A New Method for Developing Industrially Viable Nanocrystalline Cellulose-based Nanocomposites via Melt Compounding

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ABSTRACT: Due to their high crystallinity and aspect ratio, bacterial cellulose nanowhiskers (BCNW) represent an appealing choice for the development of fully biobased nanocomposite materials with high barrier performance. However, their strong tendency to self-associate, together with their highly hydrophilic character, has restricted the production of nanocomposites containing cellulose nanowhiskers by industrial processing techniques such as melt compounding.

This article presents an overview of the latest published results carried out within our group and also in other relevant literature, which have led to the development of an efficient strategy for the incorporation of highly dispersed BCNW by melt compounding through the use of electrohydrodynamic processing as a vehicle for the pre-incorporation of relatively high loadings of BCNW. First, a method for the production of highly crystalline and thermally stable BCNW was developed. These BCNW were incorporated into electrospun fibers, optimizing the process in terms of nanofiller dispersion and degree of incorporation. Finally, these hybrid fibers were used as masterbatches for the production of melt compounded nanocomposites, comparing their morphology and barrier properties with the conventional method of adding freeze-dried nanowhiskers. This method was proven to be effective for both hydrophilic and hydrophobic matrices and, thus, it provides a feasible route for the development of high barrier biobased materials.

KEYWORDS: Bacterial cellulose, nanowhiskers, nanocomposites, melt compounding, electrohydrodynamic, barrier properties

1 INTRODUCTION

Nowadays, polymeric materials are widely used in food packaging applications due to their appealing properties compared with other conventional packaging materials, and the possibility of adapting these to the product requirements within a certain range. On the other hand, there are two major issues associated with the use of polymeric materials for food packaging, which are the permeability of polymers to the transport of low molecular weight compounds and the lack of renewability of the conventional petroleum-based polymers. The introduction of biobased polymers or biopolymers throughout the industry is believed to solve this second concern.

Amongst the several biopolymers developed and studied during the last years, biopolyesters have attracted special interest as they present promising properties and can be processed by conventional industrial equipment. In particular, poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) have been extensively studied. While PLA is produced from L- and D-lactic acid, which can be derived from fermentation of natural resources such as corn or sugarcane [1–3], PHAs are produced by a wide variety of bacteria as carbon and energy storage materials [4]. While these materials present some interesting properties, there are still some drawbacks such as low thermal resistance, excessive brittleness and relatively low barrier to oxygen and water vapor as compared to other benchmark packaging materials such as PET, which need to be overcome to extend their industrial application.

The production of nanocomposite materials has been proven to be an efficient strategy to tune the properties of polymeric materials, as the matrix properties may be improved with low loadings (i.e., concentrations lower than 5 wt%) of highly dispersed nanoparticles. In particular, the use of cellulosic nanofillers in nanocomposites has numerous advantages such as their low density, high surface area, renewable nature, biodegradability, low cost and great availability of the raw material [5]. As a result, there is a growing interest in the study and use of cellulosic nanofillers for the

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production of fully biobased nanocomposites. Moreover, it has been very recently demonstrated that the migration levels of nanocomposites of PLA reinforced with both native and surface-modified cellulose nanocrystals were below the overall migration limits indicated in the current legislation in both non-polar and polar simulants [6].

This review summarizes the latest advances in the use of cellulosic nanofillers for the production of nanocomposites, with a focus on the development of strategies to guarantee a high dispersion of the nanofiller through industrial processing techniques such as melt compounding, to finally produce materials with high barrier properties for food packaging applications.

2 CELLULOSIC NANOFILLERS

Cellulose is the structural component of plant cell walls and, therefore, it is often extracted from vegetal resources such as wood, cotton, flax, hemp, etc. Nevertheless, it can also be extracted from algae and from some marine animals, such as tunicates, as well as synthesized by some bacterial species. Regardless of its source, cellulose consists of a linear homopolysaccharide of poly-β(1,4)-D-glucopyranoside chains, arranged in a highly ordered manner forming rod-like crystal units [7, 8]. This constitutes the basic structural component of cellulose and it is commonly referred to as cellulose “microfibrils”, “nanofibrils”, “nanocrystals” or “nanowhiskers”. These crystal units are held together in a paracrystalline matrix and linked along the axis by disordered amorphous domains.

2.1 Bacterial Cellulose

In the plant cell walls, cellulose is associated with other materials such as hemicelluloses, pectins and lignin and, thus, a purification step, which usually involves alkali and bleaching treatments with $NaClO_2$, is necessary to remove these other components and increase the degree of purity of the attained cellulose microfibers. On the contrary, cellulose synthesized by bacteria is directly produced as highly crystalline, nearly pure cellulose and, therefore, a purification step similar to that applied for isolating plant-derived cellulose is not required. Only bacteria cells and absorbed culture medium need to be removed after collecting bacterial cellulose pellicles and this is usually done by cleaning with boiling water and with sodium hydroxide aqueous solutions.

Bacterial cellulose (BC) is synthesised by bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium* and *Sarcina* [9], which are found in vinegar, alcoholic beverages, fruit juices, fruits and vegetables. Nevertheless, the most efficient production is carried out by the bacterial species *Gluconacetobacter xylinus,* which in a rich saccharide medium under static condition at around 28–30°C [10], produce a highly hydrated pellicle of cellulose in the liquid/air interface. This pellicle consists of a three-dimensional micro- and nanofibrillar network in which cellulose fibrils are hierarchically assembled. The low dry content of BC pellicles (ca. 1 g of dry cellulose per 100 g of hydrated pellicle) and the high cost of the sugars used as fermentation substrates are the two major issues involved in the industrial implementation of BC production. Therefore, efforts are currently being focused on the optimization of the fermentation process, to utilize cheap feedstocks such as agricultural wastes or food industry byproducts and at the same time, increase the production yields.

2.2 Extraction of Thermally Stable Cellulose Nanowhiskers by Acid Hydrolysis

For their application as nanofillers, cellulose elementary fibrils are usually isolated from native cellulose. This is usually done by subjecting cellulosic materials to either mechanical disintegration (mechanical shearing at high pressure) for the production of microfibrillated cellulose (MFC), or to an acid hydrolysis treatment for the preparation of cellulose nanowhiskers (CNW). Whereas CNWs present a highly crystalline structure, MFCs are flexible fibrils containing both amorphous and crystalline domains. Some alternative methods such as enzymatic digestion [11, 12] and TEMPO-mediated oxidation [13, 14], have been more recently investigated for production of cellulose with nanofibrillar morphologies, reducing the amount of energy required compared with the mechanical defibrillation methods.

The CNWs are usually extracted by a sulphuric acid treatment followed by filtration or centrifugation. During the hydrolysis process, preferential digestion of the amorphous domains of the material and cleavage of the nanofibrils’ bundles are produced [15], breaking down the hierarchical structure of the material. Additionally, esterification of the surface hydroxyl groups from cellulose takes place and, as a consequence, sulphate groups are introduced [15]. After hydrolysis, the suspension is subjected to several centrifugation cycles to remove the acid and the degraded cellulose, and CNWs are obtained from the turbid liquid supernatant, while fractions of larger size cellulose particles and some impurities (if the raw material contains hemicelluloses and lignin) remain in the solid precipitate. The supernatant, which usually presents a pH close to 3–3.5, is then neutralized with sodium hydroxide and subsequently subjected to dialysis. One of the drawbacks of the extraction of CNW by this acid digestion procedure is that low extraction yields, which may be as low as 5% [16, 17], are often attained. In this sense, bacterial cellulose presents a clear advantage as much higher yields may be attained by modifying the extraction procedure [16, 18]. An additional problem found with the traditional extraction method is related to the low concentration of the obtained suspensions, which have to be concentrated and, in many cases, freeze-dried before use. As shown in Figure 1, a dense network of strongly bonded CNW is

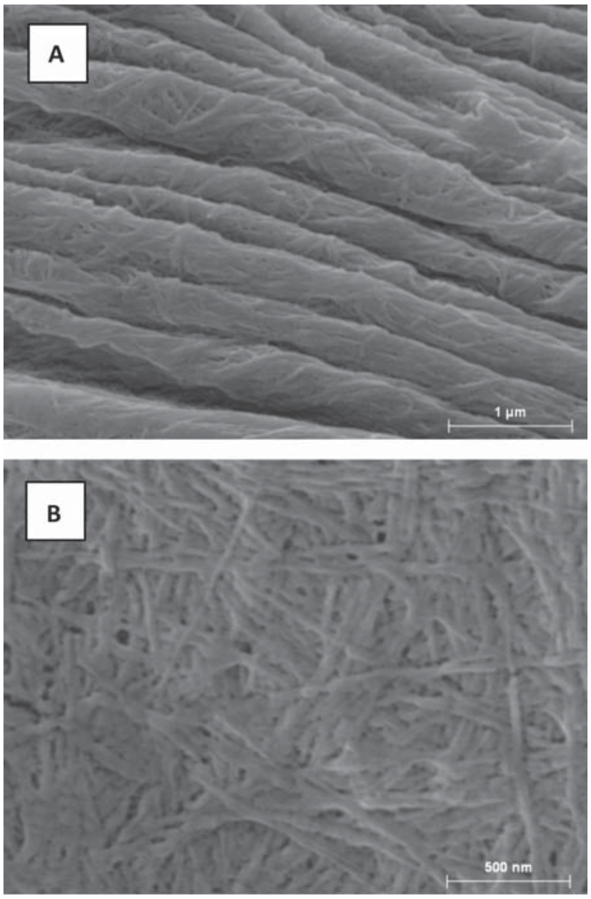

Figure 1 SEM micrographs of freeze-dried BCNW. **(A)** BCNW agglomerated into bundles with a diameter of up to 800 nm. **(B)** Within these bundles BCNW are interacting by strong hydrogen bonds, creating a highly packed structure. Scale markers correspond to 1 µm in (A) and 500 nm in (B).

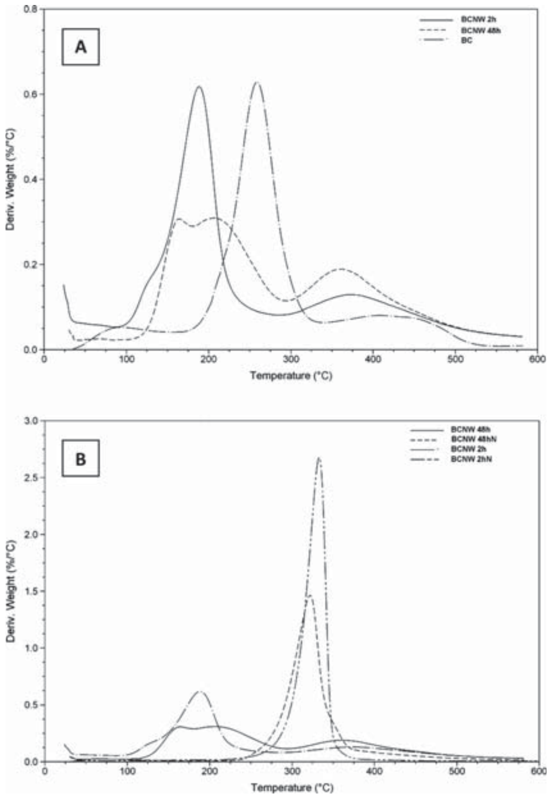

Figure 2 DTG curves showing **(A)** the effect of hydrolysis time and **(B)** the effect of neutralization. BC (native bacterial cellulose), BCNW 2h (material extracted after acid hydrolysis, 2 hours treatment), BCNW 48h (material extracted after acid hydrolysis, 48 hours treatment), BCNW 2hN (material extracted after acid hydrolysis, 2 hours treatment followed by neutralization), BCNW 48hN (material extracted after acid hydrolysis, 48 hours treatment followed by neutralization). Reproduced with permission from [20]; Copyright © 2011 Elsevier.

created as a consequence of the drying process, making it extremely difficult to redisperse them in any solvent.

To overcome these two issues, an alternative method for the extraction of bacterial CNW (BCNW) was described [18]. Taking advantage of the high purity of BC, this method suggested the extraction of BCNW from the centrifugation precipitate instead of the supernatant, after subjecting BC to a strong hydrolysis treatment. This procedure allowed increasing the extraction yield up to 85%, while obtaining highly crystalline BCNW in the form of a more concentrated gel-like fraction [16]. Extensive hydrolysis times were required to break down the hierarchical structure of the BC, which already presented a relatively high crystallinity in its native state, but at the same time hydrolysis conditions had to be carefully optimized to avoid partial carbonization or degradation of the material. Furthermore, the decreased thermal stability of the extracted BCNW was found to be a major concern, which might limit their application in nanocomposites. For instance, BCNW extracted after an extensive hydrolysis of ca. 5 days underwent significant thermal degradation when processed by melt compounding with EVOH [19].

In this context, the sulphuric acid extraction of BCNW was studied and optimized to produce a highly crystalline and thermally stable material [20]. Several hydrolysis times were tested and the effects of applying neutralization and dialysis steps after the extraction were also evaluated. Figure 2 displays the degradation profiles of several BCNW samples obtained by thermogravimetric analyses. From these results it was deduced that even short hydrolysis times, such as 2 h, led to a strong thermal stability reduction as a result of the sulphate groups incorporated onto the BCNW surface. On the other hand, neutralization after hydrolysis gave rise to an important increase in the thermostability of BCNWs, obtaining a material which could be processed at temperatures above 200°C. On the contrary, the application of a subsequent dialysis step did not show any positive effect. Regarding the crystallinity of the BCNW, short hydrolysis times were not sufficient to digest the amorphous domains of BC and a minimum of 48 h was required to significantly increase the crystallinity of the material. Increasing the hydrolysis time was seen to significantly reduce the length of the nanocrystals, while the cross-section was only slightly decreased. Thus, a hydrolysis time of 48 h was seen to be optimal in terms of maximizing crystallinity as well as preserving a high aspect ratio. This hydrolysis treatment, followed by neutralization led to thermally stable BCNW, useful as reinforcing agents in melt compoundable nanocomposites.

3 NANOCOMPOSITES CONTAINING CELLULOSE NANOWHISKERS

Cellulose nanowhiskers (CNW) are increasingly being used as reinforcing agents for new and inexpensive biodegradable materials since they present excellent mechanical properties as well as fully degradable and renewable character. However, as mentioned before, the use of CNWs as nanofillers presents some major difficulties, such as their high tendency for self-association due to their strongly interacting surface hydroxyl groups, which makes it difficult to redisperse them once they have been subjected to a drying process, and their highly hydrophilic nature, which causes incompatibility issues with most organic solvents and hydrophobic thermoplastic matrices.

Plant-derived CNWs have been incorporated into a wide variety of materials, specifically biopolymers such as PLA [17, 21], PHVB [22–24] and starch [25], by means of solution casting. Nevertheless, only a few studies have reported on the production of nanocomposites reinforced with CNWs via industrial processing techniques, such as melt compounding methods, due to the difficulty of achieving good nanofiller dispersion.

An attempt to prepare nanocomposites of PLA reinforced with CNW by pumping a suspension of CNW in DMAc/LiCl into the polymer melt during the extrusion process was described [26]. Nevertheless, aggregation and thermal degradation took place to a certain extent and no barrier property enhancement was obtained or reported. As an alternative, the use of a surfactant was seen to improve the dispersion of CNW but, at the same time, it led to PLA degradation [27]. Subsequently, the possibility of using poly(vinyl alcohol) (PVOH) as compatibilizer was investigated, but phase separation between PLA and PVOH took place and CNWs were seen to remain primarily in the PVOH phase [28]. Despite the use of PEG as compatibilizer, CNW also agglomerated when incorporated into PHBV by melt processing, leading to composites with reduced mechanical properties [22].

Other works reported approaches based on the production of masterbatches from polymer-CNW suspensions, followed by the melt compounding step. As an example, high concentrations of CNW were dispersed with PLA in organic solvents to produce masterbatches which were subsequently diluted by melt compounding [29, 30]. By this methodology relatively low contents of cellulosic fillers were uniformly distributed within the matrix, improving the mechanical properties of PLA. However, this method could have some drawbacks during the industrial implementation on top of other issues such as the efficient elimination of the entrapped solvent. In addition, surface modification of CNW by acetylation previous to the masterbatch preparation did not show either improved dispersion of the nanofiller nor improved mechanical properties as compared to the unmodified CNW [31]. Masterbatches were also produced by freeze-drying aqueous dispersions of PHBV and nanofibrillated cellulose (NFC) [32]. The addition of NFC increased the tensile modulus of PHBV, but the toughness was reduced and it caused thermal degradation of PHBV. Interestingly, none of these mentioned studies reported the effect of the nanofiller incorporation on the barrier properties.

Different strategies which have been recently addressed consist of surface modification and polymer grafting to increase the matrix-filler interactions [33–36]. Although the dispersion of CNW has been enhanced by these methods and some works have investigated the effect of grafted CNW on the mechanical properties of polymeric matrices [37–39], the impact on the barrier properties has not yet been reported.

In this context, a novel methodology based on the combination of electrohydrodynamic processing for the production of rich BCNW masterbatches, followed by melt compounding, was developed to provide nanocomposite materials containing highly dispersed BCNW with high barrier performance. The following section summarizes the main results regarding the characterization of nanocomposites produced by this approach, using both hydrophilic and hydrophobic matrices.

3.1 Electrohydrodynamic Processing to Incorporate Highly Dispersed Cellulose Nanowhiskers

Electrospinning is a versatile method to produce continuous polymer fibers down to the micrometer range through the action of an external electric field applied between two electrodes and imposed on a polymer solution or melt. When the electrical force at the interface of the polymer solution exceeds the surface tension, a charged jet is formed. The jet initially extends in a straight line, then undergoes a vigorous whipping motion caused by the electrohydrodynamic instabilities. As the solvent in the jet solution evaporates, the polymer is collected onto a grounded substrate to form a nonwoven mat with large surface-to-volume ratio [40]. Electrospinning, together with the electrospraying phenomena, in which case particles are formed instead of fibers, constitute what is known as electrohydrodynamic processing.

When intending to synthesize hybrid fibers containing BCNW, one of the major concerns was the choice of a suitable solvent, compatible with both the polymeric matrix and the hydrophilic BCNW. At the initial stage, a relatively polar matrix such as EVOH was selected as the matrix to optimize the production of hybrid fibers, minimizing the incompatibility issues. As previously mentioned, many works have been carried out using dried CNW in nanocomposite materials, ignoring that this drying step is likely to result in a significant nanofiller agglomeration. When producing EVOH-BCNW hybrid electrospun fibers, it was observed that higher levels of incorporation and more uniform morphologies could be attained when using BCNW as a partially hydrated material instead of the typically used freeze-dried BCNW [17]. By using the partially hydrated material, fibers could be produced from solutions with up to 40 wt% BCNW [18]. However, as estimated by FTIR, the actual maximum concentration of BCNW which could be effectively incorporated into the was ca. 20 wt% BCNW.

After successfully dispersing BCNWs into EVOH fibers, their incorporation into a more hydrophobic matrix such as PLA was further investigated [41]. In that case, the solvent choice was critical as, for instance, chloroform/PEG systems led to phase separation between the PLA and BCNW, while chloroform/acetone mixtures and especially 1,1,1,3,3,3-Hexafluoro-2-propanol (HFP), enabled a proper incorporation of BCNW into the fibers. Using these two latter solvent systems, electrospun fibers could be generated from solutions with up to 15 wt% BCNW by varying the total solids concentration. Between these two systems, HFP was seen to be more compatible with the BCNW, enabling higher BCNW incorporation ratios, as estimated by XRD.

By varying the electrospinning parameters, such as voltage, needle-collector distance and feeding rate, as well as the solution properties, such as the viscosity, surface tension and conductivity, the morphology of the electrospun material may be modified, thus producing fibers with different diameters, capsules or electrosprayed particles. In the above-mentioned studies, the electrospinning parameters were first optimized for the pure polymeric matrices to generate fibers and then fixed for the other compositions. However, the addition of BCNW into the solutions altered their properties and, accordingly, the morphology of the fibers was affected. For both EVOH and PLA, it was found that the incorporation of hydrated BCNW resulted in a significant increase in solution viscosity, surface tension and conductivity and led to the production of thinner fibers. In terms of maximizing the loading while preserving suitable solution properties and uniform fiber morphology, 15 wt% BCNW was found to be the optimum loading for both polymers. Table 1 gathers the solution properties for the pure polymers and their "optimized" hybrid compositions. As observed, the incorporation of BCNW increased the three measured parameters, the viscosity being more strongly affected. This increased viscosity may be provided by the high amount of hydroxyl groups present on the surface of BCNW, which enabled the creation of a strong nanocrystals network. Surprisingly, this higher viscosity did not lead to bigger sized fibers, but the opposite effect was observed when adding BCNW into the fibers (cf. Figure 3). This effect has been previously reported for several polymeric fibers incorporating CNW [42–44], indicating that the morphology of the electrospun fibers is mostly governed by the conductivity of the solutions.

3.2 Melt Compounded Nanocomposites

Given the need for developing an efficient procedure for the incorporation of highly dispersed cellulose nanocrystals by melt processing techniques, and the fact that electrospinning was proven to be an effective method for producing fibers with relatively high concentrations of dispersed BCNW, we suggested the use of hybrid electrospun fibers as masterbatches for the melt compounding process (samples coded as BCNW ES). This approach was evaluated with both EVOH and PLA, comparing it with a solution precipitation pre-incorporation method (samples coded as BCNW P) and with the conventional method consisting of the direct melt mixing of the polymer with freeze-dried cellulosic nanofillers (samples coded as BCNW FD). The procedure for generating melt compounded EVOH and PLA nanocomposites is schematically represented in Figure 4.

Figure 5 displays the cryo-fractured sections of EVOH nanocomposites. It is clear that the method for incorporating the BCNW prior to the melt compounding step determined the morphology of the obtained nanocomposites. Thus, even though EVOH and BCNW are relatively compatible, large BCNW agglomerates could be detected in the nanocomposite containing freeze-dried BCNW (cf. Figure 5D).

Table 1 Viscosity, surface tension and conductivity of electrospinning solutions and average diameter of the corresponding fibers.

	Viscosity (cP)	Surface Tension (mN/m)	Conductivity (μS)	Average fiber diameter (nm)
EVOH32	35.3	23.5	9.8	182.4 ± 79.0
EVOH32+15%BCNW	>1999	24.8	113.8	131.9 ± 53.0
PLA	119.8	19.4	4.9	484.0 ± 189.3
PLA+15%BCNW	579.6	27.7	9.7	90.7 ± 49.1

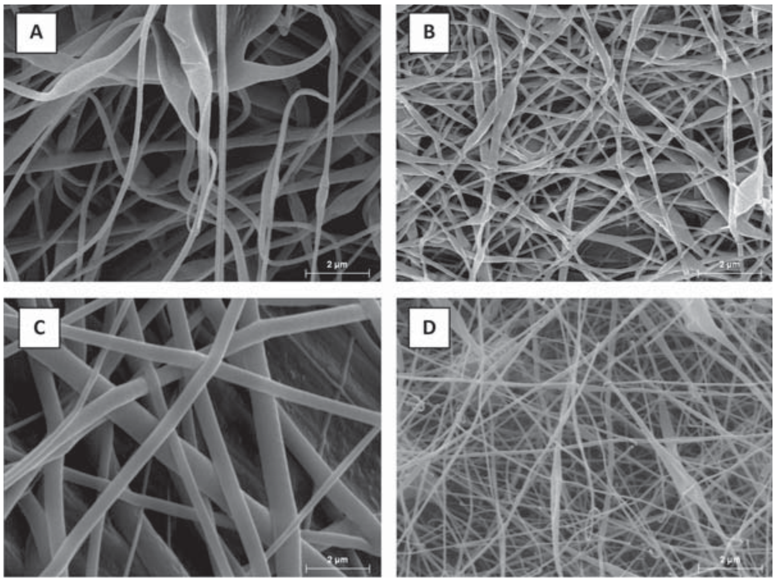

Figure 3 SEM micrographs of electrospun fibers obtained from **(A)** pure EVOH32; **(B)** EVOH32 + 15 wt% BCNW; **(C)** pure PLA, and **(D)** PLA + 15 wt% BCNW. The scale markers correspond to 2 microns. Figures 3A and 3B are reproduced with permission from [45];, Copyright © 2012 John Wiley and Sons.

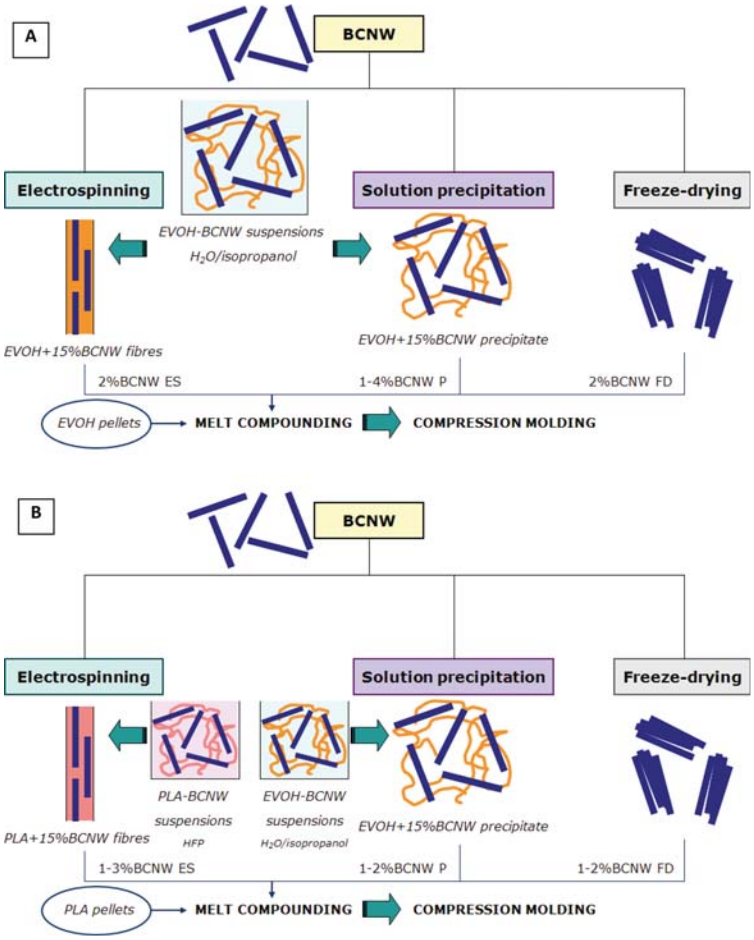

Figure 4 Approaches developed for the production of **(A)** EVOH-BCNW and **(B)** PLA-BCNW melt-processed nancomposites.

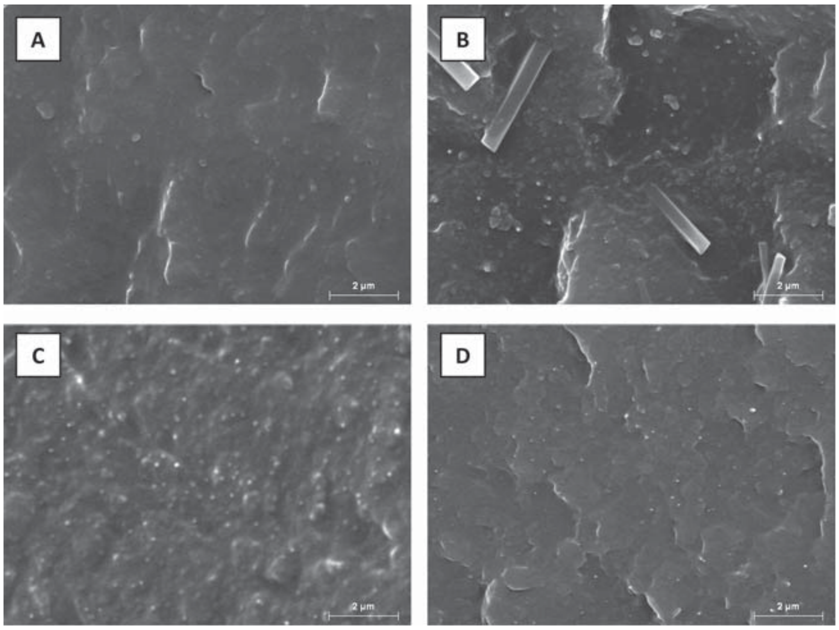

Figure 5 SEM micrographs of the cryo-fractured section obtained from EVOH films: **(A)** Pure EVOH; **(B)** 2% BCNW FD; **(C)** 2% BCNW P, and; **(D)** 2% BCNW ES. Scale markers correspond to 2 micrometers. Reproduced with permission from [45]; Copyright © 2012 John Wiley and Sons.

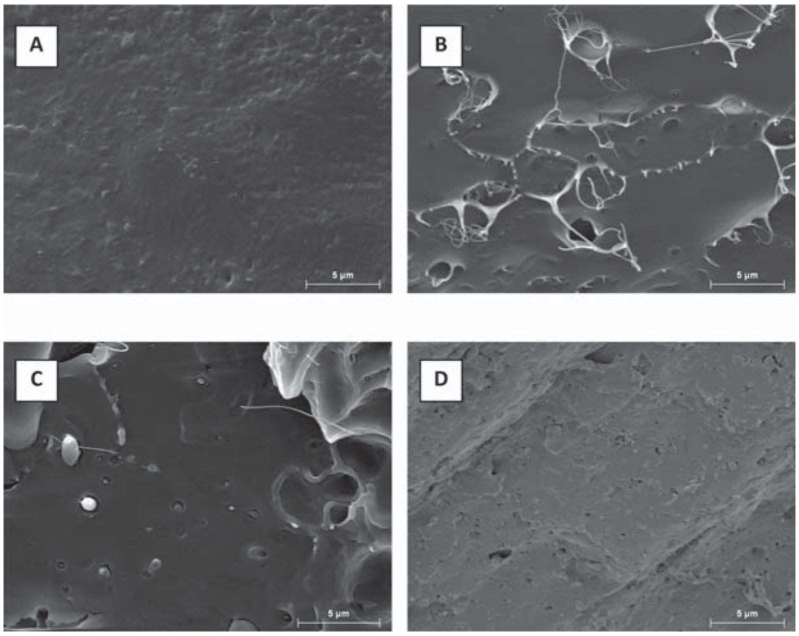

Figure 6 SEM micrographs of the cryo-fractured section obtained from PLA films: **(A)** Pure PLA; **(B)** 2% BCNW FD; **(C)** 2% BCNW P, and; **(D)** 2% BCNW ES. Scale markers correspond to 5 micrometers. Reproduced with permission from [46]; Copyright © 2012 American Chemical Society.

On the contrary, a homogeneous dispersion of the fillers was encountered using the two pre-incorporation strategies developed. In the case of PLA, the lower matrix-filler compatibility was evidenced by a certain phase separation with BCNW appearing as fiber pull-outs or voided features, as shown in Figure 6. Although the precipitation pre-incorporation resulted in a significant improvement in the nanofiller dispersion compared with the freeze-dried BCNW melt mixing, the electrospinning approach clearly provided the most optimal BCNW dispersion.

The effect of BCNW on the barrier properties was investigated through water and oxygen permeability measurements. Figure 7 summarizes the water permeability results for all the developed nanocomposites. For both polymeric matrices, the incorporation of freeze-dried BCNW resulted in increased water permeability, while this detrimental effect was not observed when using the pre-incorporation methods. For the EVOH, it was necessary to increase the BCNW loading up to 4 wt% to attain significant barrier improvement, while in the case of PLA significant permeability reductions were observed for the studied BCNW loadings (1–3 wt%). This different behavior could be explained by the effect of BCNW incorporation in the water sorption and diffusion through the system. For comparison purposes, the values of some representative samples are gathered in Table 2.

In general, the incorporation of BCNW into EVOH limited the water sorption and increased the diffusion. On one hand, the addition of highly crystalline BCNW and the possible interactions established between the hydroxyl groups from EVOH and the nanofiller were responsible for the decreased water sorption. On the other hand, these interactions led to a reduction in the amorphous density of the material through inter- and intrapolymer disruptions, which negatively affected the water diffusion. From the results, it seems that only for higher BCNW loadings, i.e., ca. 4 wt%, the positive effect of the increased crystallinity and dispersion was strong enough to counteract the negative effect of the increased free volume. It is important to note that for the nanocomposite containing freeze-dried BCNW, the diffusion was increased to a greater extent due to the creation of preferential diffusion paths as a result of the nanofiller agglomeration, hence highlighting the convenience of using the pre-incorporation methods to avoid a detrimental effect on the barrier properties.

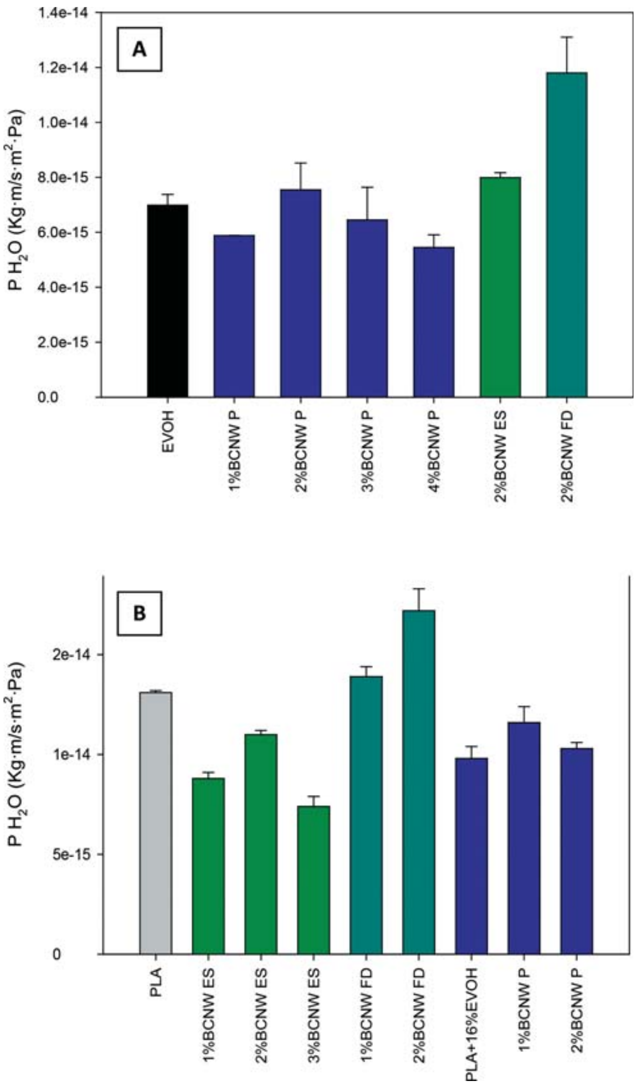

Figure 7 Water permeability of **(A)** EVOH nanocomposites and **(B)** PLA nanocomposites.

Table 2 Water permeability, water uptake and diffusion coefficient (measured for a 0%RH–100%RH gradient).

	$P\ H_2O$ (Kg·m/s·m^2·Pa)	Water uptake (%)	D (m^2/s)
EVOH32	$0.70 \pm 0.04\ e^{-14}$	9.25 ± 0.20	$0.19 \pm 0.00\ e^{-12}$
EVOH32+2%BCNW FD	$1.18 \pm 0.01\ e^{-14}$	7.12 ± 0.23	$0.42 \pm 0.01\ e^{-12}$
EVOH32+2%BCNW P	$0.76 \pm 0.10\ e^{-14}$	8.62 ± 0.43	$0.22 \pm 0.00\ e^{-12}$
EVOH32+2%BCNW ES	$0.80 \pm 0.02\ e^{-14}$	6.99 ± 0.94	$0.29 \pm 0.04\ e^{-12}$
PLA	$1.31 \pm 0.01\ e^{-14}$	0.95 ± 0.15	$3.63 \pm 0.94\ e^{-12}$
PLA+2%BCNW FD	$1.72 \pm 0.11\ e^{-14}$	0.52 ± 0.07	$8.79 \pm 0.67\ e^{-12}$
PLA+2%BCNW P	$1.03 \pm 0.03\ e^{-14}$	1.08 ± 0.12	$2.37 \pm 0.34\ e^{-12}$
PLA+2%BCNW ES	$1.10 \pm 0.02\ e^{-14}$	0.87 ± 0.01	$3.04 \pm 0.10\ e^{-12}$

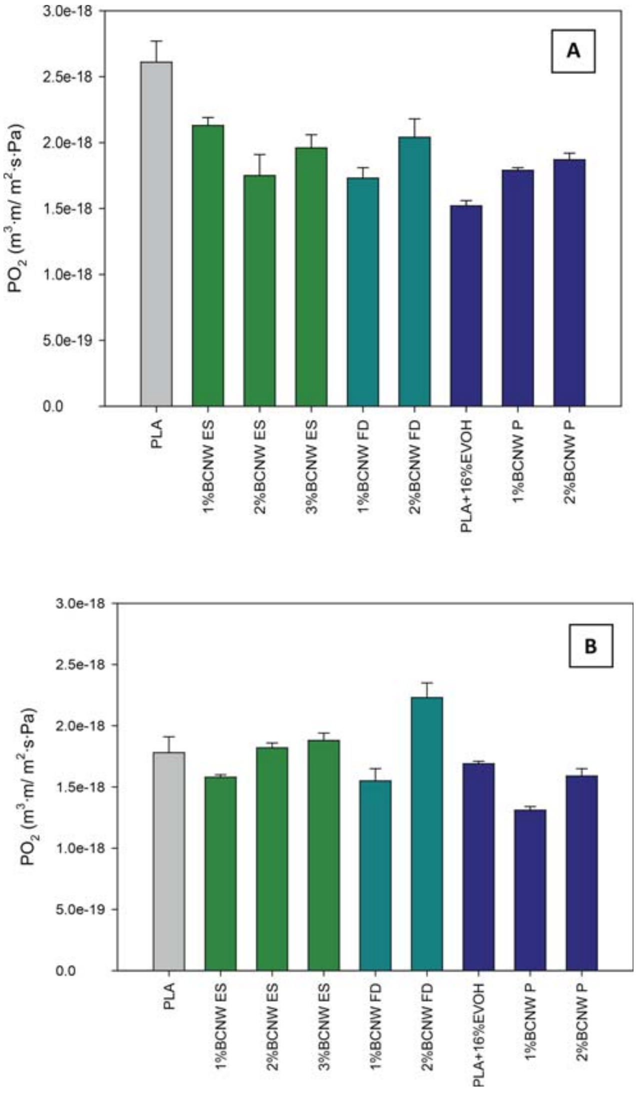

Figure 8 Oxygen permeability of PLA nanocomposites measured at **(A)** 0%RH and **(B)** 80%RH.

In the case of PLA, the same unfavorable effect was observed when incorporating freeze-dried BCNW into the material. However, the pre-incorporation methods, especially the electrospinning approach, enabled improved water barrier performance through a combination of reduced solubility and diffusion coefficients. A maximum permeability drop of ca. 43% was achieved for the nanocomposite loaded with 3 wt% BCNW through electrospinning. The oxygen permeability of PLA nanocomposites was also determined and the results are displayed in Figure 8. As it can be observed, BCNW presented a high blocking capacity which was evidenced by the higher oxygen barrier presented by all the nanocomposites at 0%RH. However, due to the high moisture sensitivity of the BCNW, barrier improvements were attained only for low nanofiller loadings when increasing the relative humidity up to 80%.

4 FUTURE PERSPECTIVES AND CONCLUSIONS

This overview gathered recent results carried out within our research group and other relevant literature to show the development of highly thermally stable nanocrystals of cellulose; and also an original and feasible approach to obtain highly dispersed and distributed nanobiocomposites of this filler. This approach permits the generation of a masterbatch of nanocrystals via electrohydrodynamic processing to freeze into a solid powder form the high dispersion of the nanocrystals existing in solution that can later be diluted by melt blending with the same or other virgin resin using conventional plastic processing technologies. The industrial implementation of this process is currently being developed since the limiting step of the mass production of electrospun material has recently been solved by companies such as BioInicia S.L. (www.fluidnatek.com). This will allow in the near future a potentially cost-effective solution to obtain fully biobased and biodegradable/compostable nanobiocomposites with tailored properties to access commodity applications such as high barrier food packaging and others.

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REFERENCES

1. R. Auras, B. Harte, and S. Selke, An overview of polylactides as packaging materials. *Macromol. Biosci.* **4**, 835–864 (2004).
2. R.E. Drumright, P.R. Gruber, and D.E. Henton, Polylactic acid technology. *Adv. Mater.* **12**, 1841–1846 (2000).
3. J. Lunt, Large-scale production, properties and commercial applications of poly lactic acid polymers. *Polym. Degrad. Stab.* **59**, 145–152 (1998).
4. D.G. Lundgren, R. Alper, C. Schnaitman, and R.H. Marchessault, Characterization of poly-β-hydroxybutyrate extracted from different bacteria. *J. Bacteriol.* **89**, 245–251 (1965).
5. G. Siqueira, J. Bras, and A. Dufresne, Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers* **2**, 728–765 (2010).

6. E. Fortunati, M. Peltzer, I. Armentano, L. Torre, A. Jiménez, and J.M. Kenny, Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydr. Polym.* **90**, 948–956 (2012).
7. D.P. Delmer and Y. Amor, Cellulose biosynthesis. *Plant Cell* **7**, 987–1000 (1995).
8. M. Mutwil, S. Debolt, and S. Persson, Cellulose synthesis: A complex complex. *Curr. Opin. Plant Biol.* **11**, 252–257 (2008).
9. R. Jonas and L.F. Farah, Production and application of microbial cellulose. *Polym. Degrad. Stab.* **59**, 101–106 (1998).
10. M. Iguchi, S. Yamanaka, and A. Budhiono, Bacterial cellulose—A masterpiece of nature's arts. *J. Mater. Sci.* **35**, 261–270 (2000).
11. T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon, and A. Isogai, Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* **7**, 1687–1691 (2006).
12. T. Saito, S. Kimura, Y. Nishiyama, and A. Isogai, Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* **8**, 2485–2491 (2007).
13. M. Henriksson and L.A. Berglund, Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *J. Appl. Polym. Sci.* **106**, 2817–2824 (2007).
14. J. George, K.V. Ramana, A.S. Bawa, and Siddaramaiah, Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. *Int. J. Biol. Macromol.* **48**, 50–57 (2011).
15. B.G. Rånby, Aqueous colloidal solutions of cellulose micelles. *Acta Chem. Scand.* **3**, 649–650 (1949).
16. M. Martínez-Sanz, R.T. Olsson, A. Lopez-Rubio, and J.M. Lagaron, Development of electrospun EVOH fibres reinforced with bacterial cellulose nanowhiskers. Part I: Characterization and method optimization. *Cellulose* **18**, 335–347 (2011).
17. M.D. Sanchez-Garcia and J.M. Lagaron, On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose* **17**, 987–1004 (2010).
18. R.T. Olsson, R. Kraemer, A. Lopez-Rubio, S. Torres-Giner, M.J. Ocio, and J.M. Lagaron, Extraction of microfibrils from bacterial cellulose networks for electrospinning of anisotropic biohybrid fiber yarns. *Macromolecules* **43**, 4201–4209 (2010).
19. M. Martínez-Sanz, R. Olsson, A. Lopez-Rubio, and J. Lagaron, Development of bacterial cellulose nanowhiskers reinforced EVOH composites by electrospinning. *J. Appl. Polym. Sci.* **124**, 1398–1408 (2012).
20. M. Martínez-Sanz, A. Lopez-Rubio, and J.M. Lagaron, Optimization of the nanofabrication by acid hydrolysis of bacterial cellulose nanowhiskers. *Carbohydr. Polym.* **85**, 228–236 (2011).
21. L. Petersson, I. Kvien, and K. Oksman, Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. *Compos. Sci. Technol.* **67**, 2535–2544 (2007).
22. L. Jiang, E. Morelius, J. Zhang, M. Wolcott, and J. Holbery, Study of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisker composites prepared by solution casting and melt processing. *J. Compos. Mater.* **42**, 2629–2645 (2008).
23. E. Ten, D.F. Bahr, B. Li, L. Jiang, and M.P. Wolcott, Effects of cellulose nanowhiskers on mechanical, dielectric, and rheological properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisker composites. *Ind. Eng. Chem. Res.* **51**, 2941–2951 (2012).
24. E. Ten, J. Turtle, D. Bahr, L. Jiang, and M. Wolcott, Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers composites. *Polymer* **51**, 2652–2660 (2010).
25. I. Kvien, J. Sugiyama, M. Votrubec, and K. Oksman, Characterization of starch based nanocomposites. *J. Mater. Sci.* **42**, 8163–8171 (2007).
26. K. Oksman, A.P. Mathew, D. Bondeson, and I. Kvien, Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. *Compos. Sci. Technol.* **66**, 2776–2784 (2006).
27. D. Bondeson and K. Oksman, Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites. *Compos. Interfaces* **14**, 617–630 (2007).
28. D. Bondeson and K. Oksman, Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. *Compos. A Appl. Sci. Manuf.* **38**, 2486–2492 (2007).
29. A. Iwatake, M. Nogi, and H. Yano, Cellulose nanofiber-reinforced polylactic acid. *Compos. Sci. Technol.* **68**, 2103–2106 (2008).
30. M. Jonoobi, J. Harun, A.P. Mathew, and K. Oksman, Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Compos. Sci. Technol.* **70**, 1742–1747 (2010).
31. M. Jonoobi, A.P. Mathew, M.M. Abdi, M.D. Makinejad, and K. Oksman, A comparison of modified and unmodified cellulose nanofiber reinforced polylactic acid (PLA) prepared by twin screw extrusion. *J. Polym. Environ.* **20**, 991–997 (2012).
32. Y. Srithep, T. Ellingham, J. Peng, R. Sabo, C. Clemons, L.S. Turng, and S. Pilla, Melt compounding of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/nanofibrillated cellulose nanocomposites. *Polym. Degrad. Stab.* **98**, 1439–1449 (2013).
33. C. Eyholzer, P. Tingaut, T. Zimmermann, and K. Oksman, Dispersion and reinforcing potential of carboxymethylated nanofibrillated cellulose powders modified with 1-hexanol in extruded poly(lactic acid) (PLA) composites. *J. Polym. Environ.* **20**, 1052–1062 (2012).
34. A.L. Goffin, J.M. Raquez, E. Duquesne, G. Siqueira, Y. Habibi, A. Dufresne, and P. Dubois, From interfacial ring-opening polymerization to melt processing of cellulose nanowhisker-filled polylactide-based nanocomposites. *Biomacromolecules* **12**, 2456–2465 (2011).
35. A.L. Goffin, J.M. Raquez, E. Duquesne, G. Siqueira, Y. Habibi, A. Dufresne, and P. Dubois, Poly(ε-caprolactone) based nanocomposites reinforced by surface-grafted cellulose nanowhiskers via extrusion processing:

Morphology, rheology, and thermo-mechanical properties. *Polymer* **52**, 1532–1538 (2011).
36. J.M. Raquez, Y. Murena, A.L. Goffin, Y. Habibi, B. Ruelle, F. DeBuyl, and P. Dubois, Surface-modification of cellulose nanowhiskers and their use as nanoreinforcers into polylactide: A sustainably-integrated approach. *Compos. Sci. Technol.* **72**, 544–549 (2012).
37. N. Lin, J. Huang, P.R. Chang, J. Feng, and J. Yu, Surface acetylation of cellulose nanocrystal and its reinforcing function in poly(lactic acid). *Carbohydr. Polym.* **83**, 1834–1842 (2011).
38. A. Pei, Q. Zhou, and L.A. Berglund, Functionalized cellulose nanocrystals as biobased nucleation agents in poly(l-lactide) (PLLA)—Crystallization and mechanical property effects. *Compos. Sci. Technol.* **70**, 815–821 (2010).
39. P. Qu, Y. Zhou, X. Zhang, S. Yao, and L. Zhang, Surface modification of cellulose nanofibrils for poly(lactic acid) composite application. *J. Appl. Polym. Sci.* **125**, 3084–3091 (2012).
40. C.W. Kim, D.S. Kim, S.Y. Kang, M. Marquez, and Y.L. Joo, Structural studies of electrospun cellulose nanofibers. *Polymer* **47**, 5097–5107 (2006).
41. M. Martínez-Sanz, A. Lopez-Rubio, and J.M. Lagaron, Dispersing bacterial cellulose in polylactides via electrohydrodynamic processing. *J. Polym. Environ.* **22**, 27–40 (2014).
42. M.S. Peresin, Y. Habibi, J.O. Zoppe, J.J. Pawlak, and O.J. Rojas, Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: Manufacture and characterization. *Biomacromolecules* **11**, 674–681 (2010).
43. O.J. Rojas, G.A. Montero, and Y. Habibi, Electrospun nanocomposites from polystyrene loaded with cellulose nanowhiskers. *J. Appl. Polym. Sci.* **113**, 927–935 (2009).
44. C. Xiang, Y.L. Joo, and M.W. Frey, Nanocomposite fibers electrospun from poly(Lactic Acid)/cellulose nanocrystals. *J. Biobased Mater. Bioenergy* **3**, 147–155 (2009).
45. M. Martínez-Sanz, A. Lopez-Rubio, and J.M. Lagaron, Nanocomposites of ethylene vinyl alcohol copolymer with thermally resistant cellulose nanowhiskers by melt compounding (I): Morphology and thermal properties. *J. Appl. Polym. Sci.* **128**, 228–236 (2012).
46. M. Martínez-Sanz, A. Lopez-Rubio, and J.M. Lagaron, Optimization of the dispersion of unmodified bacterial cellulose nanowhiskers into polylactide via melt compounding to significantly enhance barrier and mechanical properties. *Biomacromolecules* **13**, 3887–3899 (2012).