

# Preparation and Characterization of Nanocomposites Based on Linear Medium Density Polyethylene/Cellulose Nanofibers from *Agave tequilana* Bagasse Waste

José Guillermo Torres-Rendón,<sup>a</sup> Mario E. Valdez-Fausto,<sup>b</sup> José Anzaldo-Hernández,<sup>a</sup> Rosa M. Jiménez-Amezcu,<sup>b</sup> Kestur G. Satyanarayana,<sup>c</sup> Salvador García-Enriquez,<sup>a</sup> and María Guadalupe Lomelí-Ramírez<sup>a,\*</sup>

In the Mexican state of Jalisco, a significant amount of fibrous agave waste is generated from the tequila industry every year. The objective of this study was to establish the potential of obtaining cellulose nanofibers (CNF) from the bagasse waste of *Agave tequilana*, and then incorporate them into a linear medium density polyethylene matrix to obtain nanocomposites through the thermocompression process. These nanoparticles were used to prepare nanocomposites of the selected matrix, incorporating 1 to 5 wt% of CNF. All of the prepared composites had a low water absorption. Increases in tensile strength and in modulus and flexural properties occurred when the concentration of the CNF was augmented. However, in the case of nanocomposites with 5 wt%, a decrease in elongation was observed.

*Keywords:* *Agave tequilana* waste; Nanocomposite; Thermocompression moulding; Cellulose nanofibers

*Contact information:* a: Department of Wood, Cellulose and Paper, University of Guadalajara, km 15.5 at the Guadalajara-Nogales Highway, Postal Code 45220, Zapopan, Mexico; b: Department of Chemical Engineering, University of Guadalajara, Marcelino Garcia Barragan 1451, Postal Code 44430, Guadalajara, Mexico; c: Present Address: Honorary Professor, Poornaprajna Institute of Scientific Research, Sy. No. 167, Poornaprajnapura, Bidalur Post, Devanahalli, Bengaluru-562110, Karnataka, India; \*Corresponding author: glomeli@dmcyp.cucei.udg.mx

## INTRODUCTION

Industrialized countries are continually in search of raw materials, processes, and products for various technological applications. Such materials should be sustainable, low cost, low-polluting, and have good mechanical performance. Composites, particularly those that use lignocellulosic fibers, have these characteristics; therefore, there has been increased interest for these areas due to the benefits these composites offer (Khalil *et al.* 2012).

Natural fibers have been used in the production of value-added products, especially as reinforcements in polymer matrices for the production of composite materials (Zhang *et al.* 2013). It has been reported that the addition of natural fibers into a polymer matrix improves certain properties, such as the tensile and flexural properties, of the resulting composite (Darabi *et al.* 2012). The main advantages of using reinforcements obtained from renewable sources, in comparison with inorganic fillers, are their abundance, low density, high reinforcement capacity, low energy consumption, high specific mechanical properties, biodegradability, and the large amount of lignocellulosic material available in nature. However, they also have the disadvantage of having hydrophilic character. The hydroxyl groups that are present in these materials interact with water molecules. This affects the compatibility of the natural fibers with the hydrophobic polymer matrices, resulting in low matrix-reinforcing adhesion. Consequently, the physico-mechanical

properties and the resistance to environmental and biological deterioration of composite materials are affected, thus reducing their potential applications (Cao *et al.* 2012).

The generation of large quantities of agricultural waste by various industries has given rise to a prevailing need to take advantage of these ligno-cellulosic resources as raw materials. There is also a need to incorporate them into a production chain, which allows for the development of new products, such as composite materials using innovative techniques and processes, for the benefit of society and the environment (Satyanarayana *et al.* 2004; Thakur *et al.* 2017). This is the case with agave bagasse, which is a by-product that is generated by the industrial production of tequila. In Mexico, the consumption of about 649,000 tons of agave was reported in 2017, of which about 463,000 tons corresponded specifically to agave bagasse (Tequila Regulatory Counsel, 2017). This fibrous material is hardly used in the region of Tequila, Jalisco, as it is considered an industrial waste. This suggests that due to its lignocellulosic nature, the agave bagasse can be considered a raw material for producing composite materials, with a high potential for the generation of cellulose microfibrils. In fact, while the blue agave bagasse fibers of Mexico have been characterized for their physical, chemical, mechanical, and thermal properties (Satyanarayana *et al.* 2013), there have also been many studies using agave bagasse fiber and even *Agave tequilana* bagasse fiber particularly in the development of polymer-based composites (Idarraga *et al.* 1999; Santiago *et al.* 2002; Tronc *et al.* 2007; Leduc *et al.* 2008; Saucedo-Luna *et al.* 2010; Becerra-Rodríguez *et al.* 2011; López-Bañuelos *et al.* 2012; Abreu-Sherrer 2013; Frausto-Gutierrez *et al.* 2015; Cisneros-López *et al.* 2017). For example, studies of acid (Saucedo-Luna *et al.* 2010; Abreu-Sherrer 2013) and alkaline (Idarraga *et al.* 1999; Santiago *et al.* 2002) hydrolysis of agave bagasse fibers have been reported with a cellulose yield of 40 to 45 wt%, a hemicellulose yield of 20 to 22 wt%, and a lignin yield of 15 wt%. Studies on water absorption of low-density polyethylene (LDPE)-agave fiber composites have been reported by Becerra-Rodríguez *et al.* (2011). Similarly, studies of linear medium density polyethylene (LMDPE) composites with 15 wt% barley particles were reported by Frausto *et al.* (2015). Also, mechanical properties (tensile, flexural, and impact) of different polymer-based composites containing raw agave tequilana fibers (with and without chemical treatment) have been reported by several researchers (Tronc *et al.* 2007; Leduc *et al.* 2008; López-Bañuelos *et al.* 2012; Cisneros-López *et al.* 2017). There is also one study on the mechanical properties of high-density polyethylene (HDPE) containing agave-coconut fibers with two fiber contents (20 and 30 wt%) and different coconut-agave fiber ratios processed by a two-stage process using a twin-screw extruder followed by injection molding (Pérez-Fonseca *et al.* 2016). However, there seems to have been no study on the preparation of nanofibers of *A. tequilana* bagasse fiber and their polymeric composites. The present study focuses on this aspect.

In contrast, nanocellulose is being considered as the next generation of renewable reinforcement for the formation of high performance biocomposites (Lee *et al.* 2014). Based on its dimensions, functions, preparation methods, and source of cellulose, nanocellulose is classified into three categories according to Klemm *et al.* (2011): nanofibrillated cellulose (NCF or CNF), nanocrystalline cellulose (NCC or CNC), and bacterial nanocellulose (BNC). Cellulose nanofibers are obtained from lignocellulosic materials, such as wood and agricultural crops, by different processing methods such as chemical processing, mechanical methods, a combination of these, *etc.* In general, lignin is also removed from the plant cell wall before fibrillation using chemical treatment. Depending on the source and separation method used, the cellulose nanofibers are typically between 20 to 40 nm in diameter and several microns in length. Due to the specific

characteristics of cellulose nanofibers, such as a high surface area layout and good dispersion, they are of great interest for use in the improvement of the properties of polymers (Hietala *et al.* 2013). Accordingly, cellulose nanofibers of *A. tequilana* bagasse fiber were prepared in this study to develop nanocomposites with a LMDPE matrix.

From the foregoing, the following became clear, leading to the scientific gaps that exist despite the large volume of literature in books and review articles (Dufresene 2010; Cai and Niska 2011; Kalia *et al.* 2011a,b; Mariano *et al.* 2014; Satyanarayana *et al.* 2017; Thakur *et al.* 2017):

(i) A large amount of *A. tequilana* bagasse fiber is available as waste, which can be used to develop value added products; (ii) The unique properties of LMDPE have not been used in the preparation of composites, including nanocomposites; (iii) There are not many reports on the preparation of cellulose nanofibers using *A. tequilana* bagasse fiber; (iv) Although there are several studies on the development of polymeric composites using *A. tequilana* bagasse fibers, there is not a lot available on the development of composites, including nanocomposites, using LMDPE as a matrix; and, (v) The use of an inexpensive and easy thermocompression process in the preparation of the previously mentioned nanocomposites.

Accordingly, this study was conducted to address these gaps with the following objectives:

- (i) Preparing and characterizing cellulose nanofibers (CNF) using the waste of *A. tequilana* bagasse fiber;
- (ii) Preparing and characterizing nanocomposites using LMDPE as a matrix and different amounts (1 to 5 wt%) of prepared CNF from *A. tequilana* bagasse fiber; and
- (iii) Comparing the obtained properties of these nanocomposites with the reported results on macro-composites based on *A. tequilana* bagasse fibers and some of the nanofibers from other plant fibers.

It is hoped that the results of this study will not only help in finding applications for the developed nanocomposites, but also lead to further research on nanocomposites based on other nanofibers obtained from agricultural wastes of other plant materials.

## EXPERIMENTAL

### Materials

Bagasse of the Weber blue variety of the *A. tequilana* was purchased from Mundo Agave in Jalisco, Mexico. LMDPE R093650 was used as the polymer matrix and was supplied by Polímeros Nacionales (Mexico). This polymer has a melt flow index of 5 g/10 min (2.16 kg/190 °C) and a density of 0.93 g/cm<sup>3</sup>. Other chemicals used in the study include: hydrochloric acid (HCl, 37%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), sodium hypochlorite (NaOCl, 13%), sodium bromide (NaBr, 97%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95%), and sodium hydroxide (NaOH, 97%). All of these chemicals were acquired from Karal (León, Mexico). Anthraquinone (AQ, 97%), sodium chlorite (NaClO<sub>2</sub>, 90%), and 2,2,6-tetramethylpiperidine-1-oxyl radical (TEMPO, 98%) were purchased from Sigma-Aldrich (Toluca, Mexico).

## Methods

### *Preparation of bleached cellulosic fibers*

First, acid hydrolysis was carried out on the agave bagasse using a 0.5% H<sub>2</sub>SO<sub>4</sub> solution (hydromodule of 8:1) in a rotary digester at 160 °C for 30 min. Afterwards, the hydrolyzed bagasse was cooked using a solution of anthraquinone (0.1%, hydromodule of 5:1) and NaOH (23.2%) in a rotary digester at 170 °C for 150 min. These cooking conditions were based on those reported by Lomelí-Ramírez *et al.* (2018). The resulting cooked pulp was washed and purified. The bleaching process was performed by conducting four sequential chemical treatments.

The first treatment was performed in the presence of a chlorine dioxide solution (D0). The components of this process were 10 wt% pulp, 1.7 wt% ClO<sub>2</sub>, 0.15 wt% HCl 1 N. The treatment was conducted at 60 °C for 30 min, and it resulted in a final pH between 2 and 3. The second step was an alkaline extraction (E) on the 10 wt% pulp used in the previous treatment. For this treatment, a solution of NaOH (5 wt%) 1 N was employed. The alkaline extraction was performed at 70 °C for 60 min, with a final pH of ≥ 10.5.

In the third treatment, chlorine dioxide (DI) was added (1 wt% ClO<sub>2</sub>) with 0.15 wt% of NaOH 1 N. The process was conducted at 80 °C for 180 min.

In the fourth treatment, 1.5 wt% hydrogen peroxide and 1 wt% NaOH 1 N was added to obtain an initial pH between 11.5 and 11.8. This step was performed at 80 °C for 180 min. Lastly, with the aim to eliminate hemicelluloses, a chemical treatment was performed using 0.5 g of NaOH for each 100 g of pulp (dry based) at 25 °C for 30 min.

### *Preparation of cellulose nanofibers aqueous suspensions*

The bleached cellulose was subjected to a TEMPO mediated oxidation (TEMPO/NaOCl/NaBr system) under alkaline conditions (pH 10.5) for 30 min according to the method reported by Saito and Isogai (2004). The CNF suspensions were prepared by mechanical homogenization of the oxidized pulp (concentration of 4 wt%). First, an Oster blender (Oster, BLSTSOG4661B, Mexico City, Mexico) was used for homogenization at a velocity of 15,000 rpm for 120 min. Then, a second homogenization step was performed using an ultra-turrax (Janke & Kunkel, TP18, Texas City, TX, USA) at 20,000 rpm for 5 min. Finally, a sonic treatment was conducted using an ultrasonic bath (Branson, MH, Chicago, IL, USA) for 30 min. The resulting product was a gel-like suspension.

### *Preparation of nanocomposites (LMDPE-CNF) processed by thermocompression*

LMDPE was used as the matrix, and the agave cellulose nanofibers were used as reinforcements at concentrations of 0, 1, 3, and 5 wt%. Before processing, the agave nanofibers were dried for 24 h in an oven at 60 °C to eliminate moisture. Both components (LMDPE and dried CNF) were mixed manually in bags of plastic and then in a kitchen mixer (Black & Decker SmartGrind) for 2 min. The resulting mixed samples (36 g) were put in a stainless-steel mold with dimensions of 170 × 170 × 1.4 mm, applying the proportions shown in Table 1.

**Table 1.** Formulation of Samples with 0, 1, 3, and 5 wt% of CNF

Reinforcement (wt%)	LMDPE (g)	CNF (g)
0	36	0
1	35.64	0.36
3	34.92	1.08
5	34.2	1.8

For the processing conditions, the plaques of the thermocompressor (constructed in Mexico) were first heated to 160 °C. Then, a pressure of 25 bar was applied for 14 min. Finally, the mold was cooled down with circulating water until it reached 50 °C (Silva-Guzmán *et al.* 2018).

#### *Characterization of starting materials, nanocomposites, and bleached cellulose*

The quantity of residual hemicelluloses in the pulp was calculated according to TAPPI um-233 (2001). The contents of the alpha, beta, and gamma celluloses in the pulp were obtained according to TAPPI T 203 cm-93 (2009). Viscosimetry was performed to determine the degree of polymerization.

#### *Atomic force microscopy (AFM)*

Individual cellulose nanofibers were observed using an atomic force adsorption microscope (Park Systems, NX10, Suwon, South Korea). Before measurements, the samples were diluted in water until a ratio of 1:100 was reached, and then they were sonicated for 3 h. Then, the samples were deposited on cleaved mica and dried at room temperature for 24 h.

#### *Optical microscopy*

An optical microscope (OPTIKA Italy, B383PLi, Ponteranica, Italy) was used to: i) observe the morphological characteristics of the fibers before cooking and oxidative treatments, and ii) to observe delamination (fibrillation) of the cell wall induced by the mechanical treatments.

#### *Fourier transform infrared spectroscopy (FTIR)*

A spectrophotometer (Perkin-Elmer, Spectrum GX, Mexico City, Mexico) was used to perform FTIR spectroscopy. The attenuated total reflectance technique (ATR) was used, and all of the spectra were obtained by employing a resolution of 4 cm<sup>-1</sup> in the frequency range from 4000 cm<sup>-1</sup> to 700 cm<sup>-1</sup>.

#### *Lyophilization of CNF*

Prior to lyophilization, the samples (water suspensions with nanofibers) were frozen using a temperature of -21 °C for 24 h. Then, the frozen samples were put in a lyophilizer (Labconco, FreeZone, Kansas City, USA) that worked with a vacuum of 70 × 10<sup>3</sup> Mbar at -47 °C for 48 h. The lyophilized samples were grounded until a fine powder was produced.

#### *Water absorption*

Water absorption was measured according to the standard ASTM D570-98 (1998). Samples with dimensions of 10 x 50 x 3 mm<sup>3</sup> were submerged in distilled water at 25 °C. Weight changes of the samples were monitored for several weeks. The diffusion coefficient (*D*) was calculated according to the method reported by Crank (1975), which is,

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-D(2n+1)^2\pi^2/l^2) \quad (1)$$

where *M<sub>t</sub>* is the mass of absorbed water at time *t*, *M<sub>∞</sub>* is the mass of absorbed water at the equilibrium and *l* is the thickness of the samples. Five samples per type of material were measured.

### *Mechanical properties*

The tensile and flexural properties of the prepared nanocomposites were determined following the ASTM standards D638-14 (2004) and D790-17 (2017), respectively. The test samples for these three types of tests were prepared following these standards using a laser cutter (Guian, GN600LS, Shandong, China) along with the LaserWorkV6 software. The cutting speed was 5 mm/s (50 % of power laser). The samples were cut to achieve the dimensions determined by the D638-14 ASTM standard.

A universal testing machine (Instron, 3345, Barcelona, Spain) was utilized to perform the flexural and tensile tests. The cross-head speed was 1 mm/min for both types of tests. In the case of the flexural tests, a span of 30 mm was used. A total of 8 samples were measured for each types of test.

### *Scanning electron microscopy (SEM)*

The cross section of the fractured samples was analyzed with a high-resolution microscope (TESCAN, MIRA 3 LMU, Brno, Czech Republic). The fractured samples were coated with gold for 40 s in a sputtering Spi-module machine.

## RESULTS AND DISCUSSION

### **Acid Hydrolysis and Pulping Process**

Acid hydrolysis of agave fibers was performed to eliminate hemicelluloses and low molecular weight sugars. The resulting yield of cellulose was 40 wt%. This value was similar to those reported in previous studies that used 2% of sulphuric acid for hydrolysis (Idarraga *et al.* 1999; Santiago *et al.* 2002; Saucedo-Luna *et al.* 2010; Abreu-Sherrer 2013). Based on these results, the low yield obtained in the present study could be attributed to the strong chemical attack that occurred during the hydrolysis and the cooking processes.

The Kappa number was determined, according to the standard TAPPI T 236-om99 (1999), to reveal the degree of delignification in the pulp. The resulting value was 6.97, which was indicative of the strong delignification that occurred during the hydrolysis and the cooking process. This value was lower than those reported from the pulps of *A. tequilana* subjected to pulping processes, such as kraft (Kappa number of 28), soda (Kappa number of 60), and ethanol-soda (Kappa number of 33) (Idarraga *et al.* 1999).

From the four bleaching steps conducted in this work, cellulose yields of 95.6, 96, 97.7, and 98.2 wt% were obtained, respectively. Moreover, elimination of hemicelluloses was also conducted to obtain a pulp with a higher content of  $\alpha$ -cellulose. The final cellulose content of the bleaching process was approximately 15 wt%.

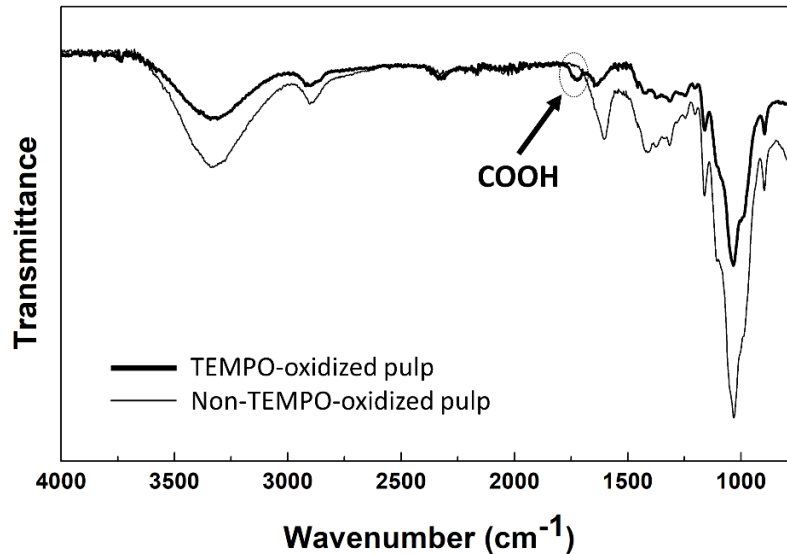
The values of the degree of polymerization were 252.2 (before bleaching) and 172.9 (after bleaching). The reduction of the degree of polymerization was due to the attacks that the cellulose chains suffered from the bleaching agents. The final content of  $\alpha$ -cellulose after bleaching was 89 wt%.

### **Characterization of CNF**

#### *FTIR*

The FTIR spectra of TEMPO-oxidized and non-TEMPO-oxidized samples (pulp) are shown in Fig. 1. The spectra of the pulp subjected to TEMPO oxidation have the characteristic bands of TEMPO-oxidized celluloses (Liang *et al.* 1959; Habibi *et al.* 2006; Ifuku *et al.* 2009). Notice that the band at 1730  $\text{cm}^{-1}$  represents the protonated carboxyl groups generated by acidification of TEMPO-oxidized samples. It is important to mention

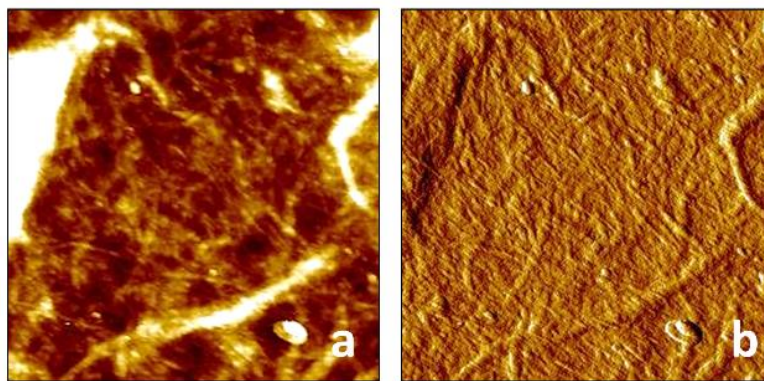
that TEMPO-mediated oxidation replaces OH groups by carboxylic groups at carbon 6 (Isogai *et al.* 2011), and it is typically used as a chemical pretreatment for preparation of cellulose nanofibers (Saito *et al.* 2006; Ishii *et al.* 2011).



**Fig. 1.** FTIR spectra of non-TEMPO-oxidized and TEMPO-oxidized agave pulps

#### Atomic force microscopy (AFM)

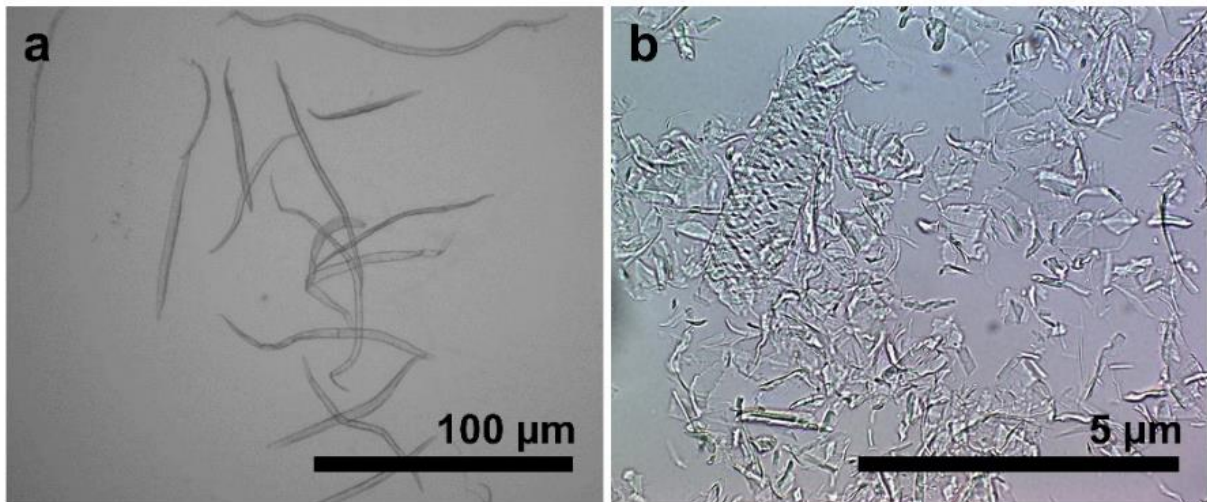
AFM was utilized to confirm the presence of cellulose nanofibers in the prepared suspensions. Figure 2 shows an (a) AFM topographical image and (b) an illumination image of the obtained nanofibers. It was observed that the mechanical treatment was successful, but only on the TEMPO-oxidized pulps in which nanofibers of approximately 10 nm in diameter were obtained. The chemical treatment (TEMPO oxidation) favored nanofibrillation, as reported by Saito *et al.* (2006). The microfibrils exhibited agglomerations due to the cellulose chains having an intermolecular hydrogen bonding and a strong hydrophilic interaction in between the cellulosic chains. These agglomerations were similar to those reported by Bhattacharya *et al.* (2008), who also reported whole microfibrillar bundles and individual nanofibers from bagasse sugarcane in AFM images. The mechanical friction in the pulp caused delamination of microfibrillar, which exposed internal areas of the cell wall and, therefore, increased the surface area.



**Fig. 2.** (a) Topographical and (b) illumination AFM images of nanofibrils

### Optical microscopy

Figure 3a shows the optical microscopic images of the agave fibers. As can be seen, the cooking, bleaching, and TEMPO oxidation steps did not degrade the cell wall, as it remained intact even after the chemical processes. Figure 3b presents both the effect of fibrillation (delamination of the cell wall) by the mechanical treatment and the sharp decrease in the length of the fibers. The mechanical friction processes produced many scattered nanofibers, as seen in the micrograph. The number of revolutions per minute, the consistency of the suspension, and the time of mechanical treatment influenced the quality of the nanofiber obtained. In addition, highly hydrated nanofibers were observed because, when the gel was formed, the suspension of the nanofibers reached about a 98% moisture content.



**Fig. 3.** Micrographs of (a) agave fibers before oxidation and mechanical treatment and (b) the resulted nanocellulose

## Characterization of Nanocomposites

### Water absorption study

The maximum water absorptions and the diffusion coefficient ( $D$ ) of all nanocomposites are shown in Table 2. The water absorptions were very low, even in 5 wt% CNF nanocomposites. This suggests that the hydrophobic matrix (LMDP) is the component that has more influence on the absorption of water. However, the absorption did increase with the incorporation of CNF, which was expected because of the hydrophilic nature of the cellulose. The highest water absorption was achieved by the nanocomposite having 5 wt% of CNF ( $2.22 \pm 0.067$ ).

Some studies have reported different amounts of water absorption for composites using natural fibers as reinforcements. For example, Becerra-Rodríguez *et al.* (2011) worked with low density polyethylene (LDPE)-agave fiber composites and observed a low water absorption. Frausto *et al.* (2015) reported water absorption values of up to 16% for LMDPE composites with 15 wt% of barley particles. In another study, Chen *et al.* (2016) reported water absorption values between 9 and 12% for composites of LDPE containing 4 to 6 wt% of bamboo particles. All these results indicated that the size of the material and their nature have a strong influence on the water absorption capacity. It is reported (Rowell *et al.* 2005; Beg and Pickering 2008a,b) that the behavior of the water absorption in polymer-based composites can be affected by three fundamental factors. First, the incorporated lignocellulosic material has a hygroscopic nature, considering that cellulose



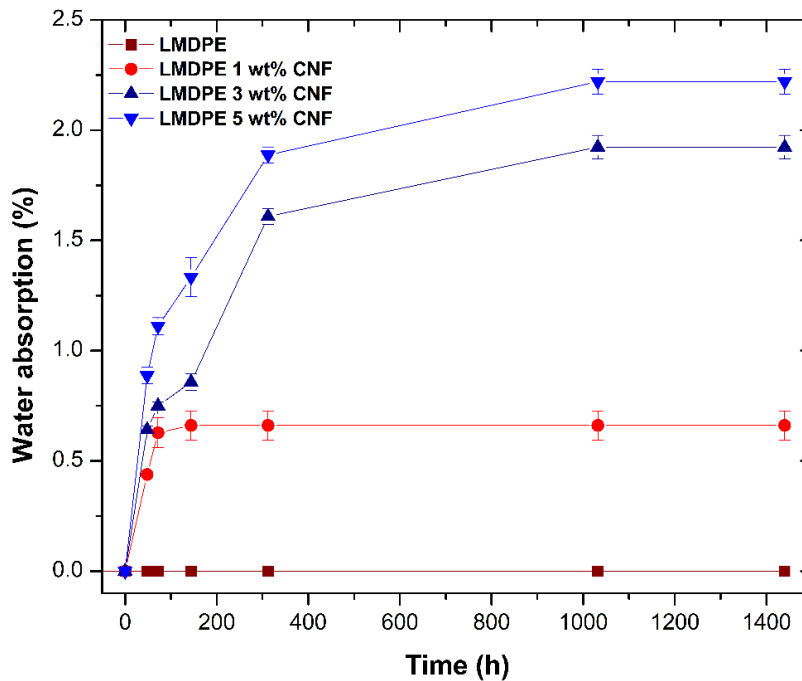
has hydroxyl groups (OH) forming the chemical structure of the cellular wall of plant fibers. Secondly, there was a low quality of encapsulation of the incorporated particles in the thermoplastic matrix because, during the preparation of the composite, free pores or fault zones could be formed and help to facilitate the entry of water in the composite (Yamada *et al.* 2009). Thirdly, results were affected by the amount of lignocellulosic material that is added because a larger percentage of incorporated hydrophilic reinforcement into the polymer matrix correlates with a greater the water absorption (Silva-Guzmán *et al.* 2018). There seems to have been a lack of water absorption studies on nanocomposites having CNFs within hydrophobic matrices. In recent years, studies dealing with nanocomposites based on CNF and thermoplastic starch (as the matrix) have all reported water absorptions of approximately 50% in 5 wt% CNF nanocomposites (Hietala *et al.* 2013; Nasri-Nasrabadi *et al.* 2014; Lomelí-Ramírez *et al.* 2018). In the case of Lomelí-Ramírez *et al.* (2018), CNF extracted from agave bagasse waste was used. This suggests that CNFs obtained from agave bagasse waste have practically the same effect on the absorption of water of composites, at least on those that have starch as a matrix, compared to other CNFs extracted from sources like softwood (Hietala *et al.* 2013) and rice straw (Nasri-Nasrabadi *et al.* 2014). It is important to mention that water absorption in composites depends on several factors, not only on the type of reinforcement. For example, it depends on the type of the matrix, the type of reinforcements, quantity of reinforcements, porosity, temperature, exposed areas of surfaces, among others (Springer 1981; Stamboulis *et al.* 2001; Deng *et al.* 2010). The maximum water absorption value found in this work was very low compared to those of starch-based nanocomposites having 5 wt% of CNF. This is believed to be due to the hydrophobic nature of the LDPE.

Figures 4 shows the water absorption kinetics of the nanocomposites. All nanocomposites have a similar kinetic behavior (high water uptake within the first 100 h, and then reaching equilibrium at around 1400 h, except for those having 1 wt% CNF, that reached equilibrium just after 100 h).

**Table 2.** Maximum Water Absorptions and Diffusion Coefficients of Materials

Material	Water absorption (%)	Diffusion coefficient, $D$ , ( $m^2/s$ ) $10^{-10}$
LMDPE	0	0
LMDPE (1 wt% CNF)	$0.66 \pm 0.007$	2.083
LMDPE (3 wt% CNF)	$1.92 \pm 0.053$	0.272
LMDPE (5 wt% CNF)	$2.22 \pm 0.067$	0.3056

The diffusion coefficients are displayed in Table 2 ( $D$ ). All values were in the range of those obtained from previous works dealing with composites having lignocellulosic reinforcements within hydrophobic matrices (Moscoso *et al.* 2012; Flores-Hernández *et al.* 2017), and also from studies about natural solids (Ochoa-Martínez and Ayala-Aponte 2005). Table 2 shows that the diffusion coefficient of nanocomposites having 1 wt% of CNF exhibited the highest value. In this case, the low quantity of CNF in the system (1 wt%) could have led to a lack of enough contact points between the reinforcements, limiting the diffusion of water through the material. In the case of the nanocomposites with 3 wt% and 5 wt% of CNF, the diffusion coefficient is higher in the later, which can be attributed to the presence of more contact points between the nanofibers.



**Fig. 4.** Water absorption kinetics of the LMDPE nanocomposites

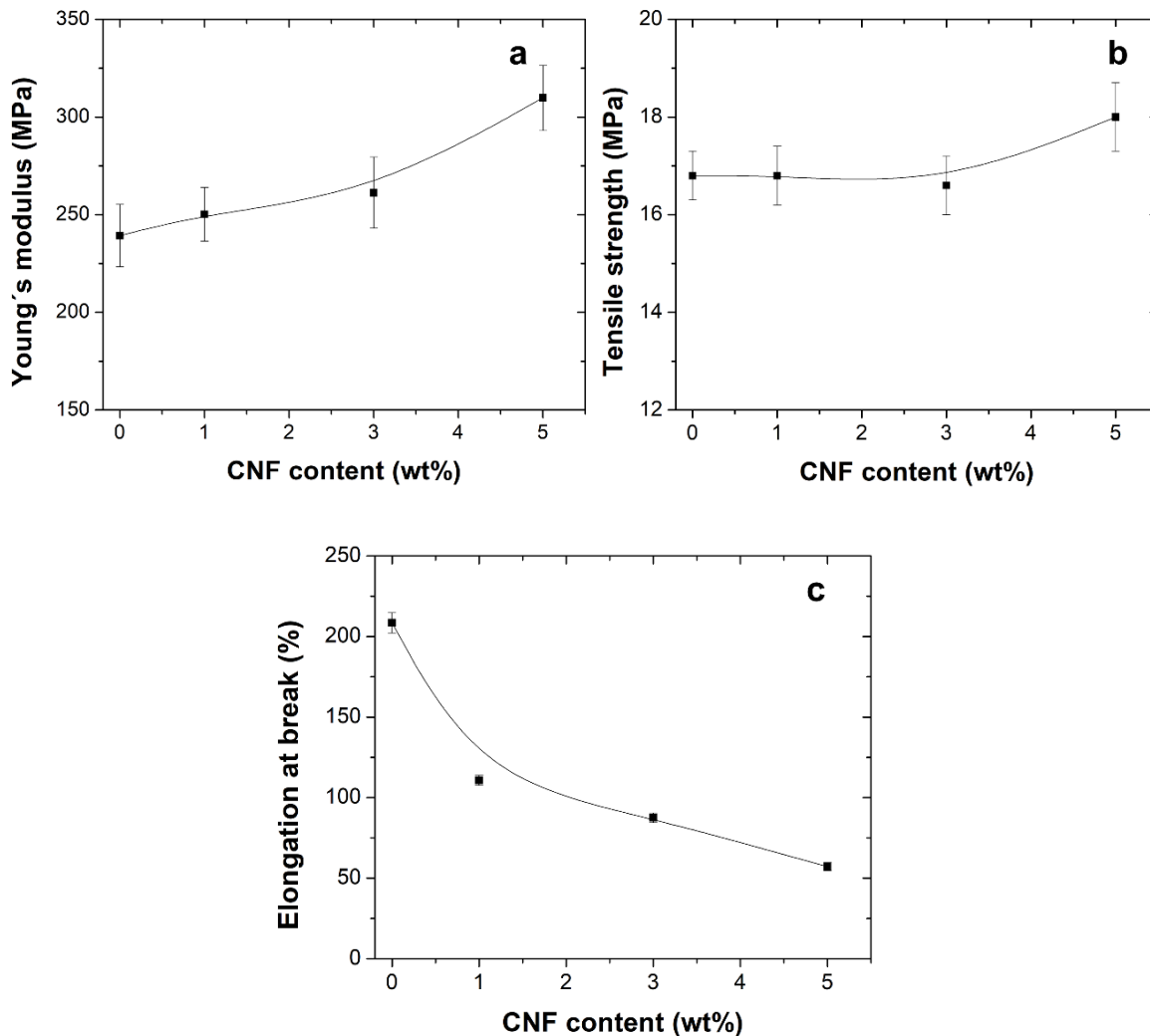
#### *Tensile properties*

Figure 5 shows the behavior of the tensile strength, Young's modulus, and the maximum elongation as functions of the amount of CNF in the nanocomposites. As can be seen in Figure 5a to b, the values of both tensile strength and Young's modulus remained practically the same compared to the matrix, suggesting that there was hardly any considerable effect on these properties with the incorporation of 1 and 3 wt% of CNF. However, both properties increased in nanocomposites containing 5 wt% of CNF, with tensile strength increasing by approximately 6% and Young's modulus increasing 29.4%. These observations are similar to those reported earlier by other researchers (Oksman 1996; Solís and Lisperguer 2005; Leduc *et al.* 2008; Gaikwad and Mahanwar 2017). For example, Oksman (1996) and Solís and Lisperguer (2005) worked with LDPE and HDPE, respectively, and with wood particles as reinforcements. They concluded that the increase in tensile strength was not significant and that compatibilizing or coupling substances were required to achieve significant increases. Gaikwad and Mahanwar (2017), who worked with HDPE/henequen microfiber composites, observed tensile strength values of 20.3 MPa and 21.1 MPa for pure HDPE and composites having 20 wt% microfibers, respectively. In that study, a maximum value of 22.4 MPa of tensile strength was reported for composites with 5 wt% of microfibers. In another study, Leduc *et al.* (2008) studied the effect of fiber content and the amount of coupling agent maleic anhydride (MAPE) on the mechanical properties of LDPE/raw *A. tequilana* fibers composites. They observed that Young's and flexural moduli increased with fiber content. However, they also observed a decrease in impact strength with an increase in fiber content. The addition of MAPE increased the effect to an optimum content between 2 and 5% on a fiber weight basis.

In another study, polyethylene-based composites with various concentrations of raw agave fibers (5, 10, and 15 wt%), processed by rotomolding, decreased in tensile strength with increasing amounts of fibers (López-Bañuelos *et al.* 2012). This has been attributed to both the difficulty of obtaining a homogeneous mixture with an increase of fibers and the resulting agglomeration of the fibers that occurs inside the rotating mold.

Furthermore, values of tensile strength and Young's modulus of composites obtained in the present study, containing 5 wt% of CNF, were comparable with those reported for composites containing 20 wt% and 30 wt% of fibers in a polyethylene matrix (Cisneros-López *et al.* 2017).

In the case of the elongation at break (maximum deformation), Fig. 5c demonstrates that a decrease in its values was correlated with an increase in CNF content. Such a decrease in elongation can be attributed to the low elasticity of the fibers, as reported earlier by Cisneros-López *et al.* (2017). It has also been reported that depending on the type of reinforcement, fibers do not contribute to elongation (López-Bañuelos *et al.* 2012).



**Fig. 5.** Plots of (a) tensile strength, (b) Young's modulus, and (c) maximum elongation as functions of the amount of CNF in the nanocomposites

#### *Flexural properties*

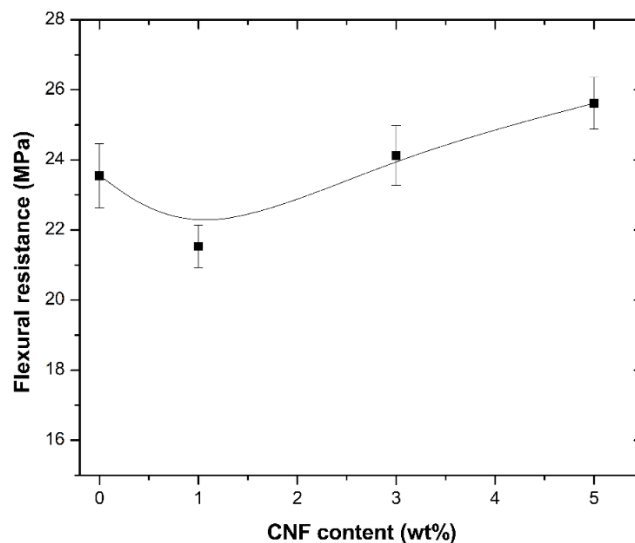
Table 3 shows the values of the flexural strength and flexural modulus, as well as the maximum deflection of the LMDPE/CNF nanocomposites. As noted, the maximum value was at 5% deflection, according to the norm, even when higher deflections were reported. Also, depending on the number of incorporated nanofibers, a noticeable effect on the deflection was observed. However, a slight decrease in the average value of the deflection was correlated with an increasing number of nanofibers added. Table 3 also

shows (i) a reduction of approximately 8% of flexural strength and flexural modulus with the addition of 1 wt% CNF and (ii) an increase in the average value of the flexural modulus with 3 and 5 wt% of CNF. Interestingly, the values of flexural modulus obtained in the present study with 5 wt% of CNF were comparable with those obtained by Tronc *et al.* (2007) with HDPE-50 wt% blue agave fiber composites (900 MPa). Similarly, the flexural modulus value of LDPE composites, obtained *via* thermocompression, containing 30 wt% of raw agave fiber, reported by Cisneros-López *et al.* (2017), could be achieved with just 5 wt% of nanofibers of blue agave in the present study.

**Table 3.** Mechanical Flexural Properties of the LMDPE Matrix Nanocomposites

Material	Flexural Resistance (MPa)	Maximum Deflection (mm/mm)	Flexural Modulus (MPa)
LMDPE	23.55 ± 0.91	6.80 ± 0.21	821.1 ± 51.6
LMDPE (1 wt% CNF)	21.53 ± 0.61	6.64 ± 0.19	758.6 ± 20.9
LMDPE (3 wt% CNF)	24.13 ± 0.85	6.61 ± 0.31	888.4 ± 45.4
LMDPE (5 wt% CNF)	25.62 ± 0.74	6.55 ± 0.13	893.4 ± 41.2

Figure 6 shows the flexural strength as a function of the amount of CNF present in the materials. The flexural strength decreased with the addition of 1 wt% CNF, while it increased when the addition of the fiber was increased to 3 and 5 wt% CNF. The values of flexural strength (FS) (19.5 MPa) and flexural modulus (FM) (700 MPa) observed by Kiziltas *et al.* (2016) in HDPE-10 wt% of nanofibers composites processed by an injection molding process were lower compared to the values obtained in the present study with 5 wt% CNF (FS: 25.6 MPa; FM: 893.4 MPa). Higher values of the observed FS and FM values in the present study can be attributed to a relatively better interaction between the nanofibers and the matrix. On the contrary, the lower values of the FS and the FM with a higher amount of nanofibers observed by Kiziltas *et al.* (2016) can be attributed to the limited interaction between the matrix (HDPE) and the nanofibers, which results in an increase in free volume and thus a decrease in the observed properties (Nakagaito *et al.* 2011; Kumode *et al.* 2017).

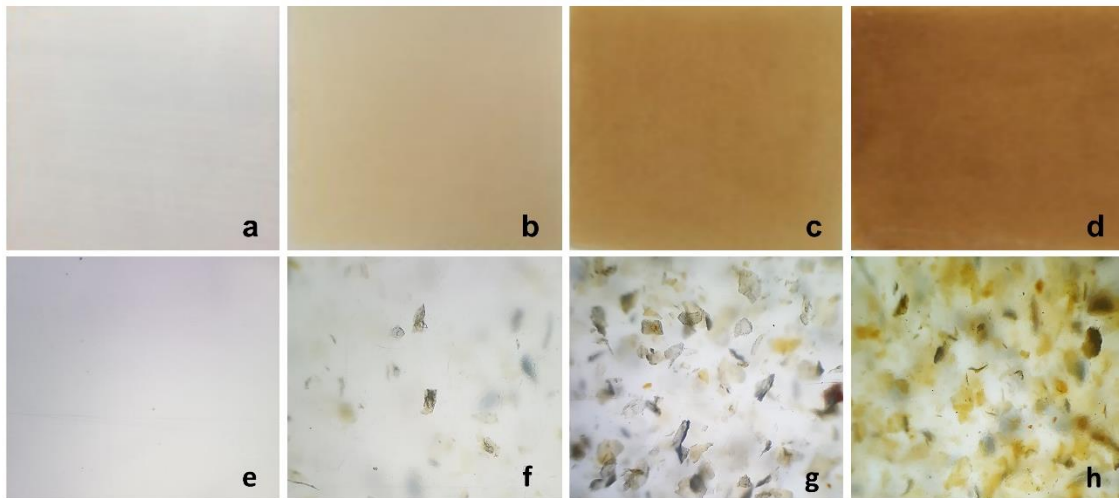


**Fig. 6.** Resistance to bending as a function of the CNF content

## Microscopy Studies of Nanocomposites

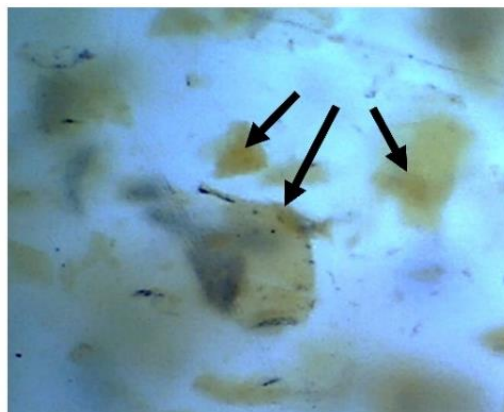
### *Optical microscopy*

Figure 7a shows a macrophotograph of the LMDPE matrix placed on a glass plate. Figure 7b to d are the macrophotographs of the LMDPE/CNF nanocomposites containing 1, 3, and 5 wt% of nanofibers, respectively, each of which was placed on a glass plate. Figure 7e to h show optical micrographs of these at 40× magnification. In these macro and microphotographs, a good dispersion of the nanofibers in the matrix was evident, with a dark color becoming more intense with an increase in the number of nanofibers in the matrix.



**Fig. 7.** Photos and micrographs of the LMDPE/CNF nanocomposites. Macrophotographs from (a) to (d) show LMDPE/CNF composites having 0 wt%, 1 wt%, 3 wt%, and 5 wt% of CNF, respectively. Optical micrographs of (e) 0 wt%, (f) 1 wt%, (g) 3 wt%, and (h) 5 wt% CNF were taken at a magnification of 40×.

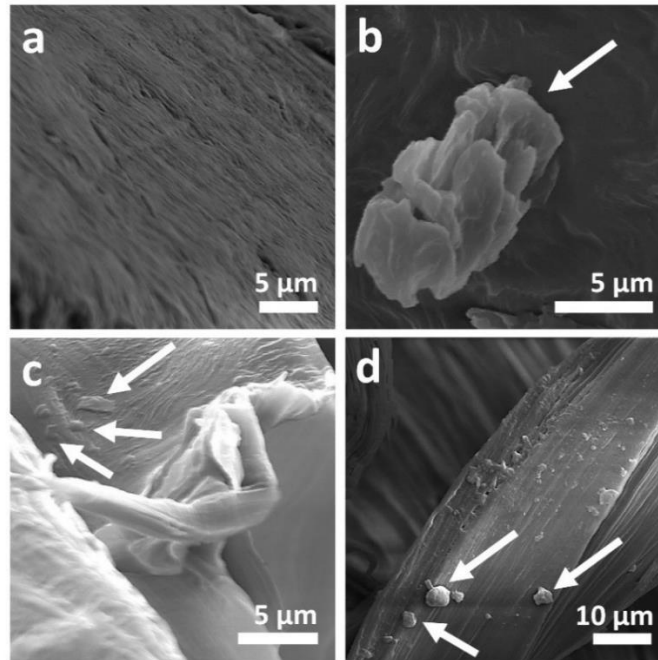
Figure 8 shows a micrograph of the LMDPE/CNF nanocomposites, revealing the aggregates formed by the cellulose nanofibers. As can be seen, most of these aggregates had a flat layer shape. These layers were probably formed by the removal of water during lyophilization. Considering that the adopted procedure in this study to prepare the LMDPE/CNF nanocomposites involved the drying of nanofibers suspensions, it was not possible to avoid the formation of aggregates.



**Fig. 8.** Photos of the LMDPE-CNF nanocomposites showing aggregates of CNF in the matrix

### Scanning electron microscopy

Figure 9a to d shows SEM micrographs of the fractured surface of tensile tested samples with Fig. 10a revealing the texture of the matrix. Figure 9b to d correspond to the nanocomposites containing 1, 3, and 5 wt% of CNF, respectively. All of the images show circular granules of CNF that were approximately 1 to 3  $\mu\text{m}$  in diameter. However, the thickness could not be determined.



**Fig. 9.** SEM images of the LMDPE matrix and LMDPE/CNF nanocomposites: (a) Pristine LMDPE, (b) Nanocomposites with 1 wt% CNF, (c) Nanocomposites with 3 wt% CNF, and (d) Nanocomposites with 5 wt% CNF

One of the most important challenges related to the use of nanocelluloses, in the form of nanofibers or nanocrystals, is their drying because of their hydrophilic nature, which tends to cause the formation of agglomerations (Peng *et al.* 2012). Hydrogen bonds can be generated during their drying, leading to their irreversible agglomeration known as hornification (Eyholzer *et al.* 2010). This process changes both the size of the nanocellulosic materials and their unique characteristics.

## CONCLUSIONS

1. A yield of 40 wt% of cellulose was obtained by the pre-treatment and pulping of the agave bagasse.
2. A yield of about 15 wt% of bleached pulp was obtained through processing agave bagasse.
3. Nanofibers could be obtained by applying mechanical treatment on TEMPO-oxidized pulps from agave bagasse waste, as observed in the AFM studies.
4. All of these treatments (cooking and bleaching of pulp followed by TEMPO treatments) did not degrade the cell walls of the fibers, as observed in the optical

microscopy studies.

5. Water absorption was very low for all nanocomposites prepared in this work.
6. An increase in both tensile strength and Young's modulus of nanocomposites containing 5 wt% CNF was observed, compared to pristine LMDPE. On the contrary, elongation of nanocomposites decreased with an increasing CNF content.
7. Flexural strength and flexural modulus of the nanocomposites decreased about 8% with the addition of 1 wt% CNF, while both of these properties increased for nanocomposites containing 3 and 5 wt% CNF. These results can be attributed to a favorable dispersion of nanofibers in nanocomposites with 3 and 5 wt% CNF. This suggests that the nanofibers functioned as the load carriers rather than as reinforcements, particularly in the nanocomposites with 1 wt% CNF.
8. One of the challenges for researchers working in the area of material science is to develop suitable drying methods to prevent agglomeration of nanocelluloses.

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