Modern Civil Engineering (ISSN 2470-4180)
January 2022, Volume 1, No. 1, pp.
Doi:10.15341/mese(2470-4180)/01.01.2022/009
Academic Star Publishing Company, 2022
www.academicstar.us

Bamboo Cellulose Nanocrystals Inserted in the Composition of Cementitious Mortars

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Abstract: This research deals with obtaining nanocrystals of cellulose from eucalyptus, which aims to insert and increase the strength of mortar, using nanotechnology for its improvement as an alternative way to reinforce the composition of the material. The methodology used to obtain this is a chemical treatment that must be carried out in two stages. The first is an alkaline treatment using sodium hydroxide (NaOH) and the second part, which is where the result is obtained, is acid hydrolysis using sulfuric acid (H_2SO_4). Briefly, cellulose, a polymer that is very abundant on the earth, when chemically treated becomes a material that can satisfactorily improve the strength of mortar or any other cementitious material. Its use in the future as a form of improvement, will become of paramount importance in civil construction, because it helps in the improvement of one of the most used materials in the industry in order to think about sustainability.

Key words: cellulose, cellulose nanocrystals, strength, mortar

1. Introduction

Considering that mortar is a cementitious compound widely used in civil construction, this work was developed with a focus on innovation and performance improvement and is one of the recurrent challenges for researchers. Considering that sustainability is increasingly on the agenda, how to improve the performance of this already existing material? Without increasing the cost and in a sustainable way becomes one of the most frequent questions.

With this in mind, one way of improvement would be to combine it with the study of cellulose nanotechnology, which, by having polymeric matrixes, has the potential to improve its mechanical properties without harming the environment.

Therefore, the present work aims to study the effect of cellulose nanocrystals, removed from bamboo (*species/genus not identified*), with the objective of inserting them in the composition of mortars, to obtain greater hydration of the cement particles and, consequently, an increase in its strength and workability.

2. Theoretical Reference

2.1 Cellulose

Cellulose is the most abundant natural polymer in nature, it is considered that 50 billion tons of this polysaccharide are biosynthesized by nature annually [1]. It has a long chain composed solely of the monomer Glucose, a polysaccharide or carbohydrate, which gives it strength and rigidity. Its empirical formula, ($C_6H_{10}O_5$), has a fibrous and wet linear structure and a semi-crystalline structure. It is a highly hydrophilic polymer without, however, being water soluble [1].

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2.2 Cellulose Nanocrystals

Cellulose is a material that has different chemical and physical properties, therefore, it can generate different cellulosic materials, one of them being cellulose nanocrystals. Cellulose nanocrystals (NCC) are termed as high crystallinity cellulose particles with at least one dimension less than or equal to 100 nm. Also reported in the literature as whiskers, crystallites or cellulose crystals, are the crystalline domains of cellulosic fibers isolated mainly through acid hydrolysis, and are so called because of their physical characteristics of stiffness, thickness and length [1-4].

The extraction of this material consists of two steps, the first one involves pre-treatments, such as wax extraction processes, bleaching and alkaline treatment, in order to remove the non-cellulosic components, and thus isolate the material that has greater tensile strength being associated with crystallinity [5].

The second step is related to the isolation of cellulosic material in its microfibrillated or crystalline form, where mechanical treatment, acid hydrolysis and enzymatic hydrolysis are the most applied isolation methods [6].

For the isolation of the crystals, acid hydrolysis is used exclusively, which performs a hydrolytic cleavage action of glycosidic bonds by the hydronium ions, penetrating the amorphous regions between the cellulose chains [7].

The main characteristics that encourage the use of NCCs as reinforcing agents in polymeric matrices are the significant specific surface area, the high modulus of elasticity (about 150 GPa), the high aspect ratio (length/diameter) (L/D) and the great reinforcement capacity at low load levels [8].

Other advantages of NCC are the low density (about 1.59 g/cm^3) [9], the non-abrasive nature (less wear on the equipment involved in its processing), the non-toxic character, biocompatibility and biodegradability [2]. Nanocrystals come from renewable natural sources that are very abundant and have a low cost. Furthermore, it is not necessary to synthesize them, their nanometric dimensions allow the production of composite films with excellent visible light transmittance and are easily chemically modified, as its molecular structure has a reactive surface with lateral hydroxyl groups, which facilitate the grafting of chemical species to achieve different surface properties [2, 4, 6]. As disadvantages, the low processing temperature (~200°C) is mentioned) and the lack of uniformity of its properties, depending on origin and seasonality.

The morphological characteristics of NCC are dependent not only on the conditions for obtaining them, but also on the acid species, concentration, reaction time, temperature and cellulose source [10].

The main method of obtaining NCC is chemical, using strong acids, and is based on the fact that the crystalline regions are insoluble in acids under the conditions in which they are used. This is due to their inaccessibility due to the organization of the cellulose molecules in their nanostructure. On the other hand, the natural disorganization of the molecules in the amorphous phases favors the accessibility of acids and consequently the hydrolysis of the cellulose chains present in these regions. Thus, the isolation of NCCs is facilitated by the faster hydrolysis kinetics presented by amorphous species compared to crystalline ones [2].

In acid hydrolysis the crystalline domains are preserved. During the reaction, the amorphous regions, which are more accessible, are rapidly attacked compared to the crystalline domains that remain intact after the process [11].

Among the reported acids, sulfuric acid is the most frequently used for the isolation of nanocrystals, with its main variables being the acid concentration, temperature, time, and acid-to-material ratio.

The sulfuric acid concentration does not vary much from a typical value of 65% by mass [12, 13]. The temperature employed can range from room temperature to 70°C, while the reaction time can vary from 30 minutes to 12 hours, depending on the temperature, with the space between 30 and 60 minutes being the most frequent [14, 15]. As for the ratio of acid to raw material, the variations are from 10 to 20 ml/g [13, 15].

The dispersion characteristics of NCCs in the aqueous system depend on the type of acid used in the hydrolysis process [2]. NCCs prepared with sulfuric acid were shown to be more stable in aqueous suspensions than NCCs prepared with hydrochloric acid, which is due to the electrostatic repulsion caused by the presence of sulfate groups on their surface [6, 11, 16].

On the other hand, although NCC isolated by hydrolysis with hydrochloric acid do not form stable suspensions, they are thermally more stable, due to the absence of sulfate groups on the surface of cellulose, whose presence can interfere in the process of cellulose degradation [17]. This occurs because the incorporation of sulfate groups on the surface of cellulose after hydrolysis has a catalytic effect on its thermal degradation reactions.

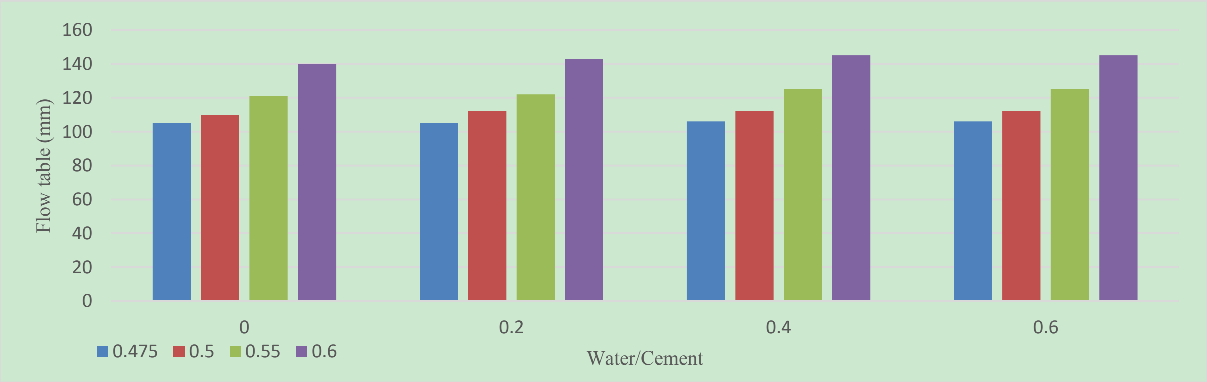
Another factor still little observed by researchers is the procedure used to stop the hydrolysis process, regardless of the type of acid used. Some studies show that water is added directly to the acid solution containing the nanocrystals in order to stop the hydrolysis before centrifugation and dialysis [18-23]. Other studies show that water is not added directly, only follow the centrifugation and dialysis steps after finishing the hydrolysis time [2, 12, 24, 25].

In addition to crystallinity, the aspect ratio (L/D) of NCCs is a crucial parameter that has a remarkable influence on the reinforcing ability of the nanoparticle when incorporated into a polymer matrix. Some publications have shown that as well as crystallinity, a large aspect ratio confers greater capacity for mechanical reinforcement in polymeric matrices [8, 20, 26, 27]. Therefore, the acid hydrolysis conditions must be carefully studied and controlled in order to obtain a material with the desired morphology.

2.3 Nanocrystals as Reinforcement for Mortar

The addition of nanocrystals in the composition of mortar can improve the strength of its structure, leaving it in a similar manner to concrete, without changing the workability and density of its composition.

Mazlan, Din, Tokoro, and Ibrahim (2016) conducted a study that addresses the use of cellulose nanocrystals (NCC) in liquid state as an additive to mortar. Mortars with different water/cement ratios (0.475; 0.50; 0.55 and 0.6) were tested and the percentages of NCC used in this work were 0%; 0.2%; 0.4% and 0.6% (Fig. 1).



	0.475	0.5	0.55	0.6
0	105	110	121	140
0.2	105	112	122	143
0.4	106	112	125	145
0.6	106	112	125	145

Fig. 1 Flow-table test for the different A/C ratios and different NCC percentages.

Source: Cellulose nanocrystals addition effects on cement mortar matrix properties.

Observing Fig. 1, the behavior of different percentages of NCC with different water/cement ratios the 0.5% ratio would be the most favorable, since it meets the requirements established by the standard used by ASTM C230, which states that the value of the creep table test should be between 110 and 115 mm.

Next, several compression tests of the different percentages of NCC at three cement curing times (7, 14, 28 days) were performed. The results obtained can be seen in Fig. 2.

The analysis of Fig. 2 allowed us to verify that the use of NCC increased the compressive strength of the mortar by about 40 to 45% compared to a mortar without cellulose.

Also Cao et al. (2014) conducted an intensive study on the insertion of NCC in mortars, making in this case an evaluation of its flexural strength.

In the experiment, 5 cm diameter cylinders of mortar with different percentages of NCC (0 up to1.5%) were made with a water/cement ratio of 0.35.

This study showed that the addition of NCC increased the flexural strength of the mortar by about 20 to 30%.

3. Methodology

3.1 Obtaining Cellulose Nanocrystals From Bamboo

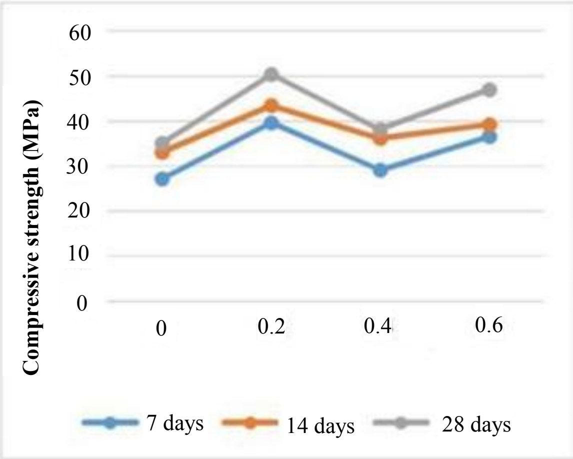


Fig. 1 Compression test results for different curing times.

Source: Cellulose Nanocrystals Addition Effects on Cement Mortar Matrix Properties.

To obtain the NCC of bamboo fiber (*unidentified species/genus*) two chemical processes are used: first, the alkaline treatment — with a 10% sodium hydroxide (NaOH) or 25% potassium hydroxide (KOH) solution — and second, the acid hydrolysis — carried out with sulfuric acid (H_2SO_4) diluted to a concentration of 65% or hydrochloric acid (HCl) 4M — described below.

The bamboo fiber was subjected to an alkaline treatment for two hours in 10% NaOH aqueous solution (10 g NaOH for every 90 g distilled water) (Fig. 3). After the two hours it was washed with deionized water to neutrality and then oven dried for 24 hours (Fig. 4);

Hydrolysis with H_2SO_4 was performed with 10 g of bamboo fiber for every 100 g of aqueous sulfuric acid solution at 65% concentration at 55°C for 30 min in a water bath (Fig. 5 and Fig. 6);

1) After completion of the reaction time, hydrolysis was stopped by adding an equal volume of ice-cold deionized water;

Fig. 3 Alkaline treatment of bamboo.

Fig. 4 Bamboo washing until neutralizing.

Fig. 5 Acid hydrolysis with H_2SO_4.

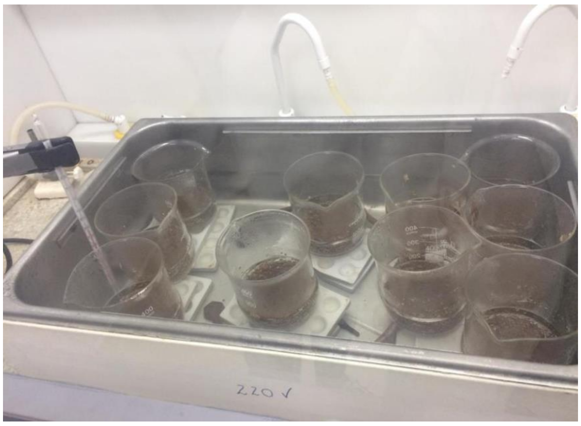


Fig. 6 H_2SO_4 solution in a water bath.

2) The excess sulfuric acid was removed by six cycles of centrifugation of 15 min duration at a frequency of 400 rpm;

At each cycle the supernatant was discarded and replaced by the same volume of deionized water until a cloudy dispersion was obtained (condition in which the nanocrystals are suspended) (Fig. 7);

The nanocrystal suspensions were neutralized by adjusting their pH with the addition of NaOH and using a pH meter to accurately measure until the pH stabilized at 7 (Fig. 8).

It was believed in obtaining the nanocrystals with the bamboo fiber, because according to Taipina (2012) [2], it was concluded that the nanocrystals would be the turbid dispersion that is suspended after the centrifugation process.

And for a better analysis the nanocrystals should be submitted to a Raman Spectroscopy, equipment that in a few seconds provides the chemical and structural information of the obtained material, thus allowing its identification.

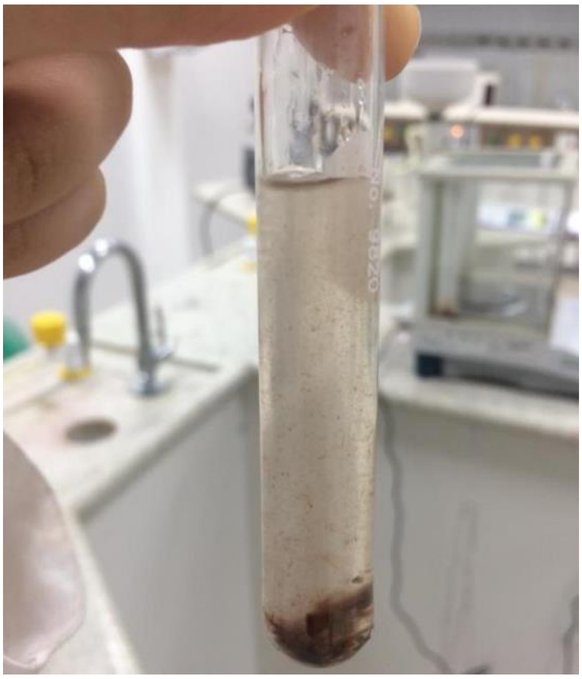


Fig. 7 Turbid dispersion (the nanocrystals become suspended).

Fig. 8 Neutrality using pH meter.

3.1 Mortar

Mortar is one of the most used cementitious compounds in the construction industry and, being mortar formed by the mixture of cement, fine aggregates and water, with or without the incorporation of adjuvants and additions, developing its properties by cement hydration.

The mortar mix used in this study was (1: 1.3: 1.7: 0.45: 0.2). The mortar composition is presented in Table 1.

Table 1 Weight of components per m^3 of mortar.

Mortar components	Cement CPV-ARI (kg/m^3)	Fine sand (kg/m^3)	Medium Sand (0.5 kg/m^3)	Water (kg/m^3)	Nanocrystals (ml/m^3)
	0.624	0.811	1.060	0.280	100

3.1.1 Cement

In the present study, high initial strength Portland cement (CP V–ARI) was used, whose main characteristic is to reach high strength in the first days of application. The development of high initial strength is achieved by using a different dosage of limestone and clay in the clinker production, as well as by finer grinding the cement, so that, when reacting with water, it acquires high strength, with greater speed. The clinker is the same used for the production of conventional cement, but it remains in the mill for a longer time. The cement continues to gain resistance until the 28th day, reaching higher values than the others, providing a higher yield.

3.1.2 Mortar Production

The mortar was produced in sequence. Fig. 9 shows the mortar obtained and its consistency. Cylindrical specimens were used. Four specimens with NCC and four specimens without NCC (control) were molded.

The specimens were kept for 24 hours in a laboratory environment, so that they acquired enough hardening (setting) to be unmolded and transported to the curing zone. The type of curing was in an environment with controlled temperature and humidity and the curing period was 12 days.

3.1.3 Strength Testing

In order to determine the resistant capacity of mortars under uniform compression stress, the mortars under study were submitted to a uniaxial compression test. This objective was achieved by taking the specimens to failure, recording the last load they resisted (Table 2).

Fig. 9 Mortar consistency.

Table 2 Resistance test result.

Portland cement: CP V-ARI **Assembly date:** 01/11/2018, **Test date:** 13/11/2018 **Age:** 12 days					
Specimen Test nº	Diameter D (cm)	Area S (cm^2)	Burst load P (kgf)	Compressive Strength	
				kgf/cm²	MPa
1 w/nano	5,042	19.97	6580	329.49	32.95
2 w/nano	5,028	19.86	6640	334.34	33.43
3 w/nano	5.01	19.71	7050	357.69	35.77
4 w/nano	4,992	19.57	6780	346.45	34.64
5 wo/nano	5,014	19.74	4900	245.37	24.54
6 wo/nano	5,017	19.77	5370	271.62	27.16
7 wo/nano	5,017	19.77	4040	204.35	20.44
8 wo/nano	4,994	19.59	5280	269.53	26.95

After the tests were performed, the arithmetic mean of the compressive strength and the maximum relative deviation (MRD) of both the specimens with the cellulose nanocrystals and the control specimens were calculated.

(1) Arithmetic mean of compressive strength and MRD of specimens with cellulose nanocrystals

Arithmetic mean of compressive strength = $\frac{32.95+33.43+35.77+34.64}{4}$ = 34.20 MPa

$$\text{MRD} = \frac{|\ 34.20-32.95|}{34.20} \times 100 = 3.7\%$$

As the MRD does not exceed 6%, the arithmetic mean of the compressive strength of the mortar with NCC can be considered equal to 34.20 MPa, whose rupture can be seen in Fig. 10.

(2) Arithmetic mean of compressive strength and MRD of specimens without cellulose nanocrystals

Arithmetic mean of compressive strength = $\frac{24.54+27.16+20.44+26.95}{4}$ = 24.77 MPa

$$\text{MRD} = \frac{|\ 24.77-20.44|}{24.77} \times 100 = 17.5\%$$

As the MRD exceeded 6% and this cannot occur, because it means that some specimen does not match the mean, a value is discarded, and the new arithmetic mean and the new maximum relative deviation are recalculated.

Arithmetic mean of compressive strength = $\frac{24.54+27.16+26.95}{3}$ = 26.22 MPa

$$\text{MRD} = \frac{|\ 26.22-24.54|}{26.22} \times 100 = 6.0\%$$

With the new MRD recalculated and not exceeding 6%, it can be said that the arithmetic mean of the Compressive Strength of the mortar without NCC is equal to 26.22 MPa, whose rupture can be seen in Fig. 11.

Fig. 10 Rupture of specimens with cellulose nanocrystals.

Fig. 11 Rupture of specimens without cellulose nanocrystals.

In conclusion, after the test it was possible to conclude that the addition of NCC to the mortar mix increased the compressive strength by 30.4%.

4. Conclusion

The research addressed the use of NCC obtained from bamboo and inserted into the mortar composition, which has the objective of increasing the strength of the material used in the study.

Cao et al. (2014) conducted a study concluding that the insertion of NCC in the mortar composition increases about 20 to 30% of its compressive strength. Also Mazlan et al. (2016) evaluated the compressive strength, obtaining a result that showed that the introduction of NCC in mortars increased about 40 to 45% of its strength.

On the other hand, the result obtained in the present work, using bamboo as a source for obtaining NCC, showed an increase of about 30% of its compressive strength.

A comparison of the various results obtained in the mentioned researches shows that strength can vary according to the material used, the type of chemical treatment, the amount of NCC inserted, and other factors that interfere in the final result.

It can be said that the insertion of NCC in the composition of mortar, regardless of how it is obtained, can improve its structure in relation to compressive strength, because all the results obtained are satisfactory.

Therefore, the research showed that nanotechnology is present in our reality and glimpses a promising future, regardless of the branch that it is used in, being able to improve the performance of construction materials which is of paramount importance for the area of civil engineering, showing that its use in cementitious materials is a technological and sustainable alternative.

References

[1] D. J. Silva and M. L. O. D'Almeida, Cellulose whiskers, *O Papel* 70 (2009) 34-52.

[2] M. A. S. A. Samir, F. Alloin, J. Sanches, N. E. Kissi and A. Dufresne, Preparation of cellulose whiskers reinforced nanocomposites from an organic medium suspension, *Macromolecules* 37 (2004) 1386-1393.

[3] J. Shi, S. Q. Shi, H. M. Barnes and C. U. Jr. Pittman, A chemical process for preparing cellulosic fibers hierarchically from kenaf bast fibers, *Bioresources* 6 (2011) 879-890.

[4] B. L. Peng, N. Dhar, H. L. Liu and K. C. Tam, Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective*, The Canadian Journal of Chemical Engineering* 9999 (2011) 1-16.

[5] A. Alemdar and M. Sain, Isolation and characterization of nanofibers from agricultural residues — Wheat straw and soy hulls, *Bioresource Technology* 99 (2008) 1664.

[6] R. Moon, A. Martine, J. Nairn, J. Simonsen and J. Youngblood, Cellulose nanomaterials review: structure, properties and nanocomposite, *Chemical Society Review* 40 (2011) 3941-3994.

[7] I. Kvien, B. S. Tanem and K. Oksman, Characterization of cellulose whiskers and their nanocomposites by atomic force and electron microscopy, *Biomacromolecules* 6 (2005) 3160-3165.

[8] A. Dufresne, Interfacial phenomena in nanocomposites based on polysaccharide nanocrystals, *Composite Interfaces* 10 (2003) 369-387.

[9] A. C. O'Sullivan, Cellulose: the structure slowly unravels, *Cellulose* 4 (1997) 173-207.

[10] M. Angle's and A. Dufresne, Plasticized starch/tunicin whiskers nanocomposites 1 structural analysis, *Macromolecules* 33 (2000) 8344.

[11] Y. Habibi, L. A. Lucia and O. J. Rojas, Cellulose nanocrystals: Chemistry, selfassembly, and applications, *Chemical Reviews* 110 (2010) 3479-3500.

[12] Y. Habibi, L. Foulon, V. Aguié-Béghin, M. Molinari and R. Douilllard, Langmuir-Blodgett films of cellulose nanocrystals: Preparation and characterization, *Journal of Colloid and Interface Science* 316 (2007) 388-397.

[13] B. Jean, F. Dubreuil, L. Heux and F. Cousin, Structural details of cellulose nanocrystals/polyeletrolytes multilayers probed by neutron reflectivity and AFM, *Langmuir* 9 (2008) 57.

[14] S. Hafraoui, Y. Nishiyama, J. L. Putaux, L. Heux, F. Dubreuil and C. Rochas, The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose, *Biomacromolecules* 9 (2008) 57.

[15] P. Podsiadlo, S. Y. Choi, B. Shim, J. Lee, M. Cuddihy and N. Kotov, Molecularly engineered

nanocomposites: Layer-by-layer assembly of celulose nanocrystals, *Biomacromolecules* 6 (2005) 2914.

[16] S. Kalia, A. Dufresne, B. M. Cherian, B. S. Kaith, L. Avérous, J. Njuguna and E. Nassiopoulos, Cellulose-based bio- and nanocomposites: A review, *International Journal of Polymer Science* (2011) 1-35.

[17] M. Roman and W. T. Winter, Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose, *Biomacromolecules* 5 (2004) 1671.

[18] M. M. K. Haafiz, A. Hassan, Z. Zakaria and I. M. Inuwa, Isolation and characterization of cellulose nanowhiskers from oilpalm biomass microcrystalline cellulose, *Carbohydrate Polymers* 103 (2014) 119-125.

[19] R. M. dos Santos, W. P. Flauzino Neto, H. A. Silvério, D. F. Martins, N. O. Dantas and D. Pasquini, Cellulose nanocrystals from pineapple leaf, a new approach for the reuse of this agro-waste, *Industrial Crops and Products* 50 (2013) 707-714.

[20] H. A. Silvério, W. P. Flauzino Neto, N. O. Dantas and D. Pasquini, Extraction and characterization of cellulose nanocrystals from corncob for application as reinforcing agent in nanocomposites, *Industrial Crops and Products* 44 (2013) 427-436.

[21] S. M. L. Rosa, N. Rehman, M. I. G. de Miranda, S. M. B. Nachtigall and C. I. D. Bica, Chlorine-free extraction of cellulose from rice husk and whisker isolation, *Carbohydrate Polymers* 87 (2012) 1131-1138.

[22] S. Belbekhouche, J. Bras, G. Siqueira, C. Chappey, L. Lebrun, B. Khelif, S. Marais and A. Dufresne, Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films, *Carbohydrate Polymers* 83 (2008) 1740-1748.

[23] E. M. Teixeira, T. J. Bondancia, K. B. R. Teodoro, A. C. Corrêa, J. M. Marconcini and L. H. C. Mattoso, Sugarcane bagasse whiskers: extraction and characterizations, *Industrial Crops and Products* 33 (2011) 63-66.

[24] G. Siqueira, J. Bras, N. Follain, S. Belbekhouche, S. Marais and A. Dufresne, Thermal and mechanical properties of bio-nanocomposites reinforced by Luffa cylindrica cellulose nanocrystals, *Carbohydrate Polymers* 91 (201) 711-717.

[25] X. Cao, C. Xu, Y. Wang, Y. Liu, Y. Liu and Y. Chen, New nanocomposite materials reinforced with cellulose nanocrystals in nitrile rubber, *Polymer Testing* 32 (2013) 819-826.

[26] S. J. Eichhorn, A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona and S. J. Rowan, Review: Current international research into cellulose nanofibres and nanocomposites, *Journal of Materials Science* 45 (2010) 1-33.

[27] M. Martínez-Sanz, A. Lopez-Rubio and J. M. Lagaron, Optimization of the nanofabrication by acid hydrolysis of bacterial cellulose nanowhiskers, *Carbohydrate Polymers* 85 (2011) 228-236.