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Naturally Occurring α-Hydroxy Acids: Useful Organocatalysts for the Acetylation of Cellulose Nanofibres

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Abstract: Cellulose nanoribbons obtained from bacterial fermentation have been esterified by means of a solventless organocatalytic route. The esterification methodology involves acetic anhydride as acylant and three different α-hydroxy acids were tested as organocatalysts. By tuning the acetylation interval, bacterial nanocellulose (BNC) with varying degree of substitution could be obtained (*i.e.* DS=0.27-0.90). Esterified BNC has been characterized in terms of its morphology, chemical structure, crystallinity, wettability and dispersibility in different solvents. The results indicate the efficacy of the present methodology for the smooth acetylation of cellulose nanoribbons at moderate conditions, thereby expanding the role of organocatalysts in reducing the hydrophilicity of bacterial cellulose nanoribbons.

Keywords: Acetylation, bacterial nanocellulose, organocatalysis, α-hydroxy acids.

INTRODUCTION

During the last decade cellulose nanoparticles (*i.e.* cellulose elements having at least one dimension in the 1-100 nm range) have received increasing attention due to a number of properties, such as abundance, low cost and renewability of the raw materials, large surface-to-volume ratio, high strength and stiffness, low thermal expansion coefficient, low weight, low density, biodegradability, and a reactive surface of hydroxyl side groups that enables surface functionalization.

Cellulose nanoparticles can be obtained by a top-down approach which involves their isolation from plant cellulose by use of mechanical, chemical and/or enzymatic methods. On the other hand, a bottom-up approach for the production of cellulose nanoparticles is based on their biosynthesis by certain bacteria which under proper conditions can synthesize high-quality cellulose organized as twisting ribbons of microfibrillar bundles [1]. During biosynthesis, carbon compounds of the nutrition medium are utilized by bacteria and polymerized into single linear β-1,4-glucan chains which are secreted outside the cells. Once Outside the cells, β-1,4-glucan chains are assembled first into subfibrils (consisting of 10–15 nascent β-1,4-glucan chains, width≈1.5 nm), then into microfibrils, then into bundles, and finally into ribbons [2, 3].

Bacterial nanocellulose (BNC) ribbons typically show rectangular cross-sections with thicknesses around 3-4 nm, 70-100 nm in width, and 1-9 μm in length [3, 4]. Although it has the same molecular formula as plant cellulose, BNC is recognized for some specially interesting features such as its high polymerization degree (*i.e.* 4000-10000 anhydroglucose units), high crystallinity (80-90%), high stability of the single cellulose fibers [5], very low thermal expansion coefficient, chemical purity (BNC is produced free of wax, pectin, lignin and hemicellulose), no requirement of further processing to obtain nanosized cellulose (*e.g.* homogenisation, fibrillation), extensive surface area originated in its well-separated microfibrils, high liquid loading capacity (*i.e.* 98-99% for water, much higher than plant cellulose), and the fact that nanofibers are immobilized in a stable network, an important aspect when considering the health risks associated with mobile nanoparticles.

In spite of the aforementioned characteristics of BNC, some of which are highly favourable for its use as nanofiller/reinforcement, the extremely high hydrophilic nature of cellulose nanoparticles associated with their OH-rich structure often results in poor compatibility with non-polar polymer matrices, which leads to poor dispersion and stress transfer efficiency between the matrix and the reinforcement. Moreover, moisture sorption results in dimensional instability and reduced mechanical properties of the composites [6].

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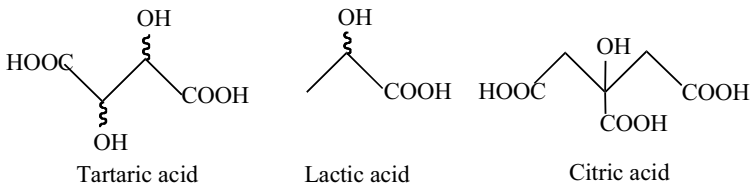

Fig. (1). Structure of naturally occurring α-hydroxy acids used as catalysts for BNC acetylation.

In this context, cellulose functionalization allows the tailoring of particle surface chemistry to facilitate controlled dispersion within a wide range of matrix polymers, and control of both the particle–particle and particle-matrix bond strength [7]. Particularly, esterification (mainly acetylation) of cellulose nanoparticles in which hydroxyl groups are partially replaced by less hydrophilic ester groups, is commonly used for tailoring cellulose nanoparticles polarity.

In reference to BNC acetylation methods, until now BNC has been mainly derivatized by the so-called "acetic acid process", in which BNC is first swelled in acetic acid and then acetylated with acetic anhydride using sulphuric acid or perchloric acid as catalysts [8-9]. Besides, in the last years, other catalyzed methodologies for BNC acetylation have been described in the literature, including among others iodine-catalyzed solvent-free acetylation with acetic anhydride [10], surface acetylation with acetic acid in presence of pyridine and *p*-toluenesulfonyl chloride [11], homogeneous acetylation with acetic anhydride in dimethylacetamide/lithium chloride [12], solvent-free surface acetylation with acetic anhydride under supercritical carbon dioxide condition [13], surface heterogeneous acetylation with acetic anhydride using ionic liquids as solvent media and catalysts [14], and more recently, solvent-free surface acetylation of BNC with acetic acid as acylant and L-tartaric acid as catalyst [15].

Particularly, the organocatalytic acetylation of cellulose nanoparticles using naturally occurring α-hydroxycarboxylic acids as catalysts appears as a promising alternative route for ecofriendly derivatization of nanocellulose. As recently reviewed by Domínguez de María (2010), interesting advantages of α-hydroxycarboxylic acids such as tartaric, lactic, and citric acids are the possibility of obtaining them by biotechnological routes, their biodegradable character, non toxicity, and easiness to apply [16]. The mentioned naturally occurring α-hydroxy acids have proven useful in the synthesis of cellulose-PCL esters by ring-opening polymerization of lactones from cotton and paper cellulose in solvent-free conditions, as well as in the solvent-free esterification of cotton fibers with hexadecanoic and pentynoic acids [17]. More recently, naturally occurring α-hydroxy carboxylic acids (*i.e.* L-tartaric acid) have been used in the acetylation and butyrylation of corn starch granules [18, 19], as well as in the surface esterification of BNC using acetic and propionic acids as acylants [15].

In the current contribution, BNC is acetylated with acetic anhydride as acylant, and not only L-tartaric acid, but also the catalytic activity of citric and lactic acids has been assayed. The effects of the acetylation level achieved in the chemical structure, morphology, crystallinity, wettability and dispersibility of esterified BNC have been studied.

RESULTS AND DISCUSSION

Organocatalytic Acetylation of BNC

The evolution of the acetylation of BNC with acetic anhydride as acylant and catalyzed by L-tartaric, citric and lactic acid (Fig. **1**) was studied within the 1-7 h interval. No solvent was added to the system. Instead, the acylant was added in excess in order to provide the reaction volume required to guarantee a proper dispersion of cellulose nanoribbons. At the chosen reaction temperature, the complete dissolution of solid catalysts (*i.e.* L-tartaric and citric acids) was guaranteed.

Results in terms of the degree of substitution (DS) achieved are summarized in Fig. (**1**).

As it is shown in Fig. (**2**), all α-hydroxy acids assayed showed catalytic activity towards the acetylation of BNC, with DS values ranging from 0.27 to 0.90. Within the first three hours of reaction, highest substitution levels were attained with L-tartaric acid as catalyst, reaching a DS value of 0.54, 37% and 54% higher than those attained with citric acid and lactic acid, respectively. In the inspiring contribution of Hafrén and Córdova (2005) dealing with the synthesis of biocompatible cellulose-PCL esters by ROP of ε-caprolactone from cotton and paper cellulose as initiators, authors reported that even if tartaric, citric and lactic acids all exhibited catalytic activity and furnished PCL, tartaric acid was the most efficient catalyst for the production of PCL-grafted cellulose [17].

However, during the following hours of BNC acetylation, reaction catalyzed by L-tartaric acid showed only marginal increments in DS, whereas citric acid-catalyzed acetylation continued with almost constant rate, achieving a DS of 0.90 within 7 h of reaction. On the other hand, out of the three naturally occurring α-hydroxy acids assayed, lactic acid showed the lowest catalytic activity, leading to DS values at the most 40% higher than the ones measured for the uncatalyzed reaction (Fig. **2**).

In reference to the acylating agent used to carry out the organocatalytic acetylation of BNC, it is noteworthy that acetic anhydride appears as much promising than acetic acid, with DS values up to 7 times higher than those achieved previously with acetic acid (identical reaction conditions, catalyst: L-tartaric acid, [15]). In fact, the use of acetic anhydride allowed attaining in 1 hour of reaction a DS value for which acetylation of BNC with acetic acid has been reported to require 6 h [15]. The differences observed are explained in terms of the higher reactivity of acetic anhydride. The carboxylate ion of the anhydride activates the carbonyl group by withdrawing electronic density and is the leaving group in nucleophilic acyl substitution reactions. Since reactivity in-

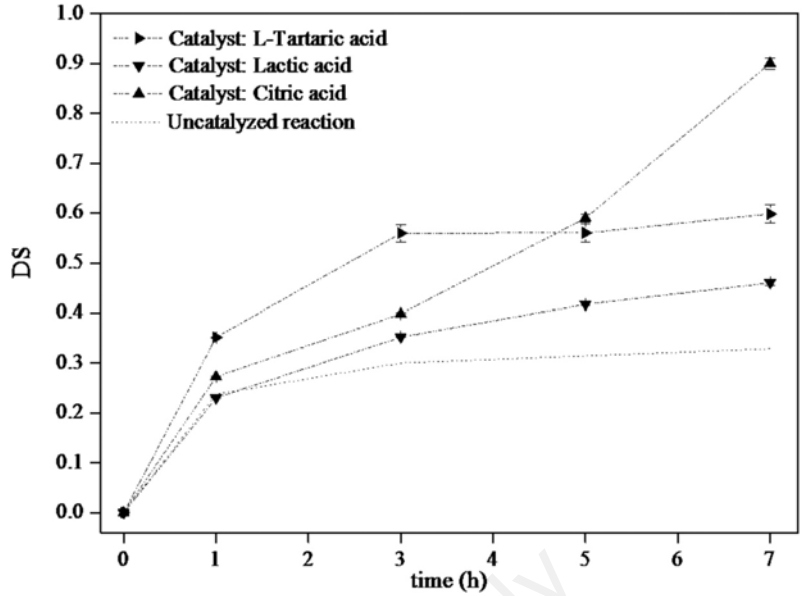

Fig. (2). Organocatalytic acetylation of bacterial nanocellulose using acetic anhydride as acylant, and L-tartaric, lactic and citric acids as catalysts at 120°C.

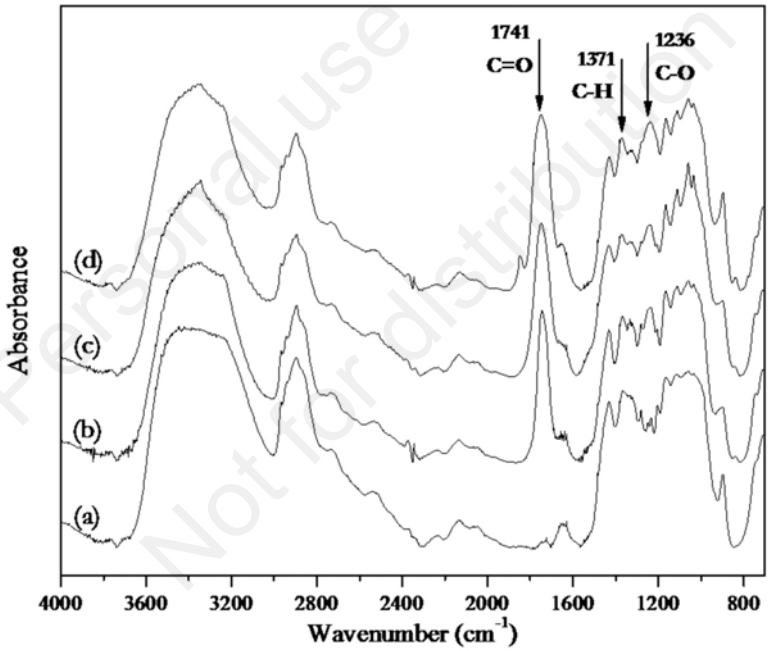

Fig. (3). FTIR spectra of native (**a**) and acetylated BNC, (**b**) DS=0.42 (lactic acid), (**c**) DS=0.56 (L-tartaric acid), (**d**) DS=0.90 (citric acid).

creases as the leaving group becomes more acidic, anhydrides are more reactive than acids [20].

FTIR Spectroscopy

Acetylation of BNC was further confirmed by FTIR spectroscopy of derivatized samples, which evidenced the appearance of signals typical of the ester groups introduced. Fig. (**3**) shows the FTIR spectra of native BNC and acetylated BNC with the highest DS obtained by use of the different organocatalysts assayed. The peaks centred at 3345, 2895, 1432, 1278, 1165, 1109, 1059, and 897 cm^{-1} are typical of native cellulose [21, 22]. Besides, the signal observed at 1645 cm^{-1} is associated with the H-O-H bending vibration of adsorbed water molecules in hydrophilic BNC. Spectra of acetylated BNC provided evidence of esterification by the appearance of new peaks at 1741 cm^{-1} (C=O stretching), 1371 cm^{-1} (C–H symmetrical deformation in CH_3), and 1236 cm^{-1} (C–O stretching) [10-11, 23-24].

Scanning Electron Microscopy

Fig. (**4**) shows FE-SEM micrographies of native and acetylated BNC. Native bacterial cellulose nanoribbons micrometric in length and 15-60 nm in width form a highly reticulated network and tend to aggregate due to the high density of surface hydroxyl groups (Fig. **4a**). Native BNC nanoribbons show smooth uniform surfaces. Figs. (**4b-4d**) show

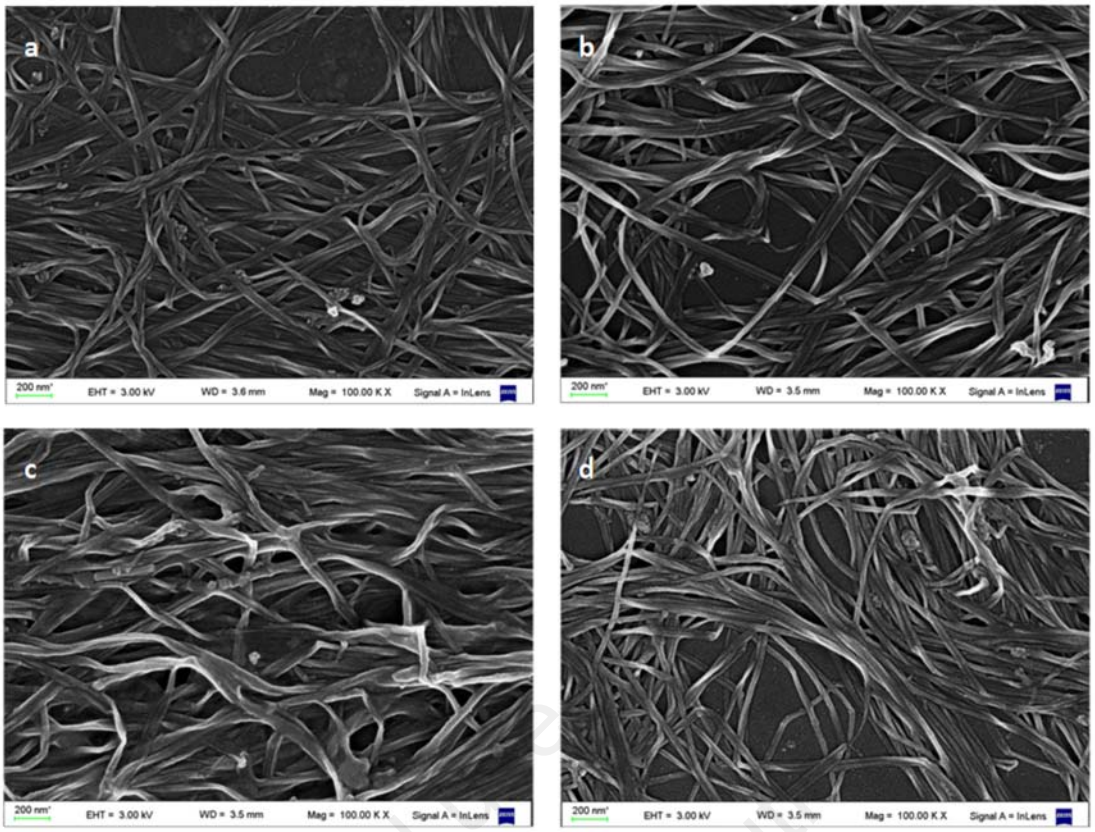

Fig. (4). FE-SEM micrographs of native (**a**) and acetylated BNC, (**b**) DS=0.42 (lactic acid), (**c**) DS=0.56 (L-tartaric acid), (**d**) DS=0.90 (citric acid).

images of acetylated BNC with the highest DS obtained by use of the different organocatalysts assayed. As it is shown, under the conditions chosen, the organocatalytic acetylation protocol did not destroy the fibrous structure of cellulose microfibrils, and the smooth appearance of microfibrils was preserved.

X-Ray Diffraction

Fig. (**5**) shows XRD results for native and acetylated BNC samples with the highest DS obtained by use of the different organocatalysts assayed. Native and acetylated BNC samples showed five diffraction peaks centred at 2θ= 14.4° (101), 16.7° (10-1), 20.1° (021), 22.5° (002), and 34.4° (040) which confirmed that only cellulose-I was present in all samples [25]. For the DS attained in this contribution, neither peak shifting nor appearance of new peaks was detected. The relative degree of crystallinity of the samples was calculated by use of the Segal equation [26]. Values of the correspondent crystallinity index (CrI) have been included within (Fig. **5**).

As it is shown, native BNC has a high proportion of crystalline material (89%), which is actually one of its distinguishing properties among nanocellulose sources. CrI values obtained for acetylated BNC evidence only a very slight decrease of crystallinity for samples with DS of 0.42 (lactic acid) and 0.56 (L-tartaric acid), with CrI values of 88% and 86%, respectively. On the other hand, acetylation with citric acid during 7 h (DS=0.90) induced a slightly more significant reduction in BNC crystallinity, with a calculated CrI of

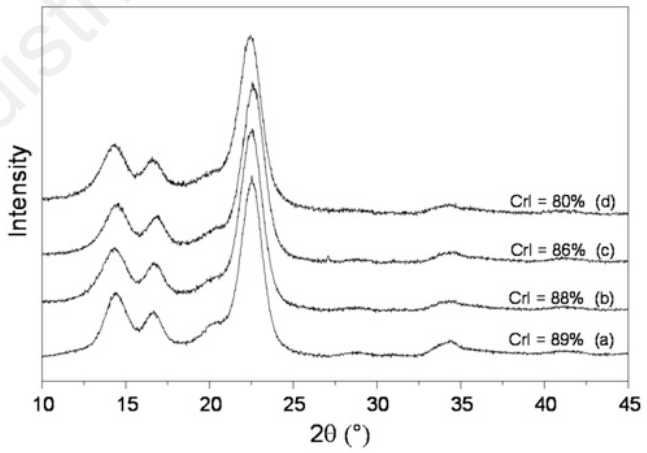

Fig. (5). XRD patterns of native (**a**) and acetylated BNC, (**b**) DS=0.42 (lactic acid), (**c**) DS=0.56 (L-tartaric acid), (**d**) DS=0.90 (citric acid).

80%. Analysis of DRX results together with the acetylation profiles observed in Fig. (**2**) suggest that, under the conditions chosen and within the studied reaction interval, acetylation of BNC catalyzed with lactic and L-tartaric acids is a surface-only process, involving essentially the OH groups on the surface or in the amorphous regions of BNC, and not affecting its ultrastructure [11, 14]. On the other hand, the ascending profile observed in Fig. (**2**), together with XRD results of Fig. (**5**) suggest that, given enough time, acetylation catalyzed by citric acid might be able to introduce a

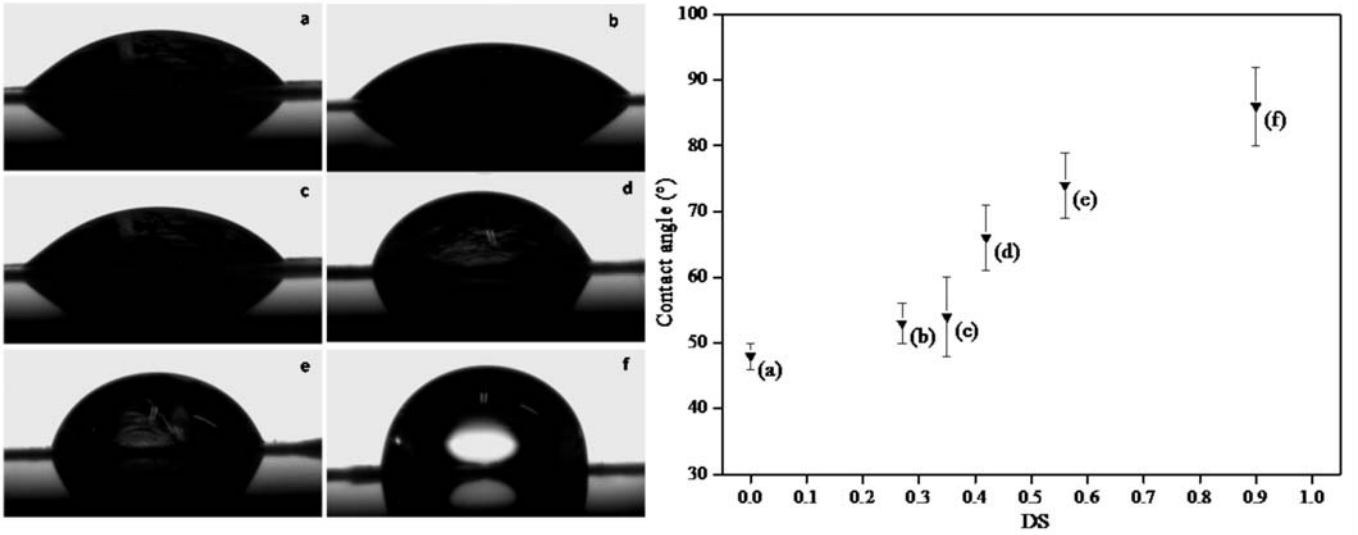

Fig. (6). Images of water drops used to determine contact angles of native and acetylated BNC, 60 s. Equilibrium contact angles measured for acetylated samples as a function of their DS. (**a**) native BNC, (**b**) DS=0.27 (citric acid), (**c**) DS=0.35 (L-tartaric acid), (**d**) DS=0.42 (lactic acid), (**e**) DS=0.56 (L-tartaric acid), (**f**) DS=0.90 (citric acid).

higher number of acetate groups in BNC, involving not only the more accessible surface-OH groups. This, in turn, would reduce the hydrogen bonding density between cellulose molecules, and partially affect the crystalline structure of BNC.

Wettability

In order to obtain qualitative information about the change in the hydrophilicity of BNC achieved by the organocatalytic acetylation proposed, equilibrium contact angles (60 s) were determined as a measure of the samples' wettability in water. Images of water drops used to determine contact angles are in shown in Fig. (**6**) for chosen samples. Fig. (**6**) also illustrates the evolution of the average equilibrium water contact angle with the DS of the samples determined by saponification. As it is shown, equilibrium contact angles continuously increased with the acetylation level of the samples, indicating that the acetylation methodology proposed effectively altered the hydrophilic character of cellulose nanoribbons surface by partial replacement of hydroxyls with less polar ester groups.

In all cases, the results illustrated no significant change in contact angles after 60 s observation. However, prior to attaining equilibrium it was observed that average contact angle values measured for native and acetylated BNC with DS lower/equal than DS=0.35 varied significantly with time due to the spreading action. On the other hand, contact angle values found for acetylated BNC samples with DS equal/higher than 0.42 decreased slightly with time and only within the first seconds of assay. The different behaviour in terms of drop spreading is also an indicative that water has a lower affinity for highly derivatized BNC.

The time required for complete drop absorption was determined as a function of DS, as further qualitative evidence of the increase in the hydrophobicity of BNC pellicles upon organocatalytic acetylation. As it is illustrated in Table **1**, the time required for complete water drop absorption significantly increased with the samples' DS, confirming that esterification significantly changed the polarity of the samples.

Table 1. Results from water drop test. a) native BNC, (b) DS=0.27 (citric acid), (c) DS=0.35 (L-tartaric acid), (d) DS=0.42 (lactic acid), (e) DS=0.56 (L-tartaric acid), (f) DS=0.90 (citric acid).

Sample	DS	Time (min)
(a)	0	25±5
(b)	0.27	40±3
(c)	0.35	38±3
(d)	0.42	70±8
(e)	0.56	74±8
(f)	0.90	83±9

Dispersibility in Solvents of Different Polarity

The high hydrophilicity of cellulose nanoparticles limits not only their use in composite materials with hydrophobic matrices, but also their dispersion in non-polar liquid media. As a qualitative indication of the change in BNC hydrophilicity due to organocatalytic acetylation, chosen esterified BNC samples were contacted with solvents of decreasing polarity (*i.e.* decreasing PI), and their dispersibility was evaluated. Fig. (**7**) illustrates the initial and 72 h-appearance of dispersions for native and acetylated BNC (DS=0.39).

As shown in Fig. (**7a**), native BNC thoroughly dispersed in water (I) and acetone (II), whereas rapid sedimentation of BNC took place in dichloromethane (III) and petroleum ether (IV). On the other hand, acetylated BNC (DS=0.39) slowly sedimented in water, whereas extensive dispersion in acetone and also in this case in dichloromethane (III) was observed (Fig. **7b**). Acetylated samples with higher DS showed the same dispersion pattern, with good dispersion in dichloromethane but still no compatibility with petroleum ether medium. Inspection of dispersions for higher times evidenced the stability of suspensions (Figs. **7c-d**). Results

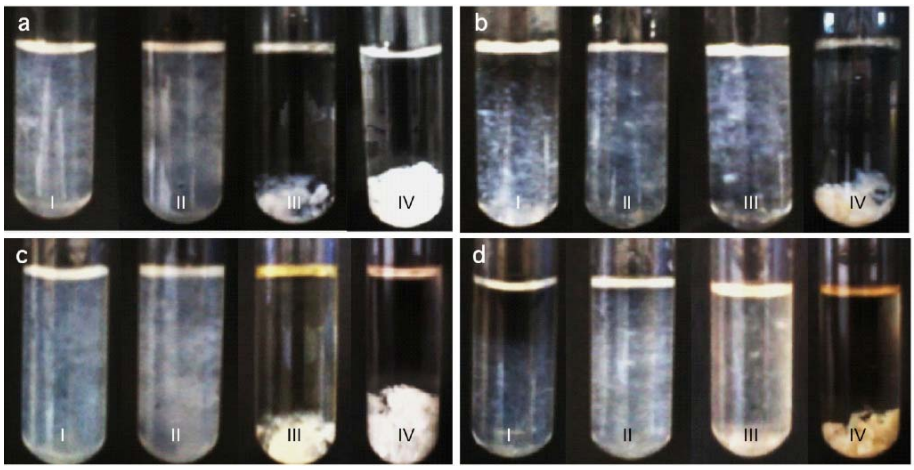

Fig. (7). Dispersibility of native and acetylated BNC (DS=0.39) in different solvents at 0 and 72 h. (**a**) native BNC, 0 h; (**b**) acetylated BNC, 0 h; (**c**) native BNC, 72 h; (**d**) acetylated BNC, 72 h. I: water (PI=10.2), II: acetone (PI=5.1), III: dichloromethane (PI=3.1), IV: petroleum ether (PI=0.1) [27].

included in this section also illustrate the change in BNC hydrophilicity achieved by partial substitution of hydrophilic hydroxyl with less polar acetate groups.

EXPERIMENTAL

Materials

The bacterial strain used for BNC production (*Gluconacetobacter xylinus*, syn. *Acetobacter aceti* subsp. *xylinus, Acetobacter xylinum,* NRRL B-42) was gently provided by Dr. Luis Ielpi from Fundación Instituto Leloir, Buenos Aires, Argentina. For inocula the formulation of BNC production medium, anhydrous dextrose (Biopack), meat peptone (Britania, Laboratorios Britania S.A.), yeast extract (Britania, Laboratorios Britania S.A.), disodium phosphate (Anedra), citric acid (Merck), glycerol (Sintorgan) and corn steep liquor (Ingredion) were used. Acetic anhydride (Merck), lactic acid (Cicarelli), citric acid (Merck), L-tartaric acid (Biopack), hydrochloric acid (Anedra) and sodium hydroxide (Biopack) were all reagent grade chemicals.

Production of BNC

Inocula of *Gluconacetobacter xylinus* NRRL B-42 were cultured in 100 mL Erlenmeyers flasks containing 20 mL of Hestrin and Schramm (HS) medium [28] and incubated under orbital agitation (200 rpm) for 48 h at 28°C. For BNC production, 10 % (v/v) inocula were transferred to Erlenmeyers flasks containing 4.0 % w/v glycerol and 8.0% corn steep liquor (flask/medium v/v ratio of 5:1), and statically incubated at 28°C for 14 days. The bacterial nanocellulose pellicles thus obtained were collected and thoroughly rinsed with distilled water in order to remove the culture medium. Then, the BNC membranes were homogenized in a blender for 5 min and maintained for 14 h in a 5 % w/v KOH solution to eliminate the bacterial cells, and they were finally rinsed with distilled water till neutralization.

Esterification of BNC Catalyzed by α-Hydroxy Acids

Homogenized bacterial nanocellulose pellicles (0.5 g, dry weight) were solvent exchanged from water through acetic acid (three times, 20 mL), into acetic anhydride (three times, 20 mL). The never-dried acetic anhydride-soaked BNC was then poured into an oven-dried 100 mL glass flask equipped with a reflux condenser, to which 3.1 mmol of the chosen α-hydroxy acid and 50 mL (*i.e.* 0.53 mol) of acetic anhydride were added. The mixture was then heated to 120°C under continuous magnetic agitation in a thermostatized oil bath. Once the target temperature was reached, esterification was alternatively run for different reaction times (1, 3, 5 and 7 h). After the chosen reaction time, the mixture was allowed to cool down to room temperature, the solid product was separated by vacuum filtration and thoroughly washed with distilled water for catalyst and unreacted anhydride removal. The progress of the uncatalyzed esterification reaction was also monitored. Reactions were performed in duplicate, being in all cases the error lower than 3%.

The level of esterification attained in BNC samples was determined by heterogeneous saponification and back titration with HCl, as detailed elsewhere [15]. The acyl content and the degree of substitution achieved were then calculated by:

$$\text{Acyl (\%)} = [(V_B - V_S) \times N_{HCl} \times 4{,}3] / W \quad (1)$$

$$DS = (162 \times \text{Acyl \%}) / [4300 - (42 \times \text{Acyl \%})] \quad (2)$$

where V_B (mL) is the volume of HCl required for blank titration, V_S (mL) is the volume of HCl required to titrate the sample, N_{HCl} is the normality of the HCl solution, and W (g) is the mass of sample used.

Characterization of Esterified BNC

Fourier Transform Infrared Spectroscopy (FTIR): Fourier transform infrared spectra of native and acetylated grinded BNC samples were acquired on an IR Affinity-1 Shimadzu Fourier Transform Infrared Spectrophotometer in transmission mode. Carefully dried (12.5 mg, 110°C, 1 h) samples were mixed with previously dried KBr (130°C, overnight) in the ratio 1:20 and pressed into a disc. Spectra were collected with 40 scans in the range of 4000 to 700 cm^{-1} with a resolution of 4 cm^{-1}, and normalized against the intensity of the absorption at 1165 cm^{-1}, corresponding to the (C–O–C) link of cellulose [11, 21].

Field Emission Scanning Electron Microscopy (FE-SEM): Drops of native and acetylated BNC/water suspensions (0.2 % w/v) were deposited on microscope glasses and dried at 100°C for 5 minutes. Samples were then coated with gold using an ion sputter coater, and observed by use of a scanning electron microscope Zeiss Supra 40 with field emission gun operated at 3 kV.

X-ray diffraction (XRD): The structure of native and acetylated grinded BNC samples was analyzed with a Rigaku D/Max-C Wide Angle automated X-ray diffractometer with vertical goniometer. The X-ray diffraction pattern was recorded in a 2θ angle range of 10 to 45° at a step size of 0.02°. The wavelength of the Cu/Kα radiation source used was 0.154 nm, generated at accelerating voltage of 40kV and a filament emission of 30 mA. In order to calculate the crystallinity index of native and esterified BNC samples Segal's method was applied [26]:

$$CrI = (I_{002} - I_{am})/ I_{002} \times 100 \quad (3)$$

where I_{002} corresponds to the maximum intensity of the 002 lattice diffraction, and I_{am} is the intensity at 2θ=18°, after the subtraction of the background signal measured without BNC. This is an empirical equation for estimating de degree of crystallinity of pure cellulose materials.

Wettability, contact angle measurements: Native and acetylated BNC samples were made into films (1.5-2 cm width, 10-13 cm length) by spreading and drying the recovered nanofibrils suspension (200 mg dried weight) between nylon-covered microscope glasses at 110°C for 30 min. Equilibrium contact angles of native and acetylated BNC pellicles were measured using a contact angle goniometer (OCA 15LHT Plus photo-microscope, Dataphysics). Immediately before analysis membranes were further dried at 80°C for 5 h. For each film five sessile contact angles were registered at room temperature during 60 s after deposition of 30 μL distilled water drops, and an arithmetic mean of the equilibrium contact angle was calculated. Images of the sessile drops were processed using SCA20 software. Besides, pellicles were also subjected to water drop tests, for which 30 μL water droplets were manually placed on the dried pellicles (80°C, 5 h) using a syringe, and the time required for complete absorption was determined.

Dispersibility: The dispersibility of native and chosen acetylated cellulose samples (DS=0.39, 0.58 and 0.9) in solvents of different polarity index (PI) such as water, acetone, dichloromethane and petroleum ether 60-80°C (*i.e.* ligroin) was studied. For this purpose, aqueous (0.35 w/v) suspensions of native and acetylated BNC were prepared and solvent exchanged (three times, 5 mL) from water through acetone into dichloromethane and petroleum ether. The suspensions were sonicated for 15 min and their stability at room temperature was observed during 14 days.

CONCLUSION

A facile acetylation route for reducing the hydrophilicity of bacterial cellulose nanoribbons has been demonstrated. The methodology involves the use of different naturally occurring α-hydroxy acids such as L-tartaric, lactic and citric acids as organocatalysts, and proceeds under solvent-free conditions at moderate temperature and atmospheric pressure.

All organic catalysts have been shown to be active in the acetylation of BNC, although different kinetic evolution of the catalyzed esterifications is observed. In particular, citric acid appears as very promising in view of the high rate at which the catalyzed reaction proceeded for time intervals for which the L-tartaric/lactic acid-catalyzed esterifications showed only marginal increments. By use of the chosen α-hydroxy acids and by controlling the reaction time, BNC with substitution degrees in the 0.27-0.90 interval could be attained. Comparison of results with data from the L-tartaric acid acetylation of BNC with acetic acid as acetylating agent, evidenced that the use of acetic anhydride as acylant leads to an outstanding increase in acetylation rate which allowed obtaining similar modification levels in much lower reaction time intervals.

Characterization of acetylated cellulose microfibrils further confirmed the occurrence of the esterification reaction and illustrated the expected change in BNC hydrophilicity. Fourier transform infrared spectroscopy showed the appearance of new signals associated with the ester groups introduced, whereas scanning electron microscopy suggested that the methodology proposed does not induce significant changes in nanofibrils morphology and preserves the fibrous structure of BNC. X-ray diffraction analysis suggested surface-only acetylation especially for samples with DS values not higher than 0.56. Assays performed in order to qualitatively demonstrate the modification of BNC polarity by the organocatalytic acetylation route, evidenced that derivatization significantly reduced the water wettability of the pellicles and effectively improved the dispersibility of the nanoribbons in less polar solvents.

The results obtained herein suggest that the organocatalytic acetylation route is a promising eco-friendly toxic-solvent free method for derivatization of BNC to be used as reinforcement of non polar polymeric matrices. Further studies devoted to assay the effect of other reaction parameters on DS are currently going on.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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LIST OF ABBREVIATIONS

Acyl (%)	=	Acyl content
BNC	=	Bacterial nanocellulose
CrI	=	Crystallinity index
DS	=	Degree of substitution
FE-SEM	=	Field emission scanning electron microscopy
FTIR	=	Fourier transform infrared spectroscopy

HS = Hestrin and Schramm

PI = Polarity index

XRD = X-ray diffraction

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