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Cellulose nanocrystals from rice and oat husks and their application in aerogels for food packaging

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ABSTRACT

This study describes the valorization of rice and oat husks by obtaining cellulose nanocrystals for the production of aerogels for food packaging applications. Commercial cellulose was used as a control sample. Nanocrystals from cellulose were obtained by enzymatic hydrolysis and mechanical treatment at high pressure. The morphology, particle size, functional groups, crystallinity, and thermal properties of the cellulose nanocrystals were analyzed. The morphology, functional groups, crystallinity, water absorption capability, and zeta potential of aerogels were also analyzed. Cellulose nanocrystals show different structural properties and crystallinity depending on the source of the cellulose. The average diameter of the nanocrystals varied from 16.0 to 28.8 nm. The aerogels prepared with cellulose nanocrystals showed a porous and uniform structure with a water absorption capacity between 264.2% and 402.8% at 25 °C. The aerogel of oat cellulose nanocrystals showed a larger pore size than that of eucalyptus cellulose nanocrystals, and this may have influenced the lowest water absorption capacity of the aerogels of eucalyptus cellulose nanocrystals. These results show that agroindustrial residues have promising applications in various industrial fields and could be used as aerogel absorbers of water in food packaging.

1. Introduction

Currently, the growing concern about the environment and the partial substitution of synthetic materials with biodegradable materials has called attention to the industrial use of polysaccharides. Cellulose is a polysaccharide that is abundant in plants and can be used in different areas for different applications [1]. One way of using cellulose is in the isolation of nanocrystals for use as reinforcement in polymer matrices. Nanocrystals of cellulose have several important characteristics such as a specific surface, high aspect ratio (length/width), high crystallinity, and excellent mechanical properties, and can be obtained by chemical or enzymatic hydrolysis, with or without mechanical treatment [2]. Enzymes, such as cellulases that degrade cellulose, are utilized under moderate temperature conditions and without the use of chemical reagents, making their use advantageous compared to other methodologies because they do not attack the environment [3]. In addition, enzymatic hydrolysis, when coupled with a mechanical treatment in a high pressure homogenizer, promotes the disintegration of the amorphous remaining regions of the cellulose, reducing the length of the cellulose crystals [4].

Cellulose nanocrystals can be used to produce materials such as absorbent aerogels. Currently, aerogels are the subject of research in several areas, such as medical, environmental and food packaging researches. These materials attract attention due to the characteristics such as large internal surface area and high surface-volume relationship [5], low density, excellent thermal properties and liquid absorption capacity [6]. In addition, aerogels can be used as absorbers in food packaging, which is a new application in this field of research [5]. Because of the high surface area of the aerogels, the functional groups present in the polysaccharides are easily accessible for interactions with the medium. This property of the polysaccharide aerogels is of interest in relation to the sorption of different compounds on the surface of the aerogel, such as water and water vapor, saline solutions, dissolved polar molecules, and surfactants [7]. In addition, the ability of aerogels to maintain their physical structure during water absorption is a result of cross-links between network chains [8].

Aerogels also can be produced from synthetic polymers. Synthetic polymers are chemically more stable, but their high mechanical strength results in a slow degradation rate. Poly (vinyl alcohol) (PVA) is a synthetic polymer that is biocompatible, biodegradable, and made by polymerization of vinyl acetate followed by a hydrolysis reaction of the poly (vinyl acetate) [9]. PVA is widely used in the preparation of physically crosslinked aerogels from freeze/thaw cycles [10]. For food

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applications, the physical crosslinking has the advantage of avoiding residual amounts of toxic chemical crosslinking agents.

The combination of different types of polymers, such as natural and synthetic polymers, to form composite materials is one alternative to improve aerogel properties. In our previous study [11], it was observed that aerogels made with cellulose and PVA presented high values of water absorption. Cellulose nanocrystals exhibit good biocompatibility and biodegradability, however, aerogels made only from them they tend to disintegrate upon contact with water. Besides, cellulose nanocrystals present higher ratio of aspect and higher surface area of contact, due to this it is expected that aerogels combined with cellulose nanocrystals and PVA will present higher values of water absorption.

In recent studies, it was observed that polysaccharide aerogels combined with other polymers presented results of great interest for application in food preservation, mainly in regards to absorption values [11,12]. Therefore, the development of these materials should be encouraged [13]. The objective of this study was the isolation and characterization of cellulose nanocrystals from rice and oat husks for the utilization of this material on the elaboration of absorbent aerogels for food packaging.

2. Material and methods

2.1. Material

Rice grains from the IRGA 417 cultivar and oat grains from the URS GURIA cultivar were used. Rice grains were husked in the Zaccaria machine (model PAZ-1-DTA, *Industrias Machina Zaccaria* S/A, São Paulo, Brazil) and oat husks were acquired from the *Cerélus Produtos Integrais* Industry, localized in the Ijuí, RS, Brazil. The rice and oat husks were used to isolate the cellulose according to the methodology reported in our previous work [11]. The commercial cellulose fibers (eucalyptus) were acquired in the *CMPC – Cellulose Rio Grandense* Industry, localized in the Guaíba, RS, Brazil. The eucalyptus cellulose was used as a control sample. All the chemical reagents used in this work were of an analytical grade.

2.2. Preparation of cellulose nanocrystals

Rice cellulose and oat cellulose were obtained according to the methodology used in our previous study [12]. The rice, oat, and eucalyptus cellulose nanocrystals were prepared according to the method suggested by Pääkkö et al. [14]. A 100 g sample of cellulose was added to 2 L of sodium acetate solution (0.05 $\text{mol}\cdot\text{L}^{-1}$) with pH 5 and 2 mL of the *cellulase reesei* enzyme solution (≥700 units/g) from Sigma. The mixture was kept at 37 °C in a thermostatic bath with mechanical stirring for 5 days. After enzymatic hydrolysis, the mixture was homogenized for 30 cycles at a pressure of 15 MPa for high-pressure homogenization (EmulsiFlex – C3, Avestin). The nanocrystals were stored at 5 °C for analysis and preparation of aerogels.

2.3. Characterization of cellulose nanocrystals

The morphology of cellulose nanocrystals was evaluated in a transmission electron microscope (TEM) (JOEL, JEM-1400) with an acceleration voltage of 150 kV. The size of nanocrystals was evaluated from TEM images using ImageJ software.

The cellulose nanocrystals were analyzed with a spectrometer (IRPrestige21, Shimadzu Corp. Japan), with an ATR (Attenuated Total Reflectance) accessory. Scans were performed in the spectral range 3600–600 cm^{-1}, and 30 readings were acquired at a resolution of 2 cm^{-1}.

The relative crystallinity of the cellulose nanocrystals was investigated by X-ray diffraction. The analysis was performed in an X-ray diffractometer (XRD-6000, Shimadzu, Brazil) with a scanning range between 5° and 40° (2θ). The calculation of the relative crystallinity of the nanocrystals was performed according to Segal et al. [15].

The thermal analysis of the cellulose nanocrystals was performed to study the degradation characteristics of the cellulose nanocrystals. The thermal stability of each sample was determined using a thermogravimetric analyzer (TGA) (TA-60WS, Shimadzu, Kyoto, Japan). Samples (8–10 mg) were heated from 30 to 600 °C at a heating rate of 10 $°\text{C}\cdot\text{min}^{-1}$. A flow of 50 $\text{mL}\cdot\text{min}^{-1}$ of nitrogen was used.

2.4. Preparation of aerogels

Nanocrystals from rice, oat, and eucalyptus celluloses and poly (vinyl alcohol) (PVA) were used for the preparation of aerogels. An aqueous dispersion of cellulose nanocrystals at 2% (w/v) was prepared under magnetic stirring in a water bath (Velp Scientifica, enzymatic Digestter-GDE, Italy) for 1 h at 35 °C. An aqueous dispersion of PVA (powder; $(C_2H_4O)_n$; hydrolysis of 86.5–89.5%) at 21% (w/v) was prepared by heating with magnetic stirring at 90 °C for 1 h in a water bath (Velp scientific, enzymatic Digestter-GDE, Italy). The two dispersions, cellulose nanocrystals, and PVA were stirred until complete homogenization, in order to obtain the gel. A sample of the gel (25 g) was added to acrylic plates with a diameter of 6 cm where physical crosslinking was performed. This consists of freezing the gel at −20 °C, followed by its total thawing at room temperature (approximately 25 °C). This freeze-thaw process was performed five times. Then, after crosslinking, the aerogel was frozen again in the ultra-freezer and freeze-dried.

2.5. Characterization of the aerogels

The morphology of the aerogels was examined by a scanning electron microscope (JEOL JSM-6610LV, Japan) according to the method described by Wang et al. [16]. The aerogel samples frozen in liquid nitrogen were fractured immediately, and then a thin film of gold was sprayed on their surface. The accelerating voltage was 15 kV, and the images were captured at a magnification of 100×.

The analysis was performed in an X-ray diffractometer (XRD-6000, Shimadzu, Brazil) with a scanning range between 5 and 40° (2θ). The calculation of the relative crystallinity of the aerogels was performed according to the method described by Rabek [17] by the equation: $RC\,(\%) = (Ac/(Ac + Aa)) * 100$; where *Ac* is the crystalline area and *Aa* is the amorphous area on the X-ray diffractograms.

The aerogels were analyzed with a spectrometer (IRPrestige21, Shimadzu Corp., Japan), with an ATR (Attenuated Total Reflectance) accessory according to Wang et al. [16]. The freeze-dried aerogel was ground and mixed with KBr in the region of 3600–900 cm^{-1}. The relative crystallinity of the aerogels was investigated by X-ray diffraction.

The thermal stability of aerogels was determined using a thermogravimetric analyzer (TGA) (TA-60WS, Shimadzu, Kyoto, Japan). Samples (8–10 mg) were heated from 30 to 600 °C at a heating rate of 10 $°\text{C}\cdot\text{min}^{-1}$. A flow of 50 $\text{mL}\cdot\text{min}^{-1}$ of nitrogen was used.

The water absorption capacity of the aerogels was evaluated in distilled water according to the method described by Demitri et al. [18], with some modifications. The water absorption capacity of the aerogels was measured by weighing the samples before and after immersion in water at 25 °C for 24 h. The water absorption capacity (WAC) was defined by the equation: $WAC = ((Ws - Wd)/Wd) * 100$, where *Ws* is the weight of the swollen aerogel and *Wd* is the weight of the dried sample.

The suspension stability of the aerogel was evaluated through zeta potential using Zetasizer Nanoseries Nano-Z equipment (Malvern Instruments, England) at 25 °C and a 90° angle.

2.6. Statistical analysis

Analytical determinations for the samples were performed in triplicate, and standard deviations are reported, except for X-ray diffraction and thermal analysis. The results of Tukey's test were compared with a 5% level of significance by analysis of variance (ANOVA).

3. Results and discussion

3.1. Morphology and size of the cellulose nanocrystals

The micrographs of nanocrystals from rice, oat, and eucalyptus celluloses observed via TEM are shown in Fig. 1. Nanocrystals of rice cellulose (Fig. 1a), oat cellulose (Fig. 1c), and eucalyptus cellulose (Fig. 1e) presented an individualized structure with different shapes and sizes. Individualization is due to the enzymatic hydrolysis process, which cleaves the amorphous and disordered domains of cellulose fiber, preserving its crystalline part, resulting in well-defined single crystals. In addition, mechanical treatment with high pressure helps with individualization of cellulose nanocrystals by providing greater uniformity of size and morphology [19,20]. According to Silvério et al. [21], cellulose nanocrystals are particles with at least one dimension equal to or <100 nm. Poaty et al. [22], who studied kraft cellulose nanocrystals, found nanocrystals with a size of 140 nm. Hebeish et al. [23] studied cotton cellulose nanowhiskers obtained by alkali treatment, treatment with perborate, and treatment with sulfuric acid and found nanowhiskers with sizes ranging from 80 to 200 nm. Therefore, from the reports of previous studies, it is possible to suggest that the size of

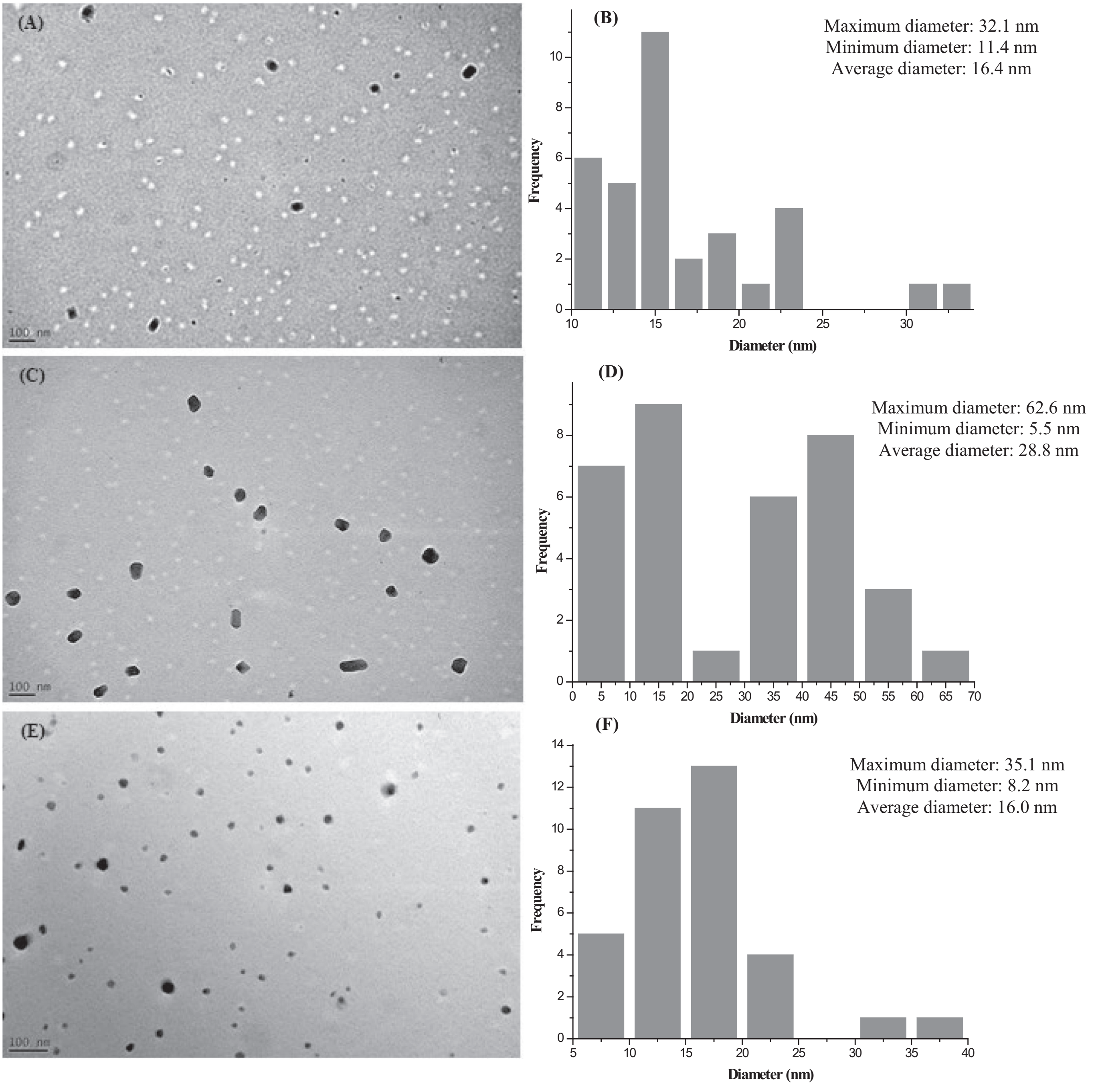

Fig. 1. Morphology and size distribution of the nanocrystals of rice cellulose (a–b), oat cellulose (c–d), and eucalyptus cellulose (e–f).

the nanocrystals varies according to the source of extraction and also according to the method of production.

The differentiated morphology of the nanocrystals of this study may be due to the longer hydrolysis time (five days) compared to other studies that used shorter times of hydrolysis, as in the study of Beyene et al. [24] in which hydrolysis time was from 2 to 10 h. According to Kargarzade et al. [25] and Beck-Candanedo et al. [26], the hydrolysis time is one of the parameters that most influence the diameter of the cellulose nanocrystals, whereas as the hydrolysis time increases there is a decrease in the diameter. Therefore, it is suggested that prolonged hydrolysis and mechanical treatment of high pressure altered the morphology of the cellulose nanocrystals of the present study.

3.2. Functional groups of the cellulose nanocrystals

The FTIR spectra of the nanocrystals of rice, oat, and eucalyptus celluloses are shown in Fig. 2. The cellulose nanocrystals showed similar spectra with bands at 3378 cm^{-1}, mainly due to the hydrogen bond of O—H stretching vibration, which indicates the hydrophilic tendency of the nanocrystals [22]. In addition, the bands at 2905 cm^{-1} and 1659 cm^{-1} were attributed to the sp^3 C—H stretching vibration and the –OH bending to the absorbed water, respectively [27]. The band around 1355 cm^{-1} represented the C—H asymmetric deformation and C—O symmetric stretching within the polysaccharide aromatic rings of cellulose [28]. The band at 1422 cm^{-1} was associated with CH_2 symmetric bending of cellulose [29].

Chen et al. [30] produced cellulose from algal biomass and reported that bands at 1245 cm^{-1} and 872 cm^{-1} are related to the non-cellulosic polysaccharides such as lignin and hemicellulose. In our study, these bands were not observed. This suggested that nanocrystals were successfully produced through enzymatic hydrolysis. These results were in agreement with other literature [29–31], in which the cellulose and nanocellulose were described as having a similar FTIR pattern.

3.3. Relative crystallinity of the cellulose nanocrystals

The relative crystallinity (RC) and X-ray diffraction of the nanocrystals are presented in Fig. 3. The nanocrystals of cellulose from rice, oat, and eucalyptus showed RC values of 60.0%, 90.0%, and 95.1%, respectively. Johar et al. [31] found an RC of 59.0% for rice cellulose nanocrystals. Hassan et al. [32] found an RC of 73.9% for nanocrystals of sheets of nanopaper, and Tibolla et al. [33] found an RC 49.2% for banana peel nanocrystals. The difference in RC between sources of cellulose nanocrystals can be attributed to the non-cellulosic components of the fibers [34]. In this case, as the rice husks have a higher amount of lignin and silica in their initial composition [12], the presence of these remaining compounds may have decreased the RC of the rice nanocrystals. The values of the aforementioned studies are presented to emphasize that the RC varies according to the source of extraction of the nanocrystals.

In addition, the hydrolysis method to obtain nanocrystals also influences the RC. High RC values indicate that the enzyme reduced the regions of amorphous cellulose caused by the preferential attack of cellulase thereon. This preference is due to the greater accessibility of glycosidic β-1,4 bonds in these domains [35]. According to Elazzouzi-Hafraoui et al. [36], differences in the relative crystallinity of cellulose nanocrystals are assigned to the hydrolysis that occurs in the amorphous regions and primarily the origin of the precursor fiber. The high crystallinity of cellulose nanocrystals is based on the chemical structure of cellulose, which has the ability to form intermolecular links within the hydrogen between the cellulose chains, allowing packaging of the crystalline cellulose chains in a highly compact system (crystalline structures) [37].

The X-ray diffraction patterns were similar, where the peak at $2\theta = 22.7°$ was the most intense in nanocrystals of rice, oat, and eucalyptus celluloses (Fig. 3). This peak is characteristic of cellulose type I and was also observed by Johar et al. [31], who prepared and characterized rice cellulose nanocrystals. However, the XRD pattern of oat cellulose nanocrystals presented a peak at $2\theta = 20.1°$ (Fig. 3) that is characteristic of cellulose type II, and this difference is attributed to the plant variety and hydrolysis conditions that can cause partial polymorphic transformation of cellulose I to cellulose II [38]. The diffraction pattern of XRD is a factor that can influence the mechanical properties of nanocrystals. According to Mariano et al. [39], nanocrystals with the diffraction pattern of cellulose I tend to have a higher longitudinal elastic modulus than those with the diffraction pattern of cellulose II. Values may vary according to methodology, but in X-ray measurements, cellulose I may have a modulus of 130 GPa, while cellulose II may exhibit a modulus of 90 GPa. The same behavior occurs with the chemical and thermal stability of these materials [40].

3.4. Thermogravimetric analysis of cellulose nanocrystals

Thermogravimetric analysis is a useful tool for understanding the thermal behavior of natural materials [39].

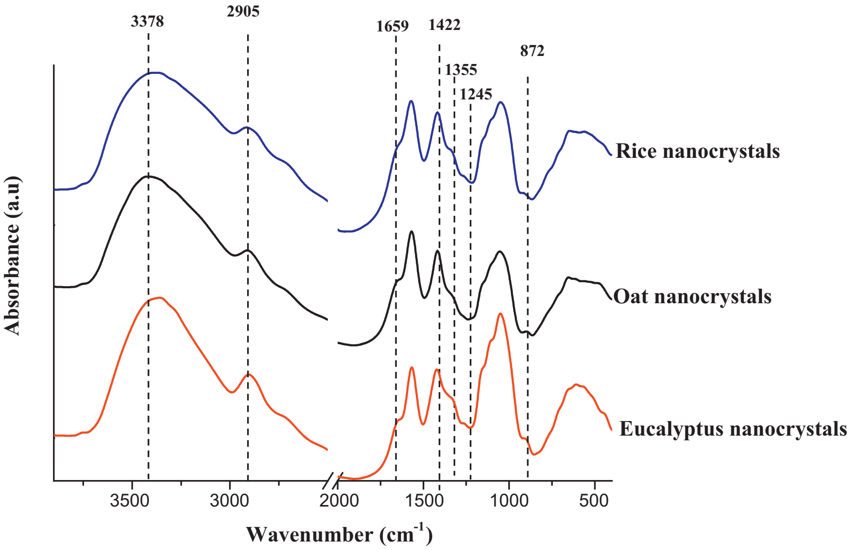

Fig. 2. Fourier-transform infrared spectroscopy (FTIR) spectra of the nanocrystals of rice cellulose, oat cellulose, and eucalyptus cellulose, in the region between 3600 cm^{-1} and 600 cm^{-1}.

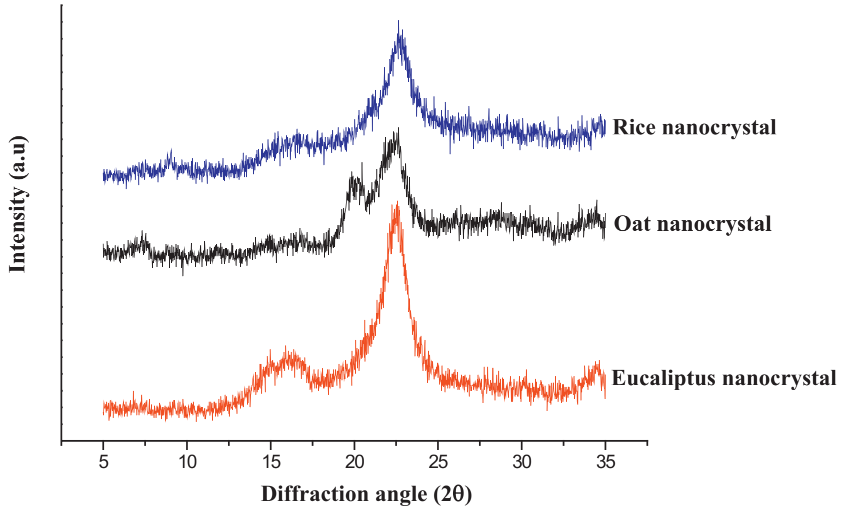

Fig. 3. X-ray diffraction pattern of the cellulose nanocrystals of the rice cellulose, oat cellulose, and eucalyptus cellulose.

From the thermogravimetric analysis, three regions of mass loss were observed (Fig. 4). The first stage, around 150 °C, corresponds to the removal of absorbed water. The second stage, around 200 to 350 °C, corresponds to the degradation of the cellulosic chain due to dehydration and decomposition of glycosidic units. The third stage of decomposition was observed around 380 °C and corresponds to the compounds from the decomposition of low molecular weight carbonic residues. These results are in agreement with similar studies [41,42].

The thermal stability of cellulose nanomaterials is dependent on numerous factors related to chemical composition and structural

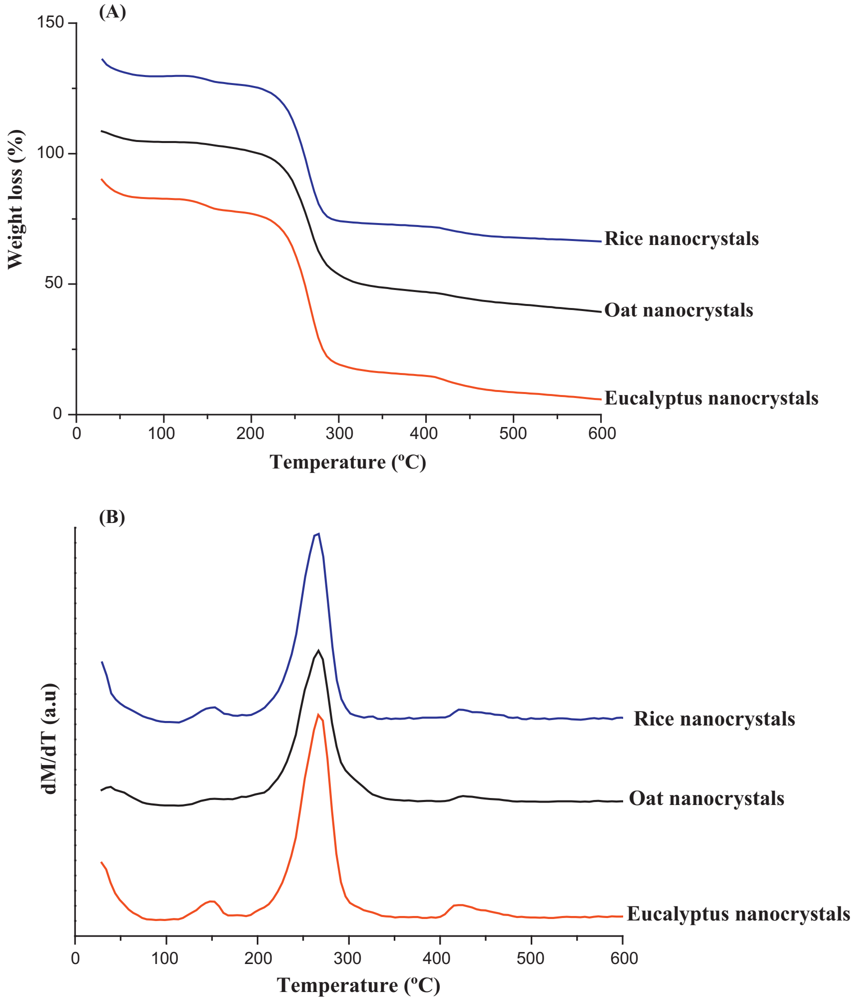

Fig. 4. Thermogravimetric analysis (TGA) (a) and its first derivatives (DTG) (b) of the nanocrystals of rice cellulose, oat cellulose, and eucalyptus cellulose.

characteristics [43–45]. In the present study, it was verified that the cellulose nanocrystals, independently of the source, presented high thermal resistance in the initial stage of degradation. This is promising in terms of applicability in composite technology, where the processing of polymers involves heat and oxygen operation under high shear, such as in the production of food packaging.

3.5. Morphology of the aerogels

The morphology of the aerogels of nanocrystals from rice, oat, eucalyptus celluloses, and PVA (control) is shown in Fig. 5. In general, aerogels were homogeneous without phase separation, which indicated a relatively unique structure. The aerogel of rice cellulose nanocrystals (Fig. 5a) showed pores interconnected throughout their length and a structure more organized into a three-dimensional network when compared to the oat cellulose nanocrystals aerogel (Fig. 5b). The aerogel of eucalyptus cellulose nanocrystals (Fig. 5c) presented an organized structure but had smaller pores compared to the aerogels of rice and oat cellulose nanocrystals. However, what most attracted our attention was the morphology of the aerogel control, that is, the aerogel created only with PVA (Fig. 5d), which presented a compacted and low-porosity structure. The freeze-drying process consists of two steps: freezing and drying. However, the final structure of the aerogels depends significantly on the freezing step. In fact, the pore size distribution, shape, and pore network connectivity are the result of the shape of the ice crystals that form during freezing [46,47]. The size and distribution of pores of aerogels are important parameters for use as absorbers in food packaging because they can influence the amount and mechanism of water absorption since aerogels with small pores present a lower ability to absorb water. Furthermore, according to Spagnol et al. [48], the presence of cellulose nanocrystals in the aerogel matrix increases the number of hydrophilic groups, which makes the diffusion of liquid into the matrix easier and faster. Therefore, the pore size is increased.

3.6. Relative crystallinity, functional groups and thermogravimetric analysis of the aerogels

The relative crystallinity (RC) and X-ray diffraction of nanocrystal aerogels are shown in Fig. 6. The aerogels of nanocrystals from rice, oat, and eucalyptus celluloses presented values for RC of 75.5%, 79.1%, and 86.4%, respectively (Fig. 6), while the control aerogel, created only with PVA, presented an RC of 35.5%. Therefore, it is possible to suggest that the high RC of the aerogels is due to the nanocellulose (Fig. 3), since it presented high RC values. PVA is a type of synthetic hydrophilic polymer that can generate a physical aerogel by freezing and thawing cycles due to the formation of crystallites; however, polymers and nanomaterials provide an effective way of improving the properties of the original polymers, such as mechanical strength, water barrier properties, and thermal stability [49]. The properties of nanocomposites depend on the individual properties of each component (matrix and reinforcement), composition (volume fraction of constituents), the morphology of each phase (spatial arrangement, dimensions, and crystallinity), and interface properties. The water absorption capacity of aerogels of cellulose nanocrystals can be influenced by the crystallinity of the cellulose nanocrystals [50].

The spectra of the aerogels and poly (vinyl alcohol) (PVA), analyzed by FTIR, are shown in Fig. 7. In the aerogels of nanocrystals of rice, oat, and eucalyptus, celluloses were identified as bands related to the PVA and cellulose. The band at 3320 cm^{-1} is related to stretching O—H, 2928 cm^{-1} is related to vibration C—H, 1718 cm^{-1} is due to vibration C═O, 1168 cm^{-1} is related to stretching C—O, and 1088 cm^{-1} refers

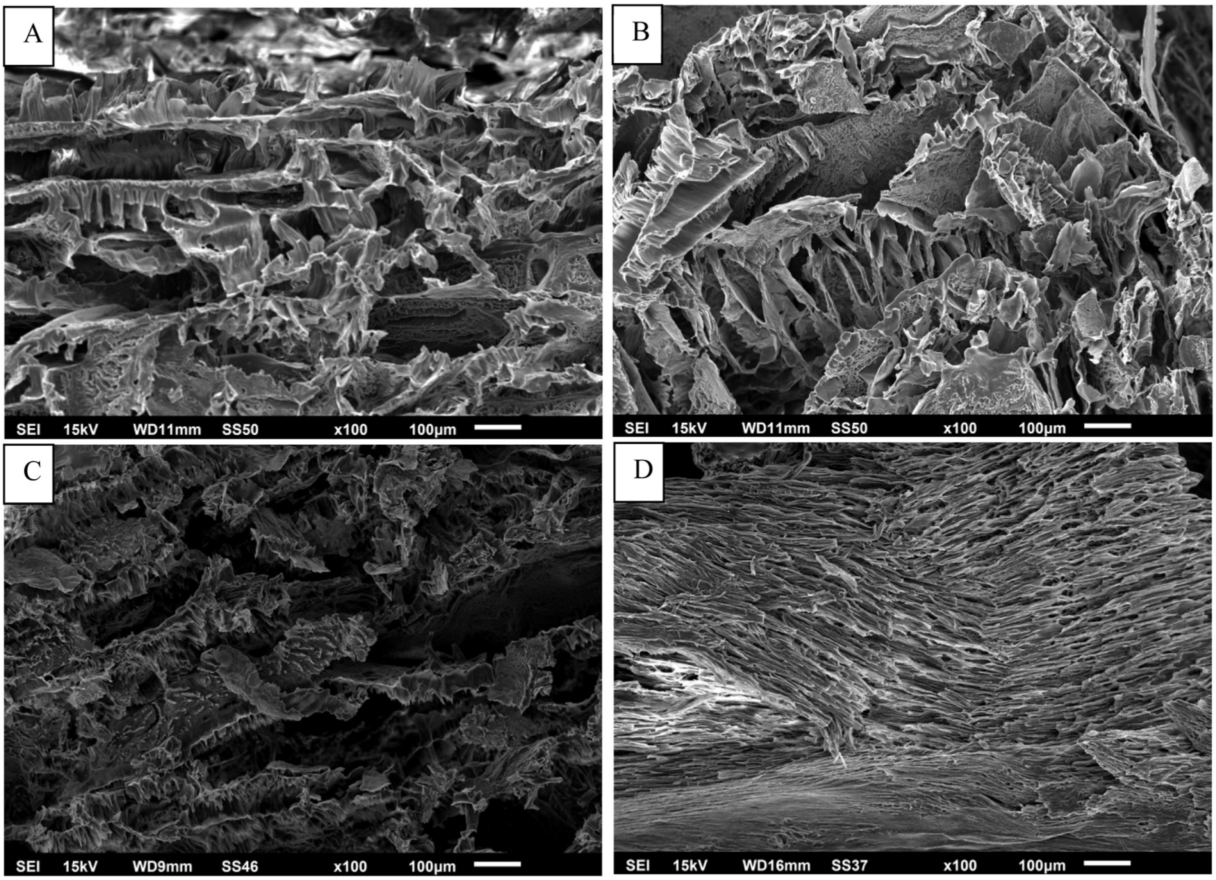

Fig. 5. Morphology of the aerogels of nanocrystals of rice cellulose (a), oat cellulose (b), eucalyptus cellulose (c), and poly (vinyl alcohol) (d).

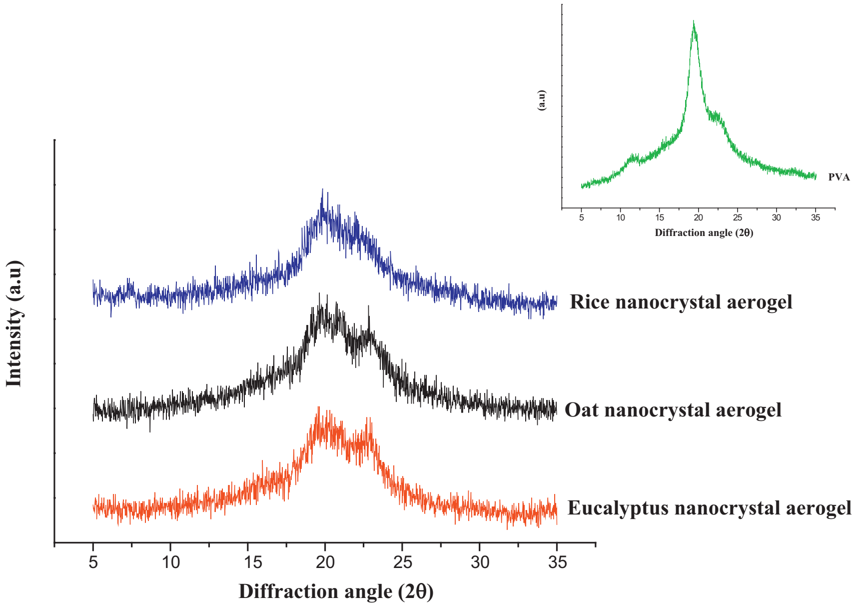

Fig. 6. X-ray diffraction pattern of the aerogel of nanocrystals of rice cellulose, oat cellulose, eucalyptus cellulose, and poly (vinyl alcohol).

the C═O. The similarity of some of the bands identified in the spectra of cellulose nanocrystals (Fig. 2) with the bands of the spectra of aerogel suggests that there was an interaction among the functional groups of the cellulose nanocrystals with the groups of the PVA. As shown in Fig. 7, the band at 1558 cm^{-1}, which refers to conjugated aromatic rings and carbonyl groups characteristic of residues of lignocellulosic materials [51], appears only in the spectra of the nanocrystal aerogels, evidencing the interaction between the nanocrystals and the PVA, since this band is not observed in the spectrum of aerogel made only with PVA. The bands indicated in the spectra of the aerogel were correlated with other studies that evaluated aerogels prepared with PVA and cellulose and found similar bands [51].

The thermogravimetric analysis of the aerogels is presented in Fig. 8. Three regions of mass loss were observed. The first region at approximately 180 °C is associated with moisture loss of the aerogels, and there is no thermal degradation in this region. The second region is defined as the main stage of mass loss, which was observed at temperatures of 265 to 309 °C (Fig. 8b). The thermal decomposition of the aerogels in this region presented a higher decomposition temperature when compared to the second thermal decomposition region of the pure nanocrystals (Fig. 4).

According to Peng et al. [52], the increase in decomposition temperature is a consequence of the drying process that the aerogels were subjected. The drying process allows the cellulose nanocrystals to reorganize in the preferred order creating a network of hydrogen bonds and thus causing a delay in the thermal decomposition of the aerogels. The third region observed at around 430 °C may be associated with carbonic residues of high molecular weight. In addition, the higher thermal stability of the aerogels may be due to the presence of PVA, since the PVA aerogel had a higher decomposition temperature (Fig. 8).

3.7. Water absorption capacity of aerogels

The water absorption capacity of aerogels of cellulose nanocrystals ranged from 264.2% to 402.8%, and the aerogel of oat cellulose nanocrystals had the highest water absorption (Table 1). The aerogel made only with PVA disintegrated completely when in contact with

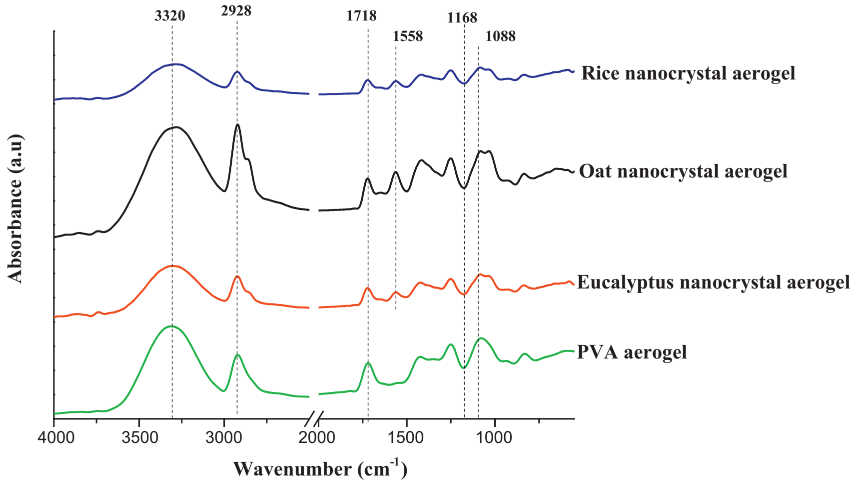

Fig. 7. Fourier-transform infrared spectroscopy (FTIR) spectra of the aerogels of nanocrystals of rice cellulose, oat cellulose, eucalyptus cellulose, and poly (vinyl alcohol), in the region between 3600 cm^{-1} and 600 cm^{-1}.

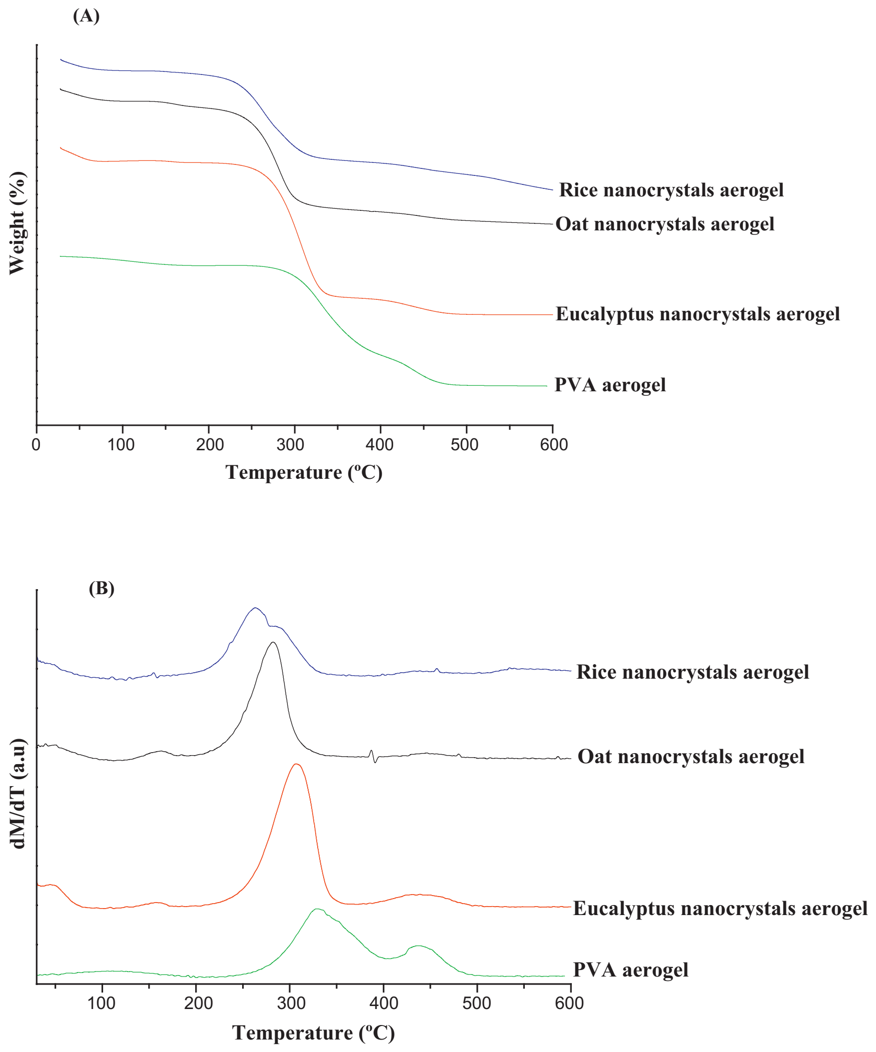

Fig. 8. Thermogravimetric analysis (TGA) (a) and its first derivatives (DTG) (b) of the aerogels of nanocrystals of rice cellulose, oat cellulose, eucalyptus cellulose, and poly (vinyl alcohol).

water. Therefore, it was not possible to perform water absorption measurements, and this was probably due to the highly hydrophilic nature of the PVA. In addition, it is possible that the disintegration of this aerogel occurred due to its low porosity and compacted structure (Fig. 5d).

The aerogel of oat cellulose nanocrystals showed a greater pore size (Fig. 5b) as compared to pores of the aerogel of eucalyptus cellulose nanocrystals (Fig. 5c). The pore size influenced the water absorption since the aerogel with smaller pores (aerogel of eucalyptus cellulose nanocrystals) showed lower water absorption capacity (Table 1). In addition, another fact that contributed to the lower water absorption of eucalyptus cellulose nanocrystal aerogels is the higher relative crystallinity of eucalyptus cellulose nanocrystals compared with that of other aerogels (Fig. 6). According to De Paula et al. [53], nanocrystals with high relative crystallinity cause a barrier effect in polymer matrices causing low diffusion of water between the polymer chains; however, this makes the polymer more resistant to degradation in hydrolytic environments.

Table 1
Water absorption capacity and zeta potential of aerogels from rice, oat and eucalyptus celluloses nanocrystals.

Aerogel[a]	Water absorption capacity (%)	Zeta potential (mV)
Rice cellulose nanocrystals	357.5 ± 2.7b	−31.5 ± 0.7a
Oat cellulose nanocrystals	402.8 ± 4.5a	−17.8 ± 1.6b
Eucalyptus cellulose nanocrystals	264.2 ± 1.7c	−11.6 ± 1.8c

[a] The results ate the means of three determinations. Values with different letters in the same column are significantly different ($p < 0.05$).

According to Das et al. [54], the water absorption inside the polymeric chain of the aerogel is related to the hydrophilicity of the polymer chains. When the dry aerogel comes in contact with water, the first water molecules absorbed hydrate the more polar molecules of the polymer backbone, leading to the first type of water bond with the polymer molecules. With the hydration of the first groups occurs an increase in the polymeric structure where more hydrophobic molecules within the polymer matrix are exposed to water. This expansion of the structure and hydration of the groups within the molecule leads to the appearance of the second type of interaction of the water molecules, which occurs with the more hydrophobic groups of the polymer. The covalent forces, as well as the interactions that maintain the three-dimensional structure, provide the elastic capacity of the aerogel. When there is a balance between the forces of absorption and water retention, the maximum water absorption of the aerogel is achieved. Furthermore, as previously reported, the incorporation of cellulose nanocrystals into the aerogel network improves water absorption capacity and reduces the time necessary to achieve the equilibrium condition [48].

Based on the high water absorption capacity, all the aerogels obtained may be used as absorbers in food packaging. Moisture absorbers can be used mainly in meat packaging to avoid condensation of water, which can reduce water activity and indirectly affect the microbial growth [55]. Another important factor observed from this analysis is that the aerogel made only with PVA, under the conditions of the present study, did not prove to be suitable for application as a moisture absorber in food packaging, since there was disintegration of its structure, which is not ideal for the storage of food in bioactive packaging.

3.8. Zeta potential of aerogels

The stability of the suspension used to prepare the aerogels of cellulose nanocrystals as measured from the zeta potential is shown in Table 1. The charges of aerogels were negative, and the charges of aerogels assigned to the PVA molecule were negative [56]. According to Araki et al. [57], the inclusion of negative charges on the surface material suspension provides stability to the suspension. The aerogel of rice cellulose nanocrystals presented a more negative zeta potential than other aerogels, and according to Greenwood [58], this behavior suggests an increase in resistance to agglomeration for this suspension. Moreover, the author reports that a suspension with a zeta potential of approximately ±30 mV is considered to have good stability.

The zeta potential reflects the surface potential of particles, which is influenced by changes to the interface with the dispersing medium, due to the dissociation of functional groups on the particle surface or adsorption of ionic species present in the aqueous dispersion medium. Moreover, according to Amiri et al. [59], the stability of the suspensions is given by the force of particle/particle interactions. According to Tibolla et al. [33], who investigated the zeta potential of nanofibers of cellulose isolated from banana peel as a reinforcing agent in composite, high zeta potential values of a colloidal suspension are related to a more stable suspension, and a high electrostatic repulsion of the fibers provides surface charge to stabilize the suspension.

4. Conclusions

In the present study, cellulose nanocrystals from different sources were obtained by enzymatic hydrolysis, a green methodology, and this method can replace acid hydrolysis, reducing the environmental impact caused by this reaction. In addition, in order to obtain biodegradable materials with absorption capacity for food packaging, aerogels with cellulose nanocrystals from different sources and PVA were produced. Cellulose nanocrystals and aerogels presented with varying structural, morphological, and crystallinity properties, depending on the source of cellulose. The aerogel of rice cellulose nanocrystals showed the highest water absorption capacity (402.8%). The use of the rice and oat husks, which are considered agroindustrial waste, for the production of cellulose nanocrystals for application in aerogels has the potential to be applied in many industrial areas, including as aerogel absorbers of water in food packaging.

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