

Article

Development and characterization of nanocellulose-incorporated Chitosan-starch-based composite films for sustainable packaging for food

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ABSTRACT

A series of edible chitosan-starch (CS-S) biocomposite films were developed by simple integration of monomers and casting process, which was tested for its physicochemical integrity through tensile strength, FTIR analysis, TGA analysis, water vapor permeability, and opacity. Microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) were used to improve the film's properties. The film with the highest tensile strength was 2:3 (CS:S) - CNF, which had a value of 8.99 MPa. According to the FTIR data, all nine types of film samples produced were found to have good integration of the added materials robust structure. Also, the film types 2:1 (CS:S) and 2:1 (CS:S) - MCC exhibited the lowest water vapor transmission rate of 0.01 ml/hr. When the prepared films were tested using a UV spectrophotometer, the film samples that did not contain MCC and CNF had the lowest reported opacity. The 2:3 (CS:S) - CNF film type exhibited the highest tensile strength, an average water vapor transfer rate, and an average opacity for all the film samples developed. The developed film has a high potential to be employed as a biocomposite film in edible coatings for food preservation.

1. Introduction

The food packaging industry raised serious concern due to the environmental effects of petroleum-based polymers, which are non-biodegradable and can cause serious environmental harm if not disposed of correctly. In recent years, researchers have investigated the use of biodegradable polymers as a potential solution to the problem of plastic waste. However, there have been several difficulties in creating biopolymer films with properties that match or exceed those of traditional petroleum-based polymers. The development of viable biodegradable polymer films has been hindered by issues such as durability, strength, temperature resistance, and water permeability. These difficulties have resulted in microbial changes in food, making food quality and safety more difficult to maintain. As a result, scientists have been looking at ways to improve the qualities of biopolymer films, such as using multilayer or blended biopolymers, using cohesive plasticizers based on the biopolymers used, adding cellulose or cellulose nanofibers, and using nanocomposite technology [1, 2]. One study used Chitosan, rosehip seed oil,

and montmorillonite nano clay biopolymer nanocomposite to prepare films with higher mechanical strength, gas and water vapor barrier characteristics, and antioxidant activity. In vitro investigations show that they are effective against bacteria [3]. Pineapple leaf fiber-enhanced chitosan and polyethylene glycol-6000 biopolymer films have superior water vapor permeability, moisture index, and solubility, making them potential polymer film substitutes in vegetable packaging [4]. Adding nano clay fillers to corn starch, biofilms reduced water absorption by 22%, moisture uptake by 40%, oxygen permeability by 30%, and swelling by 31%, according to one research. Depending on the quantity of nanoclay in the coating, biodegradation is delayed. Additional research suggests using additives to improve film handling, and starch amorphous domains can act as organic nanofillers [5]. The combination of chitosan and starch as the foundation constituents for the polymer matrix is a viable technique for developing effective biodegradable polymer films for food packaging. Chitosan is a biodegradable, non-toxic polysaccharide that has been employed in a variety of sectors,

including medicine, agriculture, food preservation, cosmetics, and wastewater treatment. Its positively charged amino group interacts with negatively charged microbial cell membranes, causing proteinaceous and other internal elements of the microbe to leak, making it a suitable material for anti-microbial food packing [6]. Moreover, chitosan has strong barrier properties because of its capacity to form hydrogen bonds, crystalline structure, electrostatic interactions, and thickness [7]. Starch is a carbohydrate and storage polymer found in plants that are made up of amylose and amylopectin. The amylose-to-amylopectin ratio determines the starch granule's crystallinity and size, as well as its physical and functional properties. Any starch consisting of a low amylopectin percentage will show the quickest onset of gelation when compared to starches with a low amylose percentage. Conversely, a starch component with a high amylose percentage is identified as hard and rigid gels compared to high amylopectin percentage starch, which disperses quickly in water, forming soft and weak gels and films [8]. Because of their high amylose content and helical linear polymer structure, high amylose starches such as peas, maize, and lotus are effective in film production [9]. Because of their hydrophilicity, starch films have poor water vapor barrier properties. However, microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) have been researched as additions to improve the characteristics of starch-based films. Cellulose is a common organic polymer found in the primary cell walls of plants, algae, and oomycetes, which is made up of a chain of glucose units. Because of its fluidity and cohesiveness when moist, microcrystalline cellulose is a common cellulose derivative utilized in various sectors, including food, cosmetics, and medications [10].

The polysaccharide comprises a linear chain of hundreds to thousands of (1-4) linked d-glucose units [11]. Because of their strength, large surface area, and diversified surface chemistry, cellulose nanofibrils form a crystalline structure and behave similarly to reinforced steel [12]. Since these nanofibrils are surrounded by hemicellulose and non-crystalline lignin, they can interact with biological nanoparticles [13]. Chitosan, starch, glycerol (plasticizer), and cellulose derivatives were combined after extensive investigation and understanding of composite biopolymers. Therefore, this research aimed to develop and test the mechanical, barrier, and chemical bonding characteristics of chitosan/starch-based composite films with and without the addition of microcrystalline cellulose (MCC) and cellulose nanofiber (CNF).

2. Methodology

2.1 Design of experiment (DOE)

Table 1 indicates the experiment's design to clearly and concisely represent the experimental design and characterize the different types of composite films developed. As shown in Table 1, nine types of film blends were synthesized.

2.1.1 Materials

All the materials used in this research study were of analytical grade. Materials were purchased or collected from the local suppliers. Chitosan (>75% deacetylation) (Sigma Aldrich), Corn-Starch (Pokok Agricore), Lactic acid (Sigma Aldrich), Microcrystalline cellulose (Sigma Aldrich), Cellulose Nano Fiber (locally collected), and Glycerin (Merck).

Table 1. Experiment design

Constituents and Amount variance				
Factors		Amount variance		
Chitosan concentration	%w/v	2		
Starch concentration	%w/v	1	2	3
MCC amount	%w/v	10		
CNF solution	%w/v	10		
Design of Experiment DOE				
Type	A	B	C	
Chitosan %	2	2	2	
Starch %	1	2	3	
Final Blends				
Control	A1	B1	C1	
MCC	A2	B2	C2	
CNF	A3	B3	C3	

2.1.2 Experimental procedure

The experimental procedure can be broken down into 4 sub-parts including, the preparation of Control Chitosan-Starch solution, the preparation of MCC Chitosan-Starch solution, the preparation of CNF Chitosan-Starch solution, and lastly, the casting and conditioning of the film. The testing procedures include FTIR analysis, Spectrophotometric analysis, tensile strength testing, and water vapor transmission analysis. Prior to all experiments in this project, necessary equipment was thoroughly washed and oven-dried before use to remove any unnecessary substances from the equipment's surface.

2.1.3 Preparation of control chitosan-starch solutions

Four grams of chitosan were dissolved in 200 ml of lactic acid solution (1%, v/v) to create chitosan solutions (2%, w/v). Following complete chitosan dissolution, the solution was filtered using a cloth strainer. By mixing corn flour in distilled water and then heating and stirring using a heating/stirrer, the mixture is gelatinized and is then kept cool down to 25 °C. Starch solutions with 1, 2, and 3% concentrations were prepared. To create a series of chitosan/starch composite films, 100 ml of a 2% chitosan solution and 100 ml of a 1, 2, or 3% starch solution were combined. 20% (w/w) of the total solid weight in the solution was added as glycerin.

2.1.4 Preparation of chitosan-starch incorporating MCC solution

The same experimental procedure for control chitosan-starch solution is followed until the solution is prepared. After preparing chitosan-starch solution, 10%(w/w) MCC was added to the solution and stirred using a magnetic stirrer at 300rpm for 1 hour. The above steps are repeated for types A, B, and C.

2.1.5 Preparation of chitosan-starch incorporating CNF solution

The same experimental procedure for control chitosan-starch solution is followed until the solution is prepared. To prepare the obtained CNF for the experiment, 10%(w/w) of the total weight of CNF was soaked in 50ml distilled water for 2 hours. After 2 hours of using the sonicator (FISHER SCIENTIFIC, FB505, 20 kHz), the CNF pulp is prepared. The equipment is set at 30% - 40% amplitude gradually in 15 minutes, pulse set at 5/10, and the total energy spent 10700 joules. Then, the prepared CNF pulp is added to the prepared chitosan-starch solution.

2.1.6 Casting and Conditioning of the film

On glass petri dishes, the mixtures were cast and kept drying in an air-conditioned room (Figure 1). The films were removed from the petri dishes after drying for at least 72 hours. Before testing, dried films were conditioned for 48 hours at 50% RH and 25°C in a desiccator. Table 2 summarizes the compositions of chitosan-starch blends.



Figure 1. Set of casted chitosan-starch films

Table 2. Compositions of chitosan-starch blends

Type A	Type B	Type C
2% Chitosan	2% Chitosan	2% Chitosan
1% Starch	2% Starch	3% Starch

3. Testing procedures of the composite films

3.1 Fourier transform infrared analysis

The chemical alterations and bonding of the different types of composite films were analyzed using FTIR spectra for a spectrum of 400 to 4000 cm^{-1} . The equipment used to conduct the FTIR was a Perkin-Elmer Spectrum 400 FTIR spectrophotometer.

3.2 Tensile strength testing

For the tensile strength testing five samples from each type of film were prepared following the below procedures. The tensile strength testing procedures were adapted from the studies (The ASTM D882 tests tensile properties of thin plastic sheeting 2022). The Testing Machine used was a GoTech Universal tensile strength testing machine. The initial grip separation and crosshead speed were both adjusted to 50 mm and 500 mm/min, respectively. By dividing the greatest load (N) by the specimen's initial cross-sectional area (m^2), the TS was expressed in MPa.

3.3 Water vapor transmission rate

The package approach is a way of figuring out the water vapor permeability (ASTM D895-79). This is accomplished by placing a desiccant or product inside a completely assembled package and sealing it conventionally. When a constant state of moisture gain is established, the packs are next subjected to the normal testing conditions, and the WVTR is calculated from the slope of the straight line.

3.4 UV spectrophotometer analysis

The opacity of the film samples was determined using the UV spectrophotometer analysis. Using a Lambda 35 UV-visible spectrophotometer, the film's opacity and transmittance parameters of 10 mm in width and 30 mm in length were tested at a wavelength of 600 nm (Perkin Elmer, USA). The transmittance spectra of the films were calculated using air as a standard. For each sample, three experimental measurements were made, and the results were averaged.

4. Results and discussion

4.1 FTIR analysis

FTIR spectroscopy was used to analyze the interactions between chitosan-starch with the incorporation of MCC and CNF. Observing, all the figures at around 3250 cm^{-1} the O-H stretching is visible overlapped with the N-H stretching of the same region. The broad observed at around 1550 cm^{-1} is the NH bending (amideII). The small peak at around $1600\text{-}1620 \text{ cm}^{-1}$ can be seen due to the C=O stretching (amideI). Moreover, the peak at 1730 cm^{-1} is due to a carbonyl group in the films. The peak 2950 cm^{-1} is correspondence to the C-H stretching (Figure 2).

4.2 Tensile strength

Tensile strength testing was performed for 9 different types of films. For each type of film, the test was repeated five times to get an average tensile strength. Observing the bar chart above, the tensile strength values for CNF Type A, B and C are greater compared to the Control and MCC based films. This could be due to the formation of hydrogen bonds between OH groups in CNF and OH/NH₂ groups in Chitosan. The tensile strength is highest for Type C CNF having 8.9974Mpa. Following this is Type B CNF having 8.88 Mpa and Type B MCC having 8.295 Mpa. When comparing the ratio type, A, B and C. Type A seems to have the lowest tensile strength spread overall. This is due to the low starch content in Type A and Type B films. However, surprisingly even though the highest recorded tensile strength is for type C (Figure 3).

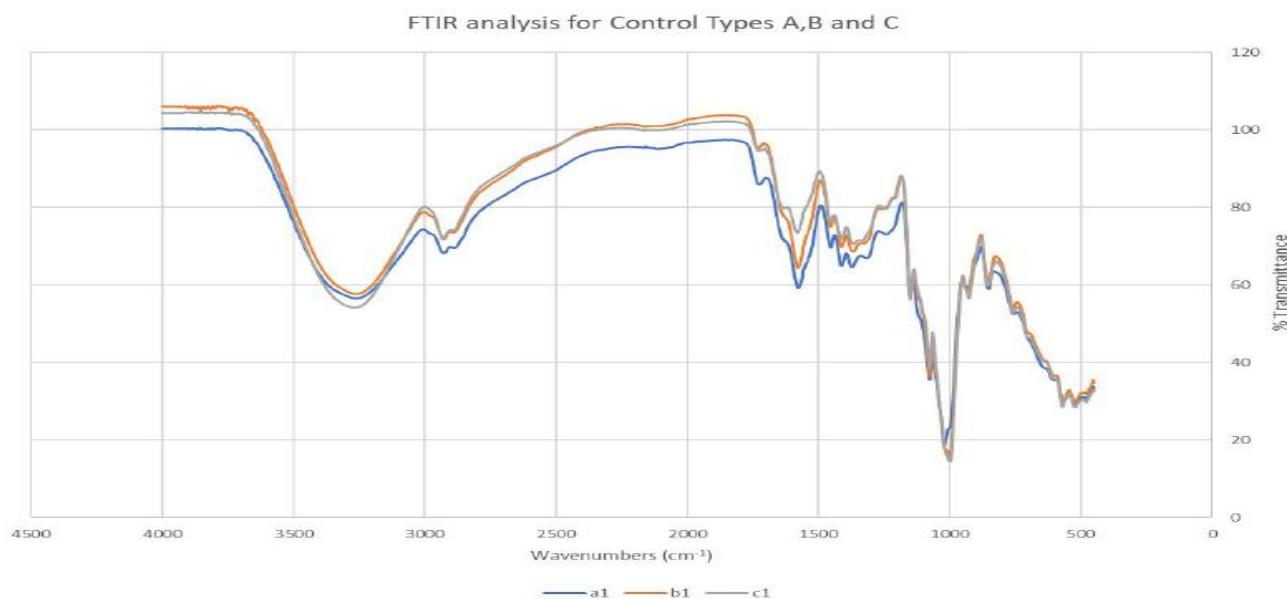


Figure 2. FTIR analysis for control Types A, B and C

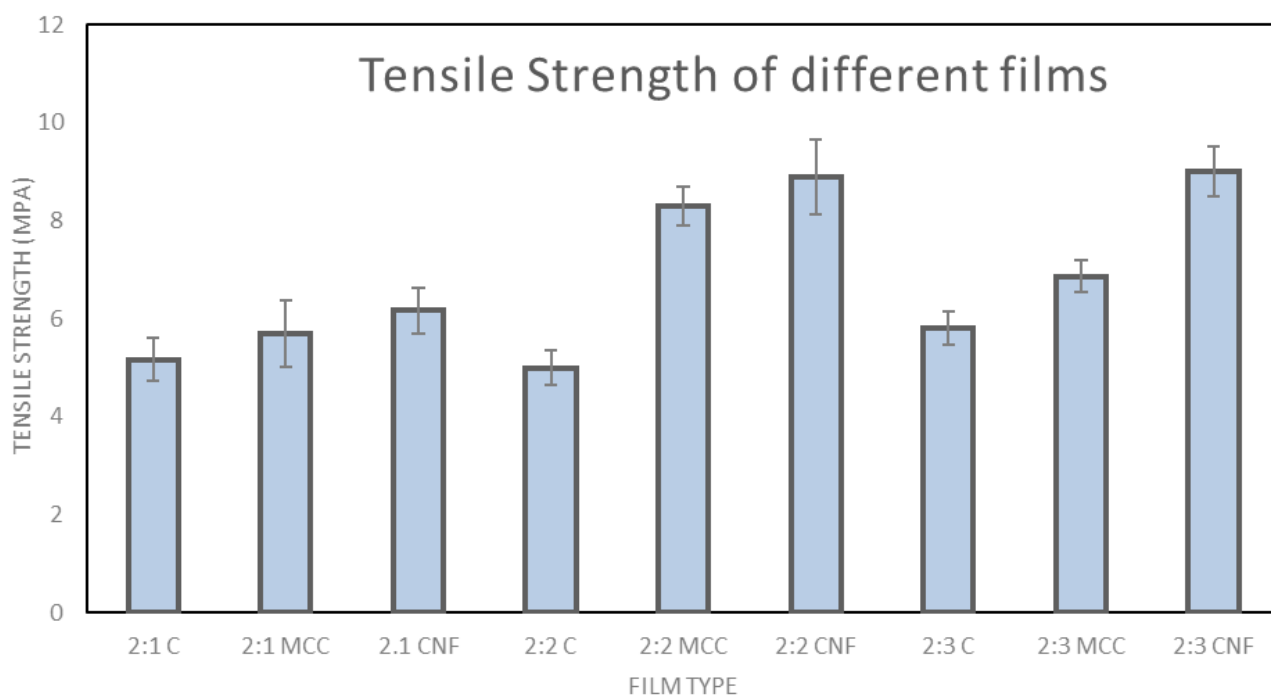


Figure 3. Tensile Strength of Type A, B and C Control, MCC, and CNF

Type B seems to have a better spread over tensile strength due to the high values obtained for MCC and CNF. To summarize, the Tensile strength property CNF shows a very good value, with Type C being the most prominent. Moreover, referring to the tensile strength results some values were obtained by errors during the experimental testing. Therefore, these values were neglected when calculating the average tensile strength of films.

4.3 Water vapor transmission

This testing was carried out to identify the water vapor transmission rate for the nine types of films.

These films showed almost similar numbers for the WVTR. However, the highest recorded WVTR was for Type B CNF and Type C control, having a value of 0.015ml/h. Surprisingly, the lowest values were recorded for the types Type A control and Type A MCC, where the value stood at 0.01ml/h. All the calculations for the WVTR were done by finding the gradient of the slope for the above nine graphs. There could be several different reasons for the fluctuations of WVTR between the blend types A, B, and C. One major reason could be the humidity in which the samples were kept (Figure 4).

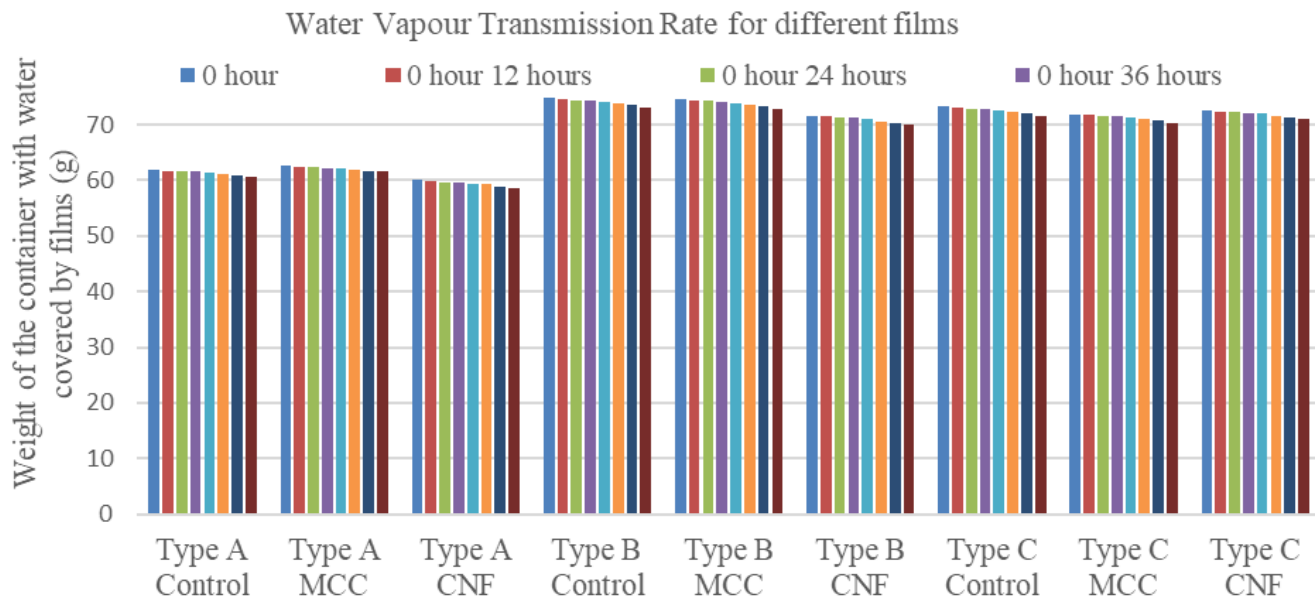


Figure 4. Water vapor transmission rate for different films

The temperature fluctuations in the lab environment could be another reason since the films tend to be quite dry and ductile in air-conditioning, whereas at normal room temperature not so much. Discussing the texture of the films, type B had the best texture at the end of the experimentation, whereas Type A had the poorest, almost fragile-like films. This shows that adding starch helps keep the film's quality texture. UV Spectrophotometer was used to evaluate the film thickness.

Table 4. Calculated opacity results

Film Type	Absorbance	AVG	b	Opacity
Type A Control	0.206	0.194	0.08	2.425
Type A Control	0.159			
Type A Control	0.218			
Type A MCC	0.499	0.536	0.09	5.96
Type A MCC	0.476			
Type A MCC	0.635			
Type A CNF	0.418	0.41	0.09	4.56
Type A CNF	0.410			
Type A CNF	0.402			

The opacity of films (Table 4) was calculated using

$$Opacity = \frac{Abs_{600}}{b} \quad (1)$$

Where, Abs_{600} is the absorbance at 600 and b is the thickness of the film.

Observing the opacities of Type A Control, Type A MCC and Type A CNF, with the addition of MCC and CNF the opacity of the film increases. Where MCC incorporated films have the highest Opacity having 5.96, followed by the CNF film having 4.56. The Opacity for control films is the lowest.

5. Conclusions

In conclusion, this experimental research was successful in the preparation and characterization of chitosan-starch films. According to FTIR readings, the favorable bonding between starch and chitosan is visible. Furthermore, the favorable attachment of MCC and CNF to the Chitosan polymer chain was observed. According to the tensile strength testing, the highest tensile strength was recorded for Type C CNF films, which had 8.99Mpa. According to the water vapor testing, the best results were depicted under the film types A control and MCC with a transmission rate of only 0.01ml/hr. When the films were tested for opacity, the highest opacity was recorded for the MCC-incorporated films. Considering all the results, the B and C films were better than the A films. However, the best film Type from the obtained results was Type C CNF, with an average opacity, an average water vapor transmission rate, and the highest tensile strength.

Ethical issue

The authors are aware of and comply with best practices in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. The authors adhere to publication requirements that the submitted work is original and has not been published elsewhere.

Data availability statement

The manuscript contains all the data. However, more data will be available upon request from the authors.

Conflict of interest

The authors declare no potential conflict of interest.

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