectrum of the pure CMCS film shows characteristic bands at 3279 cm⁻¹ (O-H and N-H stretching vibrations), 1578 and 1404 cm⁻¹ (COO⁻ stretching vibrations), and 1062 cm⁻¹ (vibrations of C-O, C-O-C glycosidic, and C-OH bands) [36,45,46]. Analysis of the composite film spectra indicates a significant similarity to the spectra of the CMCS film, with the characteristic peaks of ChA rendered invisible due to the strong absorption of the CMCS matrix. However, structural changes in composite films are observed at 3200 cm⁻¹ and 1585 cm⁻¹, as well as in the 1100–900 cm⁻¹ region. As observed, ATR-FTIR spectra exhibit a noticeable change in the shape and intensity of the –OH stretching vibration between 3300 cm⁻¹ and 3200 cm⁻¹, as well as in the amide bands within the 1660–1500 cm⁻¹ region (FIG. 5, marked with an arrow).

Thus, these infrared data suggest an interaction between CMCS and ChA, likely occurring through the formation of hydrogen bonds and electrostatic interactions. Moreover, the infrared results align with the rheological characteristics, which indicate that interactions between the CMCS matrix and the fillers modify its apparent shear viscosity.

Conclusions

This study analyzed the viscosity curves of CMCS solutions with and without ChA and GLY as components of potential materials for cosmetic and biomedical applications. The structure of CMCS film, its composite films with GLY and ChA, and the intermolecular interactions between them were confirmed by infrared spectroscopy.

The ChA dispersion and CMCS solution, as well as their mixture solutions, exhibited non-Newtonian behaviour. The addition of GLY and ChA to CMCS solution increased its apparent shear viscosity. The experimental data were fitted to the Ostwald-de Waele equation, described by the power-law relationship. The n value was found to be less than 1, indicating the pseudoplastic nature of CMCS, ChA solutions, and CMCS/GLY/ChA mixtures.

The observed changes in structure and rheological characteristics are attributed to different types of interactions, including hydrogen bonding and ionic interactions between the polymer matrix, GLY, and whiskers dispersion. The combination of the specific properties of CMCS with GLY and ChA dispersion may be beneficial for the development of materials for biomedical applications, cosmetics, and packaging.





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