Cellulose Nanoparticles Prepared by Ionic Liquid-Assisted Method Improve the Properties of Bionanocomposite Films

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Research Article

Keywords: Nanoparticles, cellulose, protic ionic liquids, cassava starch, chitosan

Posted Date: December 1st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1093986/v1>

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Version of Record: A version of this preprint was published at Journal of Polymers and the Environment on March 20th, 2022. See the published version at <https://doi.org/10.1007/s10924-022-02420-6>.

Abstract

Bionanocomposites have garnered wide interest from the packaging industry as a biocompatible alternative to non-biodegradable petroleum-based synthetic materials. This study presents a simple and eco-friendly alternative to produce cellulose nanoparticles using a protic ionic liquid, and the effects of their incorporation in cassava starch and chitosan films are evaluated. Bionanocomposite films are prepared using the solvent casting method and are characterized using X-ray diffraction, Fourier transform infrared spectroscopy, zeta potential, thermogravimetry analysis, and transmission electron microscopy. The achieved yield of cellulose nanoparticles is 27.82%, and the crystalline index is 67.66%. The nanoparticles' incorporation (concentration from 0.2 to 0.3%) results in a progressive reduction of water vapor permeability up to 49.50% and 26.97% for starch and chitosan bionanocomposite films, respectively. The starch films with 0.1% cellulose nanoparticles exhibit significantly increased flexibility compared to those without any addition. The nanoparticles' incorporation in chitosan films increases the thermal stability without affecting the mechanical properties. The study demonstrates that the use of cellulose nanoparticles obtained using protic ionic liquid can be a simple, sustainable, and viable method to produce bionanocomposites with tailored properties useful for applications in the packaging industry.

1. Introduction

Synthetic polymers have garnered significant attention from the research community and general society due to their unique properties, such as lightweight, low-cost, high surface area, and excellent mechanical properties [1]. However, despite being very efficient, most petroleum-based polymers for packaging application are non-biodegradable and harmful to the environment [2, 3], which has prompted their replacement with their benign equivalents, particularly in biomaterials derived from renewable sources [2].

Cellulose, starch, chitosan, carrageenan, and agar are good examples of polysaccharides (with thermoplastic properties) obtained from renewable sources with potential application as food packaging materials, including edible coatings [3–5]. Among the various natural polysaccharides, starch is the most abundant and economical reserve polysaccharide derived from plants, whose properties depend directly on the morphology, composition, pH, and other factors from the plant source. Starch granules are mainly composed of two types of glucose polymers: amylose and amylopectin [5, 6].

Chitosan is the second most abundant biopolymer in nature, obtained from the deacetylation of chitin (from the exoskeleton of arthropods, cell walls of yeasts and fungi). Several factors, such as source, temperature, alkali concentration, and incubation time, can affect the properties of chitin [3]. The predominant difference of chitosan from other polysaccharides relies on the antimicrobial properties against bacteria, yeasts, and fungi [3, 7, 8]. Despite their excellent properties, chitosan and starch films exhibit high water vapor permeability, which directly influences the film properties and consequently, limits their applications [9, 10].

Cellulose nanoparticles (CNPs) are promising functional materials with excellent mechanical characteristics that can be used to improve the properties of these materials because of the strong interactions of crystalline cellulose with the polymers, which increases the hydrophobicity of the films, thus improving the barrier properties [9, 10]. However, the conventional methods to obtain CNPs are often accomplished via acid hydrolysis using mineral acids such as hydrochloric and sulfuric acids, which are non-biocompatible, potentially harmful to manipulation, and non-ecofriendly [11]. Therefore, it is crucial to develop more biocompatible and environment-friendly processes using “green” solvents to produce CNPs, which can guarantee the sustainability and the biocompatibility of the nanocomposites [11]. Thus, the search for more biocompatible, low-cost, and environment-friendly solvents, such as ionic liquids (ILs), bio-solvents, and deep eutectic solvents (DES) is important [12]. Among these, the ILs defined as salts that are in liquid state at temperatures below 100°C, have emerged as one of the most fascinating classes of biocompatible solvents for cellulose dissolution and CNPs production [13–15], with several advantages, such as low volatility, high solvation capacity, and excellent thermal and chemical stabilities [16].

Numerous studies [13, 17–19] have been conducted to produce of CNPs using ILs, demonstrating that the obtained nanoparticles did not show structural changes, and ILs can be recycled and reused. Likewise, bionanocomposites incorporated with CNPs have been extensively investigated [2, 3, 10, 20–23]. However, few studies have reported using CNPs produced using IL solvents in chitosan and starch films. Following these promising reports, this study aimed to produce CNPs using a protic IL and evaluate the effect of their incorporation in starch and chitosan films. The morphology, mechanical properties, and thermal properties of the bionanocomposites are also discussed.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) and glycerol (>99.9%), both in analytical grade were purchased from Synth (Taiwan). Chitosan (MW: 50,000–190,000 Da), 3-dimethylamino-1-propylamine (DMAPA) (99%), and hexanoic acid (Hex) (99%) were purchased from Sigma-Aldrich (USA). Cassava starch (17% amylose and 83% amylopectin) was obtained from Yoki Alimentos S. A. (Brazil).

2.2. Synthesis of protic ionic liquid (PIL)

3-dimethylamino-1-propylammonium hexanoate ([DMAPA][Hex]) (pH=5.55) was acquired from Bioproducts Production and Purification Lab (BioPPuL) research group (UNESP, Araraquara, Brazil), synthesized via neutralization reaction of the base with the appropriate acid, according to the previously described procedures.^[12,16] Before use, [DMAPA][Hex]) was purified and vacuum (300 mbar) dried at moderate temperature (≈ 298 K) under constant stirring (≈ 100 rpm) for 48 h. The purity of [DMAPA][Hex]) was assessed using proton nuclear magnetic resonance (^1H NMR) spectroscopy analysis (Avance III HD, 600 MHz, Bruker, USA).

2.3. Preparation of CNP-DM using PIL

CNPs were prepared using PIL following the modified method described by Gonçalves et al [19]. Briefly, MCC was mixed with [DMAPA][Hex] at a solid/liquid ratio of 1:9 (w/w) and then homogenized at 80°C and 2800g rpm for 3 h using a magnetic stirrer hot plate mixer (C-MAG HS7, IKA, Germany). After homogenization, the tubes containing the solution were collected and centrifuged (Eppendorf Centrifuge 5702R, Germany) three times at 2800g and 25°C for 30 min to recover the PIL. The remaining solids in the tubes were washed with deionized water and centrifuged (2800g, 25°C, 30 min) until the pH neutralization. The thoroughly washed solid (CNP-DM) was then recovered and lyophilized (Lyophilizer L101, Liotop, Brazil) for 24 h.

2.4. Characterization of CNP-DM

To evaluate the CNP-DM properties, different characterizations were performed according to the following protocols:

To evaluate the yield [24], CNP-DM was dried in an oven (NI 1510, Nova Instrument, Brazil) at 105°C until constant weight, and the yield (wt.%) was calculated as the ratio between the weight of dried CNP-DM (w_f) and the initial weight of CNP-DM (w_i) in an aliquot of 10 mL of the suspension, as described by Equation 1.

$$\text{Yield (\%)} = \frac{w_i - w_f}{w_i} \times 100$$

1

Zeta potential was measured to evaluate the dispersion of CNP-DM. A cuvette containing 4 mL of CNP-DM suspension (0.3%, w/w) was analyzed at 25°C using a Zetasizer (Nano ZS, Malvern, UK).

The freeze-dried samples were analyzed using an X-ray diffractometer (D8 Advance, Bruker, USA) coupled with a high-speed data detector SSD 160 (EUA) with CuK α_1 radiation ($\lambda = 1.54 \text{ \AA}/8.047 \text{ keV}$ at 40 kV (target voltage) and 25 mA). The scanning range and rate were 5–50° and 1 ° min⁻¹, respectively. The relative crystallinity index (RCI) and average crystal size were calculated according to the previously described procedures [19, 25].

Transmission electron microscopy (TEM) was used to evaluate the morphology of CNP-DM. The images were obtained using Tecnai G2-Spirit (FEI, USA) with a 120 kV acceleration voltage. Diluted suspensions of CNP-DM (0.01% w/v) were deposited on Formvar/Carbon supported copper grids (300-mesh) and the samples were subsequently stained with 2% uranyl acetate solution [4].

The thermogravimetric analysis (TGA) was performed by heating the sample from 25 to 900°C at 30°C min⁻¹ under nitrogen flow (40 mL min⁻¹) using a Pyris 1, Perkin Elmer, USA. The sample weight ranged from 2 to 5 mg.

FTIR spectroscopy (IRPrestige-21, Shimadzu, Japan) analysis was performed in the frequency range of 4000–400 cm⁻¹. The samples were prepared using the KBr disk method [19].

2.5. Preparation of bionanocomposite films

Cassava starch and chitosan bionanocomposite films were cast, as previously described by Souza et al [26] and Kurek et al, [27] respectively. Briefly, the starch bionanocomposite films were prepared using cassava starch (4%, w/v) and glycerol (25% of starch, w/w) in water with CNP-DM addition to obtain different dispersion concentrations (0.1, 0.2, and 0.3% w/v). The film without CNP-DM was termed as sample control (SC). Each mixture batch was heated at 70°C for 1 h of continuous mixing.

Chitosan bionanocomposite films were prepared by dissolving chitosan (2% w/v) in aqueous acetic acid solution (1% v/v) with CNP-DM addition to obtain different dispersion concentrations of (0.1, 0.2, and 0.3% w/v). The film without CNP-DM was denoted as sample control (CC). The solutions were then homogenized at 25°C under magnetic stirring (2800g) for 24 h. After homogenization, a chitosan-glycerol dispersion (30% w/v) was added and mixed for 10 min to form chitosan-plasticizer-CNP-DM. Finally, 167 g of the dispersion (starch or chitosan with CNP-DM and without CNP-DM) were cast into Petri dishes (600 cm²) and dried at 30°C for 24 h. The resulting bionanocomposite films were preserved in a controlled environment to ensure equilibration of the water content. All the bionanocomposite films were prepared in triplicates.

2.6. Characterization of bionanocomposite films

2.6.1. Transmittance and opacity

The transmission spectra of the bionanocomposite films were recorded at 600 nm^[30] using a UV–vis spectrophotometer (UV-M51, Bel Engineering, Italy). The opacity values of the films were calculated using Equation 2 [21]:

$$\text{Opacity (nm/mm)} = \frac{\text{Abs}_{600}}{x}$$

2
,

where Abs₆₀₀ is the absorbance at 600 nm and X is the film thickness (mm). All measurements were taken in triplicates.

2.6.2. Thickness and moisture

The thickness of the bionanocomposite films was determined using a Mitutoyo digital micrometer (Tokyo, Japan) with a resolution of 0.001 mm. For each film, 10 measurements were randomly taken at different positions and the mean value was calculated and used for further analyses. To evaluate the

moisture, film samples (500 mg) were oven-dried at 105°C for 24 h until a constant weight and the weight loss (%) was calculated following the procedure described by Zhang et al [28].

2.6.3. Water vapor permeability (WVP)

The WVP of the bionanocomposite films was determined using the gravimetric method described by ASTM E96/E96M-12 standard [29]. Circular film samples (diameter = 4.3 cm) were covered in plastic capsules containing 10 g of calcium chloride used as a desiccant. The plastic capsules were weighed and placed in a desiccator at 25°C containing sodium chloride as the dissecting substance with a relative humidity (RH) of 75%. Hourly measurements were taken for a total period of 8 h, and the values of water permeability rate (WVP) and permeability (P) were calculated using Equation 3 and Equation 4, respectively:

$$WVP = \frac{m}{t \cdot A}$$

3

$$P = \frac{WVP \cdot e}{P_s(RH_1 - RH_2)}$$

4

where m is the mass gain, A is the permeation area, and t is the time. P_s is the steam saturation pressure at 25°C, and RH_1 and RH_2 are the relative humidity (%) within the desiccator and capsule, respectively. All tests were performed in triplicates.

2.6.4. Mechanical analysis

The mechanical characterization of the films was performed using the universal testing machine (DL-2000, EMIC, USA) according to the ASTM D882-10 standard [30]. The extension velocity was 5 mm/min and a 100 N load cell was used. Preconditioned (50% RH at 23°C) films with dimensions of 10 cm · 2.5 cm were adjusted on the grips at a distance of 50 mm for 48 h. The average thickness was calculated using a digital micrometer at 10 random points for each sample. The various mechanical parameters evaluated were tensile strength (MPa), Young's modulus (MPa), and elongation at break (%).

2.7 Statistical Analysis

For statistical analysis, the data were analyzed by ANOVA using the statistical program StatSoft version 8 (StatSoft, USA). Dunnett's and Tukey's tests were used to evaluate the average differences (95% confidence interval).

3. Results And Discussion

3.1. Characterization of CNP-DM

In the current study, [DMAPA][Hex] was directly added to the MCC suspension to prepare the CNPs (CNP-DM). The average yield of CNP-DM was 27.82% (Table 1), which is lower than that reported in the literature [11, 18]. Mao et al [18] achieved yields higher than 48% using 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO₄]) to prepare cellulose nanowhiskers at 120°C for 24 h. Abushammala et al [11] recovered cellulose nanocrystals using 1-ethyl-3-methylimidazolium acetate ([C₂mim][Ac]) at 60°C for 2 h, achieving a yield of 44%.

Table 1

CNP-DM yield (%), zeta potential (mV), crystallinity index (%), crystallite size (nm), length (nm) and diameter (nm).

	Yield (%)	Zeta Potential (mV)	RCI (%)	w (nm)	L (nm)	D (nm)
CNP-DM	27.82	-9.9 ± 1.68	67.66	5.01	320 ± 24	35 ± 15
RCI: crystallinity index (%); w: crystallite size (nm); L: length; D: diameter.						

Factors such as the strong hydrophobic character of the IL, reaction time, or temperature affect the cellulose dissolution, viscosity, and miscibility in water, thereby influencing the CNPs’ yield [31]. Interestingly, CNPs’ yields are generally affected by the anionic part of the IL, i.e., an increase in the length of the anionic alkyl chain promotes lower CNPs’ yields [32]. The results obtained in this work are in agreement with those previously reported by Arvela et al [32], highlighting that small anions are the best choice for cellulose dissolution compared to larger ones. Another factor that may have contributed to low CNP-DM yield is the dissolution temperature (60°C), which affects the viscosity and conductivity of the IL [31]. The conductivity of an IL increases with increasing temperature and more cellulose is dissolved. Therefore, a protic ionic liquid (PIL) such as [DMAPA][Hex], which exhibits relatively high viscosities, hinders cellulose dissolution at lower temperatures, resulting in less cellulose chemical degradation [32].

Table 1 also shows the zeta potential values of the CNP-DM suspensions. The average zeta potential (ζ) -9.9 ± 1.68 mV implies an unstable suspension according to the previous literature [24] reports because suspensions with ζ values greater than +30.0 mV and less than -30.0 mV are considered electrically stable because the repulsion forces exceed those of attraction values. ζ value less than ± 30 mV indicates the start of flocculation. This ζ obtained in the present study was mainly attributed to the short reaction time and low reaction temperature. Mao et al [18] and Gonçalves et al [19] achieved ζ of -30 mV and -19.1 mV using [Bmim][HSO₄] and [2-HEA][HSO₄], respectively. The effect of temperature on the production of CNPs using IL ([Bmim][OAc]) was investigated by Samsudin et al [13], observing that the hydrodynamic and polydispersity index of all CNPs increased with the synthesis temperature ($\zeta = -19.7$ mV at 70°C/1.5 h and $\zeta = -25.2$ mV at 110°C/1.5 h). This means that uniformity in size distribution is achieved when the synthesis temperature is increased due to weakened interaction between the cation and anion of the PIL.

The X-ray diffraction pattern of CNP-DM is shown in Figure 1a, exhibiting the characteristic peaks of cellulose I at 14.84°, 16.09°, 22.60°, and 34.11° and indicating that the integrity of cellulose crystals was preserved [33] and the amorphous regions were more susceptible to dissolution than the crystalline ones

[34]. The diffraction patterns are in agreement with those previously reported by Mao et al [18] (14.1°, 16.4°, 22.5°, and 34.5°), Tan et al [34] (14.9°, 16.4°, and 22.6°), and Low et al [35] (14.7°, 16.5°, 22.5°, and 34.5°).

The relative crystallinity index (RCI) of the CNP-DM increased up to 67.66%, which was higher than those obtained by Gonçalves et al [19] (58%, cellulose nanowhiskers + [2-HEA][HSO₄]) and almost similar to those achieved by Samsudin et al [13] (78.8%, CNPs + [Bmim][OAc]). The high RCI in CNP-DM results from efficient dissolution of amorphous regions (constituted by hemicellulose) by the [DMAPA][Hex], revealing a good selectivity of the PIL to this region [36].

The CNP-DM also exhibited a higher average crystal size (5.01 nm) than those obtained by Samsudin et al [13] (2.7 nm) and Tan et al [34] (4.6 nm), and lower than those reported by Gonçalves et al [19] (17.2 nm) and Man et al [17] (19.9 nm). The difference in these values is because of different cellulose sources and the synthesis conditions such as solvent concentration, time, and temperature, which strongly affect the crystal characteristics [37].

Figure 1b shows the transmission electron microscopy (TEM) images of CNP-DM, revealing the size and state of agglomerates. As expected, the CNP-DM consisted of aggregates and needle-shaped structures due to the strong surface particles' interactions by hydrogen bonds [38], supporting the result of zeta potential analyses ($\zeta = -9.9$ mV). The CNP-DM had an L of 320 ± 24 nm and a D of 35 ± 15 nm. The L/D ratio yielded a mean value of 9.14, which is consistent with the standard cellulose nanoparticle morphology. The mean L/D value confirmed the potential of CNP-DM as a reinforcing agent in composites, as demonstrated in other studies [17, 19]. Man et al [17] obtained cellulose nanocrystals with L ranging from 300 to 500 nm and D ranging from 14 to 22 nm to give a mean L/D value of 7.5–17. Gonçalves et al [19] obtained cellulose nanowhiskers with a mean L of 156.89 nm and D 4.59 nm, yielding a mean L/D of 50.23 nm. Therefore, considering that the L/D value is mainly influenced by the reaction conditions, cellulose source, and crystal size [19], the low mean L/D value (9.14) achieved in this study is a result of the larger diameter [39].

The thermogravimetric analysis (TGA) measures the samples' mass change due to chemical reactions (dehydration, oxidation, and degradation) and physical sorption as a function of temperature or time [33]. Inflections due to mass loss of CNP-DM were observed in the TG/dTG curves, as depicted in Figure 2.

Figure 2 shows the TG/dTG profile of CNP-DM in the range 25–900°C, comprising three events: the first event in the range of 31–137°C involving a mass loss of 6.72% occurred due to loss of moisture [33], the second event at 376°C (mass loss of 66.87%) was attributed to the cellulose degradation (depolymerization, degradation, and decomposition of glycosidic units) [35], and the third one in the range of 468–627°C (mass loss of 22.54%) was attributed to the oxidation and decomposition of carbonized residues (3.87% of residues) [40–42].

Similar behavior was reported by Gonçalves et al [19], who evaluated the thermal stability of cellulose nanowhiskers. In this case, three thermal events were observed at 88°C, 234°C, and 323°C without the

formation of carbonized residues, and the authors attributed these events to the presence of hydrogen sulfate and amine groups of the IL, which decreased the thermal stability of the nanowhiskers. Mao et al [18] also evaluated the thermal behavior of cellulose nanowhiskers, observing two principal events at 285°C and 346°C, and achieved more thermally stable nanowhiskers than those extracted with concentrated sulfuric acid, suggesting that the PIL allows efficient catalytic reactions and better accessibility to the cellulose amorphous regions, thus preserving the crystalline counterpart and creating smaller and homogeneous nanowhiskers.

The chemical structures of MCC, PIL ([DMAPA][Hex]), and CNP-DM were characterized using FTIR spectroscopy. Figure 3 shows the FTIR spectra of the three samples.

In the spectrum of CNP-DM, the characteristic bands at 3513 cm^{-1} and 3243 cm^{-1} were assigned to the stretching vibrations of the –OH groups [36, 43, 44]. The small band at 2901 cm^{-1} was associated with the stretching vibration of C–H in CH_2 and CH_3 groups [21, 35, 44, 45]. The band at 1643 cm^{-1} was associated with the adsorbed water on the polymer [17, 35], whereas those at 1424 cm^{-1} and 1368 cm^{-1} were attributed to the angular and symmetrical deformations of cellulose methylene groups and the C–H bond, respectively. The band at 1121 cm^{-1} emanated from the stretching vibration of C–OH, whereas those at 1056 cm^{-1} and 891 cm^{-1} were assigned to the ring skeletal vibration of cellulose. Lastly, the band at 613 cm^{-1} was assigned to the linkage between the glucose units of cellulose.

The results from the FTIR spectra also confirmed that the PIL ([DMAPA][Hex]) is an efficient solvent for cellulose dissolution, and its removal from the nanoparticles was complete as no residual PIL was detected. These results are consistent with those reported in the literature regarding cellulose dissolution using PILs [13, 17, 19].

3.2. Characterization of bionanocomposite films

3.2.1. Optical properties

Light absorption in films is one of the most important features that affect the applicability of bionanocomposites in food packaging. Therefore, it is imperative to protect the films from lipid oxidation caused by UV light, a common oxidation initiator in food systems [46]. Table 2 lists the transmittance values and opacities of starch and chitosan bionanocomposite films incorporated with CNP-DM.

Table 2

Optical properties, moisture, thickness, water vapor permeability (WVP) of bionanocomposite films.

Matrix	CNP-DM (%)	Transmittance (%)	Opacity (Abs ₆₀₀ /mm)	Moisture (%)	e (mm)	WVP (g Pa ⁻¹ . s ⁻¹ .m ⁻¹) x 10 ⁻¹⁰
Starch						
	SC	74.80 ± 0.26	1.12 ± 0.01	11.53 ± 0.34	0.09 ± 0.01	2.02 ± 0.03
	0.1	80.60 ± 0.30 *a	0.93 ± 0.13 ^b	11.3 ± 1.05 ^a	0.10 ± 0.01 ^a	2.02 ± 0.02 ^a
	0.2	77.05 ± 0.75 *b	1.09 ± 0.13 ^{a b}	10.52 ± 0.37 ^a	0.09 ± 0.01 ^a	1.03 ± 0.02* ^b
	0.3	69.60 ± 1.40 *c	1.41 ± 0.14 ^a	10.57 ± 0.38 ^a	0.10 ± 0.01 ^a	1.02 ± 0.02* ^b
Chitosan						
	CC	88.50 ± 0.1	0.68 ± 0.04	20.99 ± 0.41	0.09 ± 0.02	1.52 ± 0.01
	0.1	88.26 ± 0.77 ^a	0.61 ± 0.01 ^b	26.30 ± 1.12 ^{*a}	0.10 ± 0.02 ^a	1.63 ± 0.07 ^a
	0.2	87.46 ± 0.21* ^a	0.75 ± 0.01 ^a	26.02 ± 0.96 ^{*a}	0.09 ± 0.01 ^a	1.13 ± 0.01* ^b
	0.3	88.66 ± 0.35 ^a	0.61 ± 0.01 ^b	25.64 ± 0.89 ^{*a}	0.09 ± 0.01 ^a	1.11 ± 0.05* ^b
Means with (*), differ from the control by the Dunnett test. Means with different letters within a column indicate significant differences (p ≤ 0.05).						

The results depicted in Table 2 demonstrate that the light transmittance values of the starch and chitosan films varied from 69.60 to 80.60% and 87.46 to 88.66%, respectively. Increasing the CNP-DM concentration (%) in starch films significantly decreased (p<0.05) the transmittance values and introducing 0.3% of CNP-DM to the starch matrix, a significant reduction (≈5.2%) compared to sample control (SC) was achieved. For the chitosan films, no significant difference (p>0.05) (from 0.1 to 0.3% of CNP-DM) was observed. However, the addition of CNP-DM (0.2%) led to a reduction of ≈1.0% in transmittance as compared to CC (p<0.05). Bagde et al [20] reported a reduction in transmittance from 74 to 64% when 1% nanocellulose was incorporated into starch films. Salari et al [21] observed significant reductions in the transmittance of chitosan films at CNC concentrations above 1%. Presently, the transmittance differences among the chitosan films were not significant, probably due to the low concentrations of CNP-DM.

The opacity of starch and chitosan films varied from 0.93 to 1.41 $A_{600} \text{ nm mm}^{-1}$ and 0.61 to 0.75 $A_{600} \text{ nm mm}^{-1}$, respectively, indicating no significant difference ($p > 0.05$) with respect to the control samples. The opacity characteristics of the films obtained in this study are consistent with those obtained by Santana et al [10] for starch films with cellulose nanofibers (0%, 1%, 3%, and 5%), where no significant changes were found when compared to the control sample.

It can be surmised from these results that the addition of CNP-DM resulted in no expressive changes in transmittance and opacity sufficient to compromise the use of bionanocomposite for packaging.

3.2.2. Moisture

The moisture values of starch and chitosan films incorporated with CNP-DM ranged from 10.52 to 11.53% and 25.64 to 26.30%, respectively (Table 2). There were no statistically significant differences ($p > 0.05$) between the values of CNP-DM/starch films and the SC. In the case of CNP-DM/ chitosan films, no significant differences were observed among the formulations. However, compared to the CC, a significant increase ($\approx 6\%$) in moisture was detected. It is noteworthy that incorporating CNP-DM into chitosan led to agglomerates by hydrogen bond formation between hydroxyl groups, and the polymer chains were free to interact with water, resulting in weak dispersion that promoted water absorption [2, 6], and is desirable in food packaging materials [47].

3.2.3. Thickness and water vapor permeability (WVP) rate of bionanocomposite films

Thickness is an important parameter that must be monitored in films for maintaining uniformity and reproducibility [48]. The thickness and *WVP* of starch and chitosan films with CNP-DM (0%, 0.1%, 0.2%, 0.3%) are shown in Table 2. All films were processed under the same conditions. A thickness variation of 0.101 mm for the starch-CNP-DM films and 0.097 mm for the chitosan-CNP-DM films was observed without significant differences ($p > 0.05$). Thus, the addition of CNP-DM to the polymer matrix did not influence the film thickness. Bagde et al [20] and Salari et al [21] reported no significant changes in the thickness either when CNPs were added to starch (0.183–0.199 mm) and chitosan (0.090–0.110 mm) bionanocomposites, respectively.

WVP is one of the most significant parameters of films because of its impact on the prevention or reduction of the humidity transfer from the environment to the packaged product [24]. In this study, the *WVP* values (Table 2) were in the range of $1.02\text{--}2.02 \cdot 10^{-10} \text{ (g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1})$ and $1.11\text{--}1.63 \cdot 10^{-10} \text{ (g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1})$ for the starch and chitosan films, respectively. In both types, the high concentration of CNP-DM led to significant reductions ($p < 0.05$) compared to the control films. The highest *WVP* reductions of 49.50% (starch) and 26.97% (chitosan) were achieved using 0.2% and 0.3% CNP-DM, respectively.

Bagde et al [20] also obtained *WVP* reductions from 1.9 to $1.78 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ KPa}^{-1}$ using 1% CNPs in starch bionanocomposites. Similarly, Salari et al [21] related the *WVP* reductions ($3.65, 2.93, 2.68$, and $2.56 \cdot 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) in chitosan films when incorporated with bacterial CNPs.

Thus, it can be observed that the addition of CNP-DM to the polymeric matrices reduced the WVP due to the high crystallinity of CNP-DM. Some researchers [10, 49, 50] have suggested that the reduction in the WVP of starch mixed with CNPs can be associated with the fact that CNPs hinder the permeation of water molecules by forming crystalline domains, leading to a more compact material. Hence, it was observed in this study that the addition of CNP-DM to starch and chitosan films was sufficient to provide a physical barrier through the interaction of the CNPs with the polymer matrix, thereby reducing the permeation of water and allowing good applicability.

3.2.4. Mechanical analysis

Mechanical parameters such as tensile strength (Mpa), Young's modulus (Mpa), and elongation at break (%) were evaluated to explore the effect of CNP-DM incorporation in starch and chitosan films, and the results are listed in Table 3.

Table 3
Mechanical properties of bionanocomposite films.

Matrix	CNP-DM (%)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Starch	SC	5.6 ± 1.21	164.5 ± 31.67	91.0 ± 19.69
	0.1	2.0 ± 0 ^{*b}	16.6 ± 3.01 ^{*b}	180.6 ± 8.16 ^{*a}
	0.2	3.5 ± 0.54 ^{*a}	88.3 ± 4.88 ^{*a}	142.0 ± 21.16 ^{*b}
	0.3	3.5 ± 0.83 ^{*a}	91.6 ± 12.05 ^{*a}	128.0 ± 26.13 ^{*b}
Chitosan	CC	23.6 ± 2.94	279.1 ± 20.15	42.0 ± 5.79
	0.1	23.2 ± 2.13 ^a	212.3 ± 36.96 ^{*a}	43.0 ± 10.86 ^a
	0.2	21.6 ± 3.5 ^a	51.0 ± 4.33 ^{*b}	52.6 ± 12.75 ^a
	0.3	19.0 ± 1.89 ^{*a}	43.1 ± 8.84 ^{*b}	61.1 ± 18.44 ^{*a}
Means with (*), differ from the control by the Dunnett test. Means with different letters within a column indicate significant differences (p ≤ 0.05).				

For starch films, the tensile strength of 2–3.5 Mpa, elongation break of 128–180%), and Young's modulus of 16–91 Mpa were achieved. The incorporation of CNP-DM afforded a more flexible material (less stiff), i.e., the addition of CNP-DM (0.1%) decreased the tensile strength by 64.28% compared to the SC. However, increasing the concentration of CNP-DM noticeably increased (p<0.05) the tensile strength of the bionanocomposites. A significant increase (98.4%) in elongation at break with the incorporation of 0.1% (CNP-DM) was observed compared to the SC, indicating the film's excellent mechanical flexibility.

For chitosan films, no significant changes were observed in the tensile strength and elongation at break with the addition of CNP-DM (0.1, 0.2, 0.3%). However, the addition of 0.3% CNP-DM reduced the tensile

strength by 19.49% and increased the elongation break by 45.47% compared to the CC. All films exhibited significant reductions in Young's modulus compared to the control samples.

Taheri et al [44] reported no significant differences in tensile strength (99.61 MPa) and Young's modulus (31.20 MPa) for chitosan films with 3% nanocellulose. In another study, Silva et al [4] prepared starch films reinforced with CNPs (0–5%) and found an increase of 90% and 92% in tensile strength with the addition of 0.1% and 0.2% CNPs, respectively, in addition to 400% increase in Young's modulus. However, in the present study, this behavior was not observed, and the incorporation of CNP-DM lowered the tensile strength of the films, suggesting that the low concentrations of CNP-DM were not sufficient to improve the mechanical properties of both bionanocomposites. Silva et al [4] reported a mean L/D value of 24 for cellulose nanocrystals, which is superior to that achieved in this study (9.14). The L/D value is an important parameter for mechanical reinforcement, i.e., the higher the L/D value, the higher is the reinforcement capacity [51, 52].

Another factor that affected the mechanical parameters is the instability of the CNP-DM suspensions ($\zeta = -9.9$ mV), which hindered their effective dispersion in both matrices and thus reduced the capacity of mechanical reinforcement [53].

3.2.5. Thermogravimetry

The TG/dTG curves for the different films are shown in Figure 4. For starch films (Figure 4a), two main events were observed. The first event involved moisture loss in the range of 27.9–192.5°C, and the second involved a mass loss of 76.95% in the range of 221.8–504.9°C, corresponding to the degradation of starch and glycerol [6]. For the chitosan films (Figure 4b), the first event was observed in the range of 28.6–153.7°C, attributed to the loss of acetic acid and moisture [22, 45]. The second mass loss of 15.11% in the range of 147.5–278.5°C represents glycerol degradation [54], whereas the third mass loss of 37.99% in the range of 282.4–492.4°C was attributed to the degradation of chitosan.

Interestingly, glycerol thermal degradation (147.5–278.5°C) was only observed in chitosan films, probably due to its low interaction with the polysaccharides [54].

Incorporating 0.1% and 0.3% of the CNP-DM suspension into starch films promoted a reduction of approximately 7°C in the T_{onset} of the second thermic event. Santana et al [10] evaluated the thermal stability of starch films incorporated with CNPs (1–5%) and observed that the main degradation event occurred between 257.4°C and 352.8°C with 80% of mass loss. The authors suggested that the decrease in thermal stability is due to the reduced flexibility of amylopectin chains. For chitosan films reinforced with CNPs (5% and 10%), Khan et al [50] reported the major mass loss in the range of 280–460°C and found no changes in thermal behavior with the addition of CNPs.

In summary, the CNP-DM's incorporation into starch and chitosan polymeric matrices affected thermal stability in different ways. The presence of 0.1% CNP-DM reduced the thermal stability of starch films by 9°C in contrast to chitosan films, where stability increased by 13°C with the incorporation of 0.2% CNP-DM.

4. Conclusions

Cellulose nanoparticles (CNP-DM) were successfully prepared using a protic IL ([DMPA][Hex]) while maintaining crystal integrity. The IL exhibited high selectivity to the amorphous region during the dissolution process. Incorporating CNP-DM improved the thermal stability, flexibility, and WVP of the starch and chitosan bionanocomposite films. For both polymeric matrices, the incorporation of 0.2% CNP-DM was sufficient to significantly reduce the WVP, allowing the application of these bionanocomposites in food packaging.

The results obtained in this study are associated with low-cost production, biocompatibility, low toxicity, and recyclability, making [DMPA][Hex] a simple, efficient, and sustainable solvent to produce cellulose nanoparticles.

Further research will be conducted to improve the bionanocomposites' mechanical properties, which are essential for food packaging.

Declarations

Author Contributions

The material preparation, data collection, and analysis were performed by Suellen Rocha Vieira, Jania Betânia Alves da Silva, and Denílson de Jesus Assis. The first draft of the manuscript was written by Suellen Rocha Vieira and Jania Betânia Alves da Silva. Janice Izabel Druzian, Cassamo Ussemane Mussagy, Jorge Fernando Brandão Pereira, Ederlan de Souza Ferreira, Paulo Vitor França Lemos, Paulo Romano Correia, and Carolina Oliveira de Souza contributed on the funding management, conceptualization, and revision of the whole manuscript. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Acknowledgments

This research was supported by the Bahia State Research Support Foundation (FAPESB; APP0091/2016 and BOL0684/2019) and the National Council for Scientific and Technological Development-CNPq (313641/2019-6 and 311392/2016-4). The authors also thank the Ministry of Science and Technology, High Education and Technical Vocational Training of Mozambique (MCTESTP, Maputo, Mozambique) and FAPESP (São Paulo Research Foundation Brazil) for their projects (2015/50058-0 and 2017/50303-0).

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Figures

Figure 1

X-ray diffraction (XRD) (A) and Transmission Electron Microscopy (TEM) (B) of CNP-DM.

Figure 2

Thermal behavior of CNP-DM obtained using ionic liquid ([DMAPA][HEX]).

Figure 3

FTIR spectrum of cellulose nanoparticles (CNP-DM), microcrystalline cellulose (MCC) and ionic liquid ([DMAPA][Hex]).

Figure 4

Thermogravimetric (TGA and dTG) vs temperature curves of (a) starch matrix; (b) chitosan matrix for the different biopolymer and bionanocomposite films.

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