ENVIRONMENTALLY FRIENDLY LIGNOCELLULOSE NANOFIBRES FROM BARLEY STRAW

MONTSERRAT JUÁREZ,[*] RAFAEL SÁNCHEZ,[*] EDUARDO ESPINOSA,[*]
JUAN DOMÍNGUEZ-ROBLES,[*] ISABEL BASCÓN-VILLEGAS[*,**] and
ALEJANDRO RODRÍGUEZ[*]

[*]*Chemical Engineering Department, Faculty of Science, University of Córdoba, Building Marie Curie,*
Campus of Rabanales, Córdoba, Spain
[**]*Food Science and Technology Department, University of Córdoba, Building Charles Darwin,*
Campus of Rabanales, Córdoba, Spain
✉ *Corresponding author: Rafael Sánchez, rafael.sanchez@uco.es*

This paper is dedicated to the 70th anniversary
of Acad. Bogdan C. Simionescu
in acknowledgement of his major contribution
to the quality of the research in Romania.

Due to the environmental awareness in our society, this paper explores the possibility of obtaining high value-added products from agricultural wastes, such as cereal straw. The raw material chosen for this study was barley straw, which was pulped by a Specel® pulping process. This process uses soda (7% on oven dried material) as reagent. The chemical composition of both barley straw and unbleached pulp was determined through different parameters (alcohol extractives, α-cellulose, hemicelluloses, lignin and ash). Lignocellulose nanofibres (LCNF) were obtained by subjecting the pulp to mechanical pretreatment, followed by a high-pressure homogenizer step. The produced LCNF were characterized with regard to the nanofibrillation yield, viscosity, cationic demand and carboxyl content. The LCNF were added to a papermaking slurry based on virgin eucalyptus (bleached Kraft hardwood pulp), in amounts of 1, 3 and 5% as reinforcement. Paper sheets were made and characterized with regard to their mechanical properties. The results indicated that paper strength was improved after the addition of LCNF.

Keywords: barley straw, cellulose pulp, lignocellulose nanofibres, papermaking, paper strength, PFI-beating

INTRODUCTION

The concept of bioeconomy is gaining increasing importance and one of the pillars on which this concept is based is the effectiveness with which natural resources are exploited. Natural biomass constitutes an important source of lignocellulosic materials, which can be harnessed efficiently by separating different components (cellulose, lignin and hemicelluloses) and using them in applications with high added value.

The largest source of renewable lignocellulosic raw material in the world is cereal straw. The world cereal production was close to 2607.5 million tons in 2016, and the barley production accounted for 5.7% of the total (148.7 million tons).[1] From this high production of barley worldwide, a huge amount of by-products or residues are obtained during the processing of barley grain. Thus, a large amount of barley straw results and could be used to obtain products with high added value. Nevertheless, nowadays this agricultural residue is mainly burned in the fields or used as cattle feed. It must be considered that 530 kg of straw results from each ton of grain obtained.[2,3]

In this work, barley straw was pulped using a semichemical process known as Specel® process. This pulping process was investigated in preliminary studies, which showed that the optimum conditions for pulping cereal straw (100 °C, 7% NaOH o.d.m., 150 minutes of cooking time and 10 liquid/solid ratio) led to good results with regard to the mechanical properties of paper sheets.[4] The Specel® process uses soda as a single reagent, so it is an environmentally friendly process, unlike the processes used in the paper industry. The procedure is a very versatile one, which can be suitable to obtain both large and small productions. This feature is important when considering the objective of

achieving a sustainable economy, because it is essential that this technology can be implemented in small industries and in areas near to the source of raw materials.

From cellulosic fibres, it is possible to obtain cellulose nanofibres (CNF) or lignocellulose nanofibres (LCNF), which can be used as an additive to the papermaking slurry to achieve an increase in the physical properties of paper.[5-8] The addition of LCNF in the papermaking process improves the formation of hydrogen bonds between fibres, and this increases the paper strength and density, as well as decreases its porosity.

Nanofibres can be produced by three different pretreatments, which are applied to facilitate the mechanical stage of the process and to reduce the energy consumption. The first is a chemical process, which consists of an oxidation with a catalyst (TEMPO), which in turn causes an electrostatic repulsion due to the induction of negative charges on the carboxylate groups at the surface of the fibrils.[9] The second is a mechanical pretreatment, which uses high-speed mechanical beating to individualize the fibres before the homogenization step.[10-13] Finally, the third pretreatment is an enzymatic hydrolysis that employs β-1,4-endoglucanases, which randomly hydrolyse accessible intramolecular β-1,4-glucosidic bonds in cellulose chains, exposing the individual cellulose polysaccharide chains.[14,15] From the three pretreatments mentioned above, the TEMPO process presents the best results, but it is expensive, since the reagents used are costly, making this process not competitive. The enzymatic process is also an expensive one and it does not yield very good results. The mechanical process does not use any chemical reagent and presents satisfactory results, and that is why this pretreatment has been selected to perform this work.

Usually, cellulose nanofibres are obtained from bleached pulp, which increases the cost of the process because higher consumption of energy and chemical reagents. However, in this work, nanofibres were obtained from unbleached barley straw pulp, which makes the process more economical and environmentally friendly. Moreover, eliminating the bleaching step means less degradation of the fibres.

In this paper, lignocellulose nanofibres were obtained by mechanical pretreatment from unbleached barley straw pulp and added as reinforcement to bleached Kraft hardwood pulp (BKHP) for manufacturing paper sheets.

EXPERIMENTAL

Raw material

The barley straw used in this work was harvested in Alcalá la Real (Jaén, Spain) and was provided by local farmers. Once harvested, the barley straw was dried and kept in plastic bags at room temperature. A dried sample of barley straw was prepared according to TAPPI standard T-257 and characterized according to corresponding TAPPI standards to determine α-cellulose (T-9m54), lignin (T-203os61), holocellulose (T-222), ash (T-211), ethanol extractives (T-204), solubility in 1% soda (T-212) and solubility in hot water (T-257). The analyses for the chemical characterization were done in triplicate and the mean values were calculated.[16]

Pulping process and characterization of paper sheets

The barley straw was pulped in a 15 L reactor heated by an outer jacker heater and under stirring by rotating the reaction vessel *via* a motor, following the Specel® process. The pulping conditions wew as follows: 7% NaOH (oven dried material), 100 °C, 150 minutes and a liquid/solid ratio of 10:1. These conditions have been selected because of the similarity of the barley straw with other raw materials, such as wheat straw, and because this process was previously used at an industrial level to obtain cellulose pulp from wheat straw.[4]

After the pulping process, the cooked material was unloaded from the reactor, washed with water at room temperature to remove residual cooking liquor, and treated in a disintegrator at 1200 rpm for 30 minutes. Then, the pulp was treated by beating in a Sprout-Bauer refiner. Finally, the fiberised material was passed through a filter of 0.16 mm pore size to remove uncooked particles and was dried at room temperature. The pulp obtained was characterized according to TAPPI standards: beating degree (T-227), yield (gravimetric method), α-cellulose (T-9m54), lignin (T-203os61), holocellulose (T-222), ash (T-211), ethanol extractives (T-204), solubility in 1% soda (T-212) and solubility in hot water (T-257), Kappa number (T-236cm-85) and viscosity (T-230om-94).

In the final step, paper sheets were prepared from the barley straw pulp on an ENJO-F-39.71 according to TAPPI standard T205ps-95. The paper sheets were characterized by measuring the tensile index, burst index and tear index, following the corresponding TAPPI standards (T494om-96, T403om-97 and T414om-98, respectively).

Figure 1: Mechanical lignocellulosic nanofibres of barley straw

Preparation of mechanical lignocellulosic nanofibres (Mec-LCNF)

The lignocellulosic nanofibres were obtained by mechanical pretreatment, beating the barley pulp in a PFI beater (Metrotec), according to ISO standard 5264-2:2002, until a drainage rate of 90 ºSR was achieved.

Once the mechanical pretreatment was finished, the pulp was passed through a high-pressure homogenizer (PANDA GEA 2 K NITRO). In this process, nine passes through the homogenizer were performed, following the sequence described by Espinosa et al.[17]

Characterization of Mec-LCNF
Yield of nanofibrillated cellulose

The Mec-LCNF suspension was centrifuged in order to separate the fibrillated part from the partially or non-fibrillated materials. More precisely, a 0.1 wt% solid content suspension (Sc) was centrifuged at 4500 rpm for 30 minutes to separate the nanofibrillated material from the non-fibrillated fractions. The sediments (non-fibrillated fraction) were dried to a constant weight at 100 °C. The yield was calculated from the following relation:

$$Yield \% = \left(1 - \frac{Weight\ of\ dried\ sediments}{(Weight\ of\ diluted\ sample * \%SC)}\right) * 100 \qquad (1)$$

Optical transmittance

Optical transmittance is an indirect indicator of the nanofibrillation yield.[18] The Mec-LCNF suspensions were introduced into a quartz cuvette and the transmittance was measured from 400 to 800 nm, using a Lambda 25 UV Spectrometer. The spectrum of a cuvette filled with distilled water was used as reference.

Cationic demand

The cationic demand was determined by a Mütek PCD 05 particle charge detector. Following the methodology described by Espinosa et al.,[17] the cationic demand was calculate by the equation:

$$CD = \frac{\left(C_{Poly-D} * V_{Poly-D}\right) * (V_{Pes-Na} * C_{Pes-Na})}{W} \qquad (2)$$

where CD is the cationic demand (µeq g^{-1}), C_{Poly-D} = cationic polymer concentration (1 meq L^{-1}), C_{Pes-Na} = anionic polymer concentration (1 meq L^{-1}), V_{Poly-D} = used volume of cationic polymer and V_{Pes-Na} = used volume of anionic polymer and w = sample's dry weight.

Carboxyl content

The carboxyl content (CC) was determined using conductometric titration, as described by Besbes et al.[19] The Mec-LNFC samples (15 mg dried weight) were suspended in 15 mL of 0.01 M HCl solution. After stirring for 30 minutes, the suspension was titrated with 0.05 M NaOH. The titration curves showed three characteristic regions with two intersection points (V_1 and V_2). The first region corresponds to the excess of HCl, and the second one corresponds to the volume of NaOH required to neutralize the weak acidic (carboxylic) groups, and finally, the third region corresponds to the excess of NaOH. The volume of NaOH (mL) in the second region was used to determine the carboxyl content of the fibres:

$$CC = \frac{162\ (V_2 - V_1) * c}{w - 36(V_2 - V_1) * c} \qquad (3)$$

where c is the concentration of the NaOH (mol L^{-1}) solution and w is the oven-dry weight of cellulose (g). The results indicate the average mmols of -COOH groups per gram of Mec-LCNF.

Degree of polymerization

The intrinsic viscosity value was obtained according to UNE 57-039-92. An amount of 0.1 mg dried weight of sample was dissolved in cupriethylendiamine (1N). Three measurements for each sample were realized to determine the intrinsic viscosity at 25 °C and the mean values were calculated. The degree of polymerization was calculated using the following equation (Marx Figini):

$$DP\ (<950)\ DP = \left[\frac{\eta_s}{0.42}\right] DP\ (>950)\ DP^{0.76} = \left[\frac{\eta_s}{2.28}\right] \tag{4}$$

Production and characterization paper sheets

Paper sheets were made mixing bleached Kraft hardwood pulp (BKHP), which was kindly supplied by La Montañanesa (Spain), with barley Mec-LCNF. In this case, three percentages of nanofibres were used for the mixtures: 1%, 3% and 5% o.d.m., based on the findings of a previous study.[17] The mixtures were processed in a disintegrator with the following conditions: 3000 rpm for 30 minutes and 1.5% consistency.[20,21]

After the mixture was disintegrated during 30 min, 1% solution of cationic starch (Vector SC 20157) and colloidal silica (LUDOX HS-40 colloidal silica) were added at 0.5 and 0.8%, expressed on dry BKHP, respectively. These retention agents were added under soft agitation of the suspension at 1% consistency for 30 minutes. This step is necessary in order to avoid LCNF loss during the dewatering process. The LCNF presents an anionic charge, so a cationic element is needed to be used as microparticle retention system.[22]

After the retention of LCNF and cellulose, paper sheets with LCNF were obtained in a sheet former (ENJO-F-39.71) according to ISO standard 5269-2, and conditioned in a conditioning chamber at 25 °C and 50% humidity for 48 hours, before the mechanical test was performed. Then, the mechanical characteristics (tensile index, burst index and tear index) of the paper sheets were measured, following TAPPI standards: T494om-96, T403om-97 and T414om-98, respectively.[16]

RESULTS AND DISCUSSION
Raw material characterization

The results obtained for the chemical characterization of barley straw are shown in Table 1, along with the values found in the literature for other raw materials.[4,24]

The barley straw presents a similar composition to that of other alternative raw materials, especially to that of wheat straw, which is used in paper making at an industrial level. Despite the high ash content of the barley straw, which could cause corrosion problems, this agricultural residue is suitable for the Specel® process. This statement is based on the equipment and the operating conditions employed, which minimize the appearance of inorganic particles (100 °C). Lignin (16.3%) and α-cellulose (34.0%) contents are lower than for the rest of the raw materials studied, which makes the barley straw a less hard material and therefore the cooking treatment does not have to be so aggressive to isolate the cellulose. The content of hemicelluloses is lower in comparison with that of other alternative raw materials, but it is the same as the content of hemicelluloses in eucalyptus and higher than that of pine.

Chemical characterization of pulp

Table 2 shows the results obtained from the chemical characterization of the unbleached barley straw pulp, in comparison with those for other alternative raw materials, including different unbleached cereal straw pulps.[4,26]

Table 1
Chemical characterization of barley straw and different alternative raw materials

Raw material	Ethanol extractives (%)	α-Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
Barley straw	8.1	34.0	27.7	16.3	9.49
Oat straw[4]	6.4	37.9	37.7	16.6	7.00
Corn straw[4]	6.8	44.0	30.7	18.2	5.95
Rapeseed straw[4]	7.9	37.0	36.5	17.2	6.38
Wheat straw[4]	5.2	39.7	30.6	17.7	7.72
Pinus pinaster[23,24]	2.57	55.92	13.7	26.2	0.54
Eucalyptus globulus[23,24]	1.15	53.00	27.7	19.9	0.60

Table 2
Chemical characterization of barley straw pulp and of those from other alternative raw materials

Raw material	Ethanol extractives (%)	α-Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
Barley straw	1.31	69.9	18.3	10.9	2.64
Oats straw[4]	0.89	69.2	16.4	13.1	2.50
Corn straw[4]	0.86	71.0	20.0	8.9	1.36
Rapeseed straw[4]	0.82	62.7	10.5	21.6	2.33
Wheat straw[4]	3.37	73.0	16.3	2.80	10.90
Bleached Kraft eucalyptus pulp (BKHP)[26]	0.53	77.4	16.3	6.61	0.13
Mechanical pine pulp[26]	2.59	58.4	22.8	22.6	0.654

Table 3
Characterization of cellulose pulps

Raw material	Yield (%)	Beating degree (ºSR)	Kappa number	Viscosity (mL/g)
Barley straw	45.2	22	57.5	516
Oats straw[4]	66.9	36	71.5	465
Corn straw[4]	65.5	47	56.7	996
Rapeseed straw[4]	63.1	29	115.1	184
Wheat straw[4]	70.0	28	38.6	536

Some significant differences can be observed among the pulps. The content of lignin, α-cellulose and hemicelluloses in the barley straw cellulosic places it on a middle position among the values of other cellulosic cereal straw pulps. Comparing the barley straw pulp with wood pulps (eucalyptus and pine), it is observed that the extractives content is higher in barley than in the bleached eucalyptus Kraft pulp, but smaller than in the mechanical pine pulp. The contents in α-cellulose, hemicelluloses and lignin present the same trend as the extractives. Finally, the ash content is greater in barley pulp than in the two wood pulps.

Table 3 shows the values of the yield, beating degree, Kappa number and viscosity for the cellulose pulp of the barley straw and those of other raw materials.[4]

The yield of the cellulose pulp of the barley straw is the lowest (45.2%), this is because the content of the extractives is higher than for the other raw materials, and these are removed in the pulping process. The same is valid for the beating degree, *i.e.* it is the lowest (22 ºSR). Kappa number is a measure of delignification that the raw material has undergone. High values of kappa number imply that the pulp may not be well suited for bleaching because of the high cost involved. The pulp of the barley straw presented intermediate values of kappa number (57.5), between that of rapeseed, which is the highest (115.1) and that of wheat, which is the lowest (38.6).

Also, the barley straw pulp presented a viscosity value of 516 mL/g, which is slightly lower than the value of the wheat straw pulp (536 mL/g). In general, the viscosity values in all the cases were low.

Characterization of paper sheets

Table 4 shows the results obtained for the mechanical properties of the paper sheets prepared from barley straw cellulose pulp and from other wood raw material.[26]

The values obtained for the barley straw are higher than those obtained for the bleached Kraft eucalyptus pulp and are much higher than those obtained for mechanical pine pulp, which is used to mix with the virgin pulp in the manufacture of moulded pulp and thus reduce production costs because this pulp is cheaper. Therefore, the barley straw pulp can be considered as a suitable alternative to produce paper and paperboard.

Characterization of LCNF

Table 5 shows the values of the characterization of the LCNF and these values are compared with those obtained for other raw materials.[27]

Table 4
Characterization of paper sheets

Raw material	Tensile index (Nm/g)	Breaking length (m)	Burst index (KPa/g)	Tear index (mN²/g)
Barley straw	37.0	3778	2.165	5.134
Bleached Kraft eucalyptus pulp (BKHP)[26]	20.89	2132	1.061	4.370
Mechanical pine pulp[26]	6.15	627	0.256	0.892

Table 5
Characterization of LCNF

LNFC	Yield (%)	Transmittance (%)	Carboxyl content (μmols/g)	Cationic demand (μeq/g)	Diameter* (nm)	Length** (μm)
Mec-LCNF Barley	20.16	11.96	57.93	146.23	59.52	2.48
Mec-LCNF Wheat[27]	55.6	75.00	53.41	441.06	13.23	3.72
Mec-LCNF Corn[27]	25.80	21.00	-	144.70		-
Mec-LCNF Oats[27]	30.07	15.00	48.78	149.97		-

*Caculated using cationic demand and carboxyl content;[17] **Calculated from length (nm) = 4.286·DP − 757.[28]

Table 6
Characterization of paper sheets

Raw material	Tensile index (Nm/g)	Breaking length (m)	Burst index (KPa/g)	Tear index (mN²/g)
BKHP	20.89	2132.0	1.061	4.370
BKHP + 1% LCNF barley	26.92	2747.2	2.098	7.137
BKHP + 3% LCNF barley	29.86	3047.7	2.701	7.394
BKHP + 5% LCNF barley	42.91	4378.8	4.009	7.722

The values obtained for the Mec-LCNF of barley straw were lower than those obtained for wheat straw, except for cationic demand. This indicates that the nanofibres of barley straw have a greater specific surface area than the nanofibres of wheat straw. The specific surface area is related to the size of the nanofibres. Thus, the greater cationic demand is related to a greater specific surface, and therefore, a smaller diameter of the nanofibres.[29] Considering this, the barley straw Mec-LNFC presents a greater size, compared with the LCNF obtained from wheat straw.

Light transmittance is wavelength-dependent and it is related to the nanofibre size due to the Rayleigh scattering effect.[30] Hence, if the LCNF presents a larger size, it scatters light less, resulting in a lower transparency degree.[29] For this reason, this parameter can be used as an indirect indicator of the nanofibrillation yield – a lower nanofibrillation yield results in higher scattering. In our case, barley straw LNFC presented lower transmittance than the wheat straw LNFC, which is corroborated by its lower yield (20.16%).

Reinforcement effect on papermaking slurries

The LCNF are suitable for use as reinforcement in papermaking, as they form bonds with other fibres, increasing the strength of paper sheets. To check the viability of the usage of barley straw LCNF as a reinforcement agent in papermaking slurries, the evolution of physical properties of the paper sheets was studied by adding different percentages of the LCNF (1, 3 and 5%) to bleached Kraft hardwood pulp (BKHP). The results obtained are shown in Table 6. This table shows that the values of all the properties increase significantly with increased barley straw LCNF percentage. The strengthening effect of LCNF to the properties of paper sheets may be explained by two possible mechanisms: in the first one, LCNF act as an adhesion promoter by bridging adjacent fibres and favouring the fibre–fibre bonding; in the second one, LCNF may generate a different network embedded among larger fibres, which contributes to boosting the load-bearing capacity of the paper.[31]

CONCLUSION

Barley straw soda pulp was used to produce lignocellulose nanofibres (LCNF) by mechanical pretreatment, followed by high pressure homogenization. These LCNF were then applied as a reinforcement agent in papermaking. The results obtained showed that all the tested mechanical properties of the paper sheets increased markedly. Therefore, it can be concluded that the LCNF obtained from barley straw are suitable for being used as reinforcement in papermaking.

REFERENCES

[1] FAO 2017, httsp://www.fao.org/worldfoodsituation/csdb/es/, accessed November 2017.

[2] A. Rodríguez, R. Sánchez, A. Requejo and A. Ferrer, *J. Clean Prod.*, **18**, 1084 (2010).

[3] F. Vargas, E. Domínguez, C. Vila, A. Rodríguez and G. Garrote, *Energ. Fuels*, **30**, 8236 (2016).

[4] F. Vargas, Z. González, R. Sánchez, L. Jiménez and A. Rodríguez, *BioResources*, **7**, 4161 (2012).

[5] F. W. Brodin, Ø. W. Gregersen and K. Syverud, *Nord. Pulp Pap. Res.*, **29**, 156 (2014).

[6] I. González, S. Boufi, M. A. Pélach, M. Alcalá, F. Vilaseca *et al.*, *BioResources*, **7**, 5167 (2012).

[7] T. Taipale, M. Österberg, A. Nykänen, J. Ruokolainen and J. Laine, *Cellulose*, **17**, 1005 (2010).

[8] Ø. Eriksen, K. Syverud and Ø. Gregersen, *Nord. Pulp Pap. Res.*, **23**, 299 (2008).

[9] T. Saito, S. Kimura, Y. Nichiyama and A. Isogai, *Biomacromolecules*, **8**, 2485 (2007).

[10] M. Nogi, S. Iwamoto, A. N. Nakagaito and H. Yano, *Adv. Mater.*, **21**, 1595 (2009).

[11] K. Spence, R. A. Venditti, O. J. Rojas, Y. Habibi and J. J. Pawlak, *Cellulose*, **18**, 1097 (2011).

[12] H. Yousefi, M. Faezipour, T. Nishino, A. Shakeri and G. Ebrahimi, *Polym. J.*, **43**, 559 (2011).

[13] E. Afra, H. Yousefi, M. H. Hadilam and T. Nishino, *Carbohyd. Polym.*, **97**, 725 (2013).

[14] M. Henriksson, G. Henriksson, L. A. Berglund and T. Lindström, *Eur. Polym. J.*, **43**, 3434 (2007).

[15] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola *et al.*, *Biomacromoleecules*, **8**, 1934 (2007).

[16] TAPPI standards, TAPPI Test Methods, 2002.

[17] E. Espinosa, Q. Tarrés, M. Delgado-Aguilar, I. González, P. Mutjé *et al.*, *Cellulose*, **23**, 837 (2016).

[18] M. Delgado-Aguilar, I. González, Q. Tarrés, M. A. Pélach, M. Alcalá *et al.*, *Ind. Crop. Prod.*, **86**, 295 (2016).

[19] I. Besbes, S. Alila and S. Boufi, *Carbohyd. Polym.*, **84**, 975 (2011).

[20] M. Alcalá, I. González, S. Boufi, F. Vilaseca and P. Mutjé, *Cellulose*, **20**, 2909 (2013).

[21] M. Delgado-Aguilar, I. González, Q. Tarrés, M. Alcalá, M. A. Pélach *et al.*, *BioResources*, **10**, 5345 (2015).

[22] X. Xu, J. Zhou, L. Jiang, G. Lubineau, Y. Chen *et al.*, *Int. J. Biol. Macromol.*, **60**, 241 (2013).

[23] A. Rodríguez, L. Serrano, A. Moral and L. Jiménez, *Biochem. Eng.*, **42**, 243 (2008).

[24] A. Rodríguez, A. Moral, L. Serrano, J. Labidi and L. Jiménez, *Bioresour. Technol.*, **99**, 2881 (2008).

[25] E. Espinosa, J. Dominguez-Robles, R. Sánchez, Q. Tarrés and A. Rodríguez, *Cellulose*, **24**, 2605 (2017).

[26] E. Espinosa, R. Sánchez, R. Otero, J. Domínguez-Robles and A. Rodríguez, *Int. J. Biol. Macromol.*, **103**, 990 (2017).

[27] R. Shinoda, T. Saito, Y. Okita and A. Isogai, *Biomacromolecules*, **13**, 842 (2012).

[28] I. Besbes, M. R. Vilar and S. Boufi, *Carbohyd. Polym.*, **84**, 1198 (2011).

[29] Q. Meng, S. Fu and L. A. Lucia, *Carbohyd. Polym.*, **144**, 187 (2016).

[30] S. Boufi, I. González, M. Delgado-Aguilar, Q. Tarrés, M. A. Pélach *et al.*, *Carbohyd. Polym.*, **154**, 151 (2016).