INFLUENCE OF NANOCELLULOSE ADDITION INTO A CARBOXYMETHYL CELLULOSE-BASED POLYMERIC MATRIX

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ABSTRACT

Nanocellulose, a remarkable nanomaterial derived from cellulose, has attracted considerable attention in various fields due to its exceptional properties and versatile applications. With its nanoscale dimensions, high surface area, and biocompatibility, nanocellulose has emerged as a promising candidate for numerous technological advancements. The addition of nanocellulose, such as cellulose nanocrystals (CNC), can reinforce the polymer matrix, improving its strength and durability. One area where nanocellulose has shown considerable potential is in the agricultural field of microbial encapsulation. The aim of this study was to evaluate the influence of incorporating cellulose nanocrystals (CNC) into carboxymethyl cellulose (CMC)-based polymeric matrix with potential for microbial encapsulation. The films were prepared by the casting method and characterized by scanning electron microscopy (SEM), thermogravimetry (TGA), swelling degree (SD) and solubility (SS). The results obtained indicate that CMC-based matrices reinforced with CNC showed better results in terms of slower solubility profiles in water, a lower degree of swelling and higher thermal stability. The CMC-based matrices can be considered for future studies with potential applications in different industrial and agricultural sectors.

Keywords: Carboxymethyl cellulose. Polymeric matrix. Nanocellulose

1 INTRODUCTION

The increase in agricultural productivity to meet the growing global demand for food, fiber, and energy is one of the major challenges of today[1]. Thus, the use of chemical fertilizers and agricultural pesticides is essential to increase productivity and controlling pests and pathogens. However, the intensified use of agrochemicals in agriculture results in negative environmental impacts and compromises food quality[2].In order to address this issue, the implementation of alternative methods, especially those based on natural, biodegradable, and sustainable resources, becomes necessary. A promising alternative is the use of bioinputs containing beneficial microorganisms[2]. Through microbial inoculation, it is possible to introduce various types of microorganisms into agriculture with different functions, and this procedure has shown good results compared to conventional agricultural techniques, as it can increase agricultural productivity and reduce environmental impacts caused by the excessive application of herbicides, pesticides, and chemical fertilizers[3].

However, the efficiency of microbial inoculants as biofertilizers and/or biocontrol agents is limited due to the low survival rates of these products[4]. Therefore, the development of new formulations to improve the quality and preservation of strains during production, storage, and field application becomes a crucial step in the development of microbial inoculants. Studies suggest that one way to overcome this problem is through the encapsulation of microorganisms using biodegradable polymeric matrices.

Among the commonly employed polymers for this purpose are polysaccharides due to their biodegradability, non-toxicity, and excellent film-forming properties[5]. Carboxymethyl cellulose (CMC), a derivative of the polysaccharide cellulose, has emerged as a prominent material in the production of biodegradable and edible films, recognized for its non-toxic properties, biocompatibility, water solubility, renewable origin, and low cost[6]. The properties of CMC, including film formation, gels, and hydrogels (through cross-linking with bi- and trivalent cations), confer its relevance in various applications, including controlled release of pesticides and nutrients in agriculture[7]. However, CMC exhibits limited mechanical properties for various applications, prompting research into the incorporation of reinforcing agents to improve these characteristics[8].

In this context, cellulose nanocrystals (CNC) have emerged as a promising alternative to inorganic reinforcing agents, offering the potential for developing polymeric films with enhanced mechanical properties[9].Therefore, the current study aims to develop and characterize microbial encapsulation matrices based on carboxymethylcellulose (CMC) reinforced with CNC.

2 MATERIAL & METHODS

The matrices were formulated based on carboxymethyl cellulose sodium salt (CMC - specific average of 2040 cps, 0.7 degrees of substitution and molecular weight of 265,000 g/mol) (Synth, Brazil), in the absence and presence of cellulose nanocrystals (CNCs) as a reinforcing agent. CNCs were obtained commercially from the company Celluforce (Canada). According to the manufacturer, it has an average nominal diameter of 7.5 nm and a length of 150 nm, with an aspect ratio of 20.

Films were prepared by the casting method. For pure CMC film, a 1.5% (w/v) CMC solution was prepared. This solution was shaken (850 rpm) for 5 hours, then spread in a Petri dish and dried at 30°C for 48 hours. The same procedure was used to prepare CNC reinforced CMC films, where 0.25% (p/v) CNC was added to the 1.5% CMC solution. The surface morphology of the films was evaluated by scanning electron microscopy (SEM) using a microscope (JEOL: JEOL JSM-6510). The equipment used operated with an acceleration voltage of 5 kV and a secondary electron detector.

The thermal behavior of the films was evaluated by thermogravimetric analysis (TGA - TA Instruments, model TGA Q500). A weight of approximately 5 mg of the sample was transferred to a platinum crucible and heated from room temperature to 700 ˚C at a rate of 10 ˚C.min^{-1} under an inert nitrogen atmosphere supplied at a flow rate of 40 mL.min^{-1}.

Swelling and solubility analyzes were carried out in the same experiment[10]. The films were cut (2x2 cm) and dried in an oven at 100°C for 24 hours, and their weight was recorded (m_0). Samples in triplicate were placed in a Falcon tube containing 50 mL of sterile distilled water and placed in an orbital incubator at 25ºC with gentle shaking. Time points of 0.5, 2, 4, and 24 hours were observed for both analyzes to determine the swelling. The films were carefully removed from the water with tweezers, and their surface was lightly dried on absorbent paper to remove excess water and weighed again (m_1). The degree of swelling of the materials could be determined from the relationship between wet and initial weight as a function of immersion time (Equation 1).

$$SD\ (\%) = \frac{m_1 - m_0}{m_0} * 100 \qquad (1)$$

After weighing the wet films, the samples were dried again in an oven at 100°C for 24 hours, and their dry weight (m_2) was recorded. The materials' solubility was calculated from the difference between initial and final weights using Equation (2).

$$SS\ (\%) = \frac{m_0 - m_2}{m_0} * 100 \qquad (2)$$

3 RESULTS & DISCUSSION

The images in Figure 1 illustrate that the pure CMC film has a smooth, compact and regular surface within the detection limits of the instrument. In contrast, the CMC:CNC film shows some agglomerates and irregular points on the surface, which may be attributed to difficulties in homogenizing CMC and CNC during the preparation process.

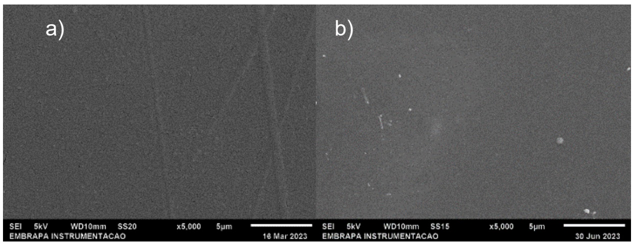

Figure 1 Scanning Electron Microscopy (SEM) micrographs of the surfaces of films a) pure CMC b) CMC:CNC.

Analysis of the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves, as shown in Figure 2 (a and b), it was observed that all the films showed a water evaporation phase between 40°C and 160°C. The loss of mass during this phase is mainly due to the evaporation of free or bound water, which is influenced by the hydrophilic nature of the materials[11]. All materials exhibited a first thermal degradation event above 220°C, with mass losses ranging from ~12 to ~15%. These losses can be attributed to the degradation of the polysaccharide side chains and the release of CO_2[12].In the second thermal degradation event, there was also a weight loss between ~24 and ~26% for all films, these weight losses were due to the degradation of the polymer backbones[13]. At the end of the analysis, it was possible to observe that the addition of CNC to CMC (CMC: CNC) matrices reduced the total weight loss by 10%. This can be attributed to the formation of hydrogen bonds between CMC and CNC[14].

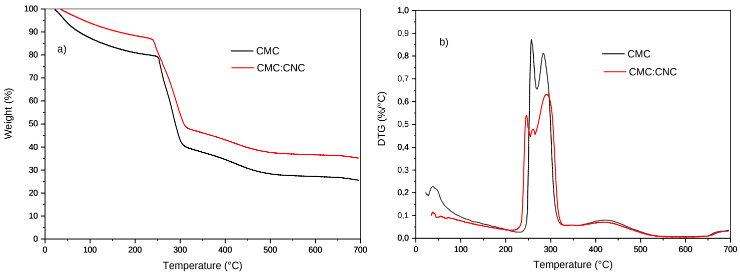

Figure 2 a) TG and b) DTG curves of CMC and CMC:CNC films.

The swelling behavior of CMC, particularly significant within the first 30 minutes of testing, aligns with its known hydrophilicity, a trait exploited in agriculture for water retention in soil as a superabsorbent hydrogel[15]. Analyzing Figure 3a, it is observed that the DS of the pure CMC matrix is higher compared to the nanocomposite (CMC: CNC). This increase can be attributed to the incorporation of CNC, which resulted in a denser polymer network and reduced water absorption capacity[16].

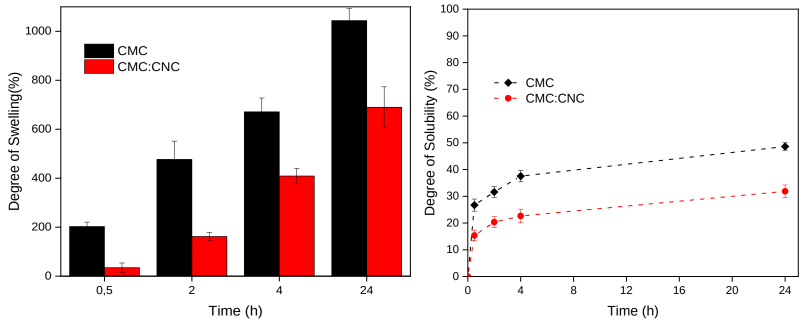

Figure 3 a) Swelling and b) Solubility profiles of the CMC and CMC:CNC films.

Notably, pure CMC films, illustrated in Figure3b exhibited a higher degree of solubility, suggesting a greater propensity for degradation or dissolution of the materials. The solubility of the films is directly related to the opening of polymer chains and/or the breaking of chemical bonds during testing[16]. On the other hand, CMC: CNC films showed the lowest degree of solubility, indicating greater structural stability and less susceptibility to dissolution.

4 CONCLUSION

Based on the results obtained, it can be concluded that the addition of CNC to the CMC-based matrices had a positive effect on the physical, chemical and thermal properties of the films. The matrices reinforced with CNC showed higher thermal stability and a reduction in the degree of swelling compared to matrices without reinforcement, indicating a potential for application in different industrial and agricultural sectors.

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