

Manufacture of a bio-tissue based on nanocrystalline cellulose from chilean bamboo *Chusquea quila* and a polymer matrix using electrospinning

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ABSTRACT

Polymers of renewable origin have aroused great interest among researchers due to their sustainable, environmentally friendly nature. This work presents a biopolymer called bio-tissue, as it is created by electrospinning. This bio-tissue was formed with a polymer matrix of cellulose acetate (CA) reinforced with crystalline cellulose (NCC) derived from an autochthonous Chilean bamboo species of no commercial value which is considered a pest, *Chusquea quila* or quila. Bio-tissues were produced with three concentrations of NCC (1, 5 and 10% as a dry weight proportion of cellulose acetate) and their technological potential as an interior coating in small constructions was assessed. The morphology of the bio-tissues showed that the CA nanofibers containing NCC were of better quality and more uniform diameter than pure CA. The thermal profile showed that the highest concentration of NCC (10% as a dry weight proportion of cellulose acetate) induced earlier degradation; it was less thermally stable and decomposed at lower temperatures. The bio-tissue with 5% as a dry weight proportion of cellulose acetate showed the greatest resistance to traction with a break-point of 30 MPa and an elasticity module of 1.597 MPa. Finally, it was shown that the permeability to water vapour, oxygen and carbon dioxide was low, allowing regulated passage of these molecules. These results show the feasibility of using cellulose nanofibers as a reinforcement in polymer matrices; this could have various applications in fields ranging from the construction industry to food packaging.

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1. Introduction

Growing environmental concerns about issues such as sustainability raise challenges associated with the life of non-degradable products, implying the eventual elimination of these materials. Compounds derived from renewable resources have been strongly recommended as their potential replacements. Increasing environmental awareness associated with predicted future shortages of fossil resources has aroused growing interest in the use of environmentally friendly polymers, encouraging the development of new materials produced from alternative sources which are biodegradable and non-toxic [1].

Among the types of polymer currently being produced, those which contain nanoparticles in their structure have attracted much attention due to their unique properties, such as biocompatibility with cellulose derivatives. The properties of these new

polymer biocompounds depend to a large degree on the size, content and structure of the nanoparticles incorporated into them. One of the most widely used techniques for generating these bio-products is electrospinning [2]. This method consists in passing polymer solutions through highly-charged electric fields. Sufficient electrical force is applied to overcome the surface tension of the charged polymer solution; at a certain voltage, fine threads of the solution are expelled from the capillary to the collector plate. Subsequently, the thread moves in the direction of the electric field, stretching in response to internal and external forces. The solvent used in the polymer evaporates and the fibre segments are deposited on a substrate or collector [3].

This method has been widely used in recent decades to manufacture polymer nanofibers. Many researchers have shown that these nanofibers have applications in various areas of industry such as filter materials, tissue engineering, protective clothing, coating materials for the health and construction industries, and the development of controlled-release drugs. The factors governing nanofiber formation by electrospinning are polymer concentration (viscosity), the conductivity of the solution and the electric

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field [4]. The physical–chemical structure of the final product and the morphology of the nanofibers have been extensively studied and have proved to have a great impact on the evolution of the technique. Two factors which are not so clearly defined but which also play an important role in electrospinning are the type and molecular weight of the solvent used to dissolve the polymer. An appropriate solvent, especially the composition of a mixed solvent, will have a decisive effect on the feasibility of producing nanofibers from a polymer using this technique [5].

The so-called nanocelluloses (nanofibrillated cellulose and nanocrystalline cellulose) are cellulose nanoparticles which have been studied as reinforcements in polymer structures formed by electrospinning [6]. They present nanometric dimensions, high crystallinity and the capacity to bond with hydrogen. The principal particularity of these cellulose nanoparticles is that molecules have to pass through their strong network structure, suggesting excellent barrier properties [7].

Nanocrystalline celluloses (NCC) are the most promising nanofibers of the 21st century due to their unique properties, which mean that they may have applications in various fields of scientific and technological progress [8]. NCC are the crystalline domains of cellulose. They present a rod-like morphology and are generally obtained from renewable lignocellulosic resources by controlled acid hydrolysis. High contact surface, chemical functionality, anisotropic mechanical properties and – most importantly – non-toxicity are some of their attractive features [9]. The abundant negatively charged hydroxyl groups on the surface of NCC act as nucleation sites and reducing agents for the growth of metallic nanoparticles [10]. There are various studies of nanoparticles of metals, including gold, platinum, silver, copper and iron, supported on NCC. These studies have been reported in the literature as the “green chemistry pathway”, with potential applications as high-performance polymer nanocompounds and biocatalysts for contaminant remediation [11].

As mentioned previously, the main process by which nanocrystalline cellulose is isolated from cellulose fibres is acid hydrolysis. The amorphous regions of cellulose are hydrolysed preferentially, while the crystalline regions, which have greater resistance to acid attack, remain intact. Thus, acid treatment eliminates microfibrils by default, producing cellulose nanocrystals [12]. Specific hydrolysis and separation protocols have been developed for cellulosic fibres of different origins. The most common sources of cellulose include wood [13], bamboo [14], wheat straw [15], New Zealand flax (*Phormium tenax*) [16], banana skins [17], orange peel [18] and palm oil industrial waste [19]. The present study considered an autochthonous Chilean bamboo species as the source from which to produce nanocrystalline cellulose.

Bamboo species belong to a sub-family of the graminids or Poaceae. They are abundantly distributed across the world's tropical regions. Bamboo is composed of cellulose fibres encrusted in a lignin matrix and is therefore considered to be a compound material. Bamboo canes have been used in the construction industry for floors, walls, windows, doors, roofs and beams [20]. They are also considered very strong structural materials and have been used in bridges, water transport pipes and as scaffolding for high-rise buildings. Bamboo fibres are a very versatile raw material, used in household products like food containers, chopsticks, handicrafts, toys, furniture and musical instruments [21].

The genus *Chusquea* belongs to the Bambusoideae sub-family. It contains approximately 180 species world-wide, of which some 12 are present in Chile. *Chusquea quila* is one of the autochthonous species in the country [22]. The chemical properties are: extractables 4.55%, ash 2.17%, lignin 13.78% and cellulose 54.65%.

This bamboo has no other commercial value; however, its cellulose content makes it a renewable resource for extracting cellulosic fibres for potential new applications in the nanotechnology industry [23].

Recent studies have focused on its properties as a barrier to gases and water vapour in biocompounds reinforced with cellulose nanostructures. One factor which must be considered in these studies is how the transport of material occurs. The gas molecules must first be dissolved in the membrane or tissue before diffusion. Although the surface of the membrane affects the molecules of the permeating gases, the most important factor in molecular migration is mass flow, i.e. the rate of molecular diffusion in the membrane [24]. Their properties as a good oxygen barrier when mixed with cellulose nanostructures may be attributed to the dense network formed by the smallest and most uniform nanofibrils and nanocrystals. In view of the above, the pores in the films serve as the principal pathway for permeation by the gas molecules [25]. Fig. 1 shows a diagrammatic representation of the augmented diffusion trajectory within the membranes or tissues reinforced with cellulose nanostructures. The highly crystalline structure inside the nanofibrils or nanocrystals contributes to their gas barrier properties [26].

There are many studies of barrier properties for use in the construction industry in which cellulose nanostructures are used for reinforcement. One such use is in films composed of nanofibrillated cellulose and montmorillonite (clays) [27]. The compound films in this study were transparent and flexible, and presented very high mechanical and oxygen barrier properties through the nano-layer structures. A film composed of 5% cellulose nanofibers had an Elasticity Module of 18 GPa, resistance to traction of 509 MPa, and oxygen permeability of $0.006 \text{ ml } \mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$.

Torgal et al. [28] present the current state of knowledge on nanomaterials and their use in buildings, including energy efficiency, optimisation of barrier properties, isolation, heating and electricity storage; they also discuss recent applications in organic photovoltaic materials, photo-bioreactors, bioplastics and foams. This is therefore a very interesting work and provides abundant references to current investigation and applications for anyone who wishes to pursue possible future research lines. The authors describe how greater energy efficiency in new and existing buildings can help to reduce overall emissions of greenhouse gases, as well as new technologies, manufacturing processes and products which could help to reduce emissions from the energy sector and offer a sustainable environment.

In view of the above, the object of the present study was to create a bio-tissue from nanocrystalline *Chusquea quila* cellulose inserted in a polymer matrix of cellulose acetate made by electrospinning. The bio-tissue was subjected to traction tests and water vapour transmission tests, and its thermal degradation profile was assessed with a view to use in small buildings for its barrier properties.

2. Experimental

2.1. Preparation of nanocrystalline cellulose from *Chusquea quila*

The *Chusquea quila* used as raw material for this work was obtained according to Oliveira et al. [23]. The chemical and physical properties were determined by ASTM standards. The extractives, ash content, lignin, and alpha cellulose were 4.55%, 2.17%, 13.78%, and 54.65%, respectively. The higher heating value were 5106 kcal/kg and basic density obtained were 290 kg/m^3 . The moisture content was studied during four seasons and found to be the highest in winter (73%). Regarding the nanomechanical profiles, hardness varied from 0.16 GPa in the cortex to 0.21 GPa in the nodule. The average elastic modulus in the nodule and internode was 12.5 GPa, while in the cortex it was 7.45 GPa.

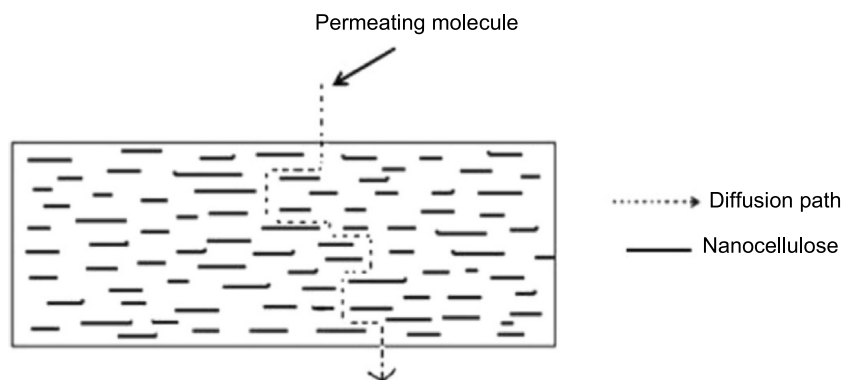


Fig. 1. Diagrammatic representation of the diffusion trajectory within films reinforced with cellulose nanostructures [26].

The cellulose fibre, produced by an oxidative delignification process using peracetic acid, had an apparent crystallinity index of 78% and a residual lignin content of less than 2% (Kappa number 12.34). The nanocrystalline quila cellulose was produced by treatment in the following stages: (1) Acid hydrolysis of pure cellulosic material (15 g of quila cellulose) under strictly controlled conditions: temperature (45 °C in a thermo-regulated bath), time (45 min), shaking (35 rpm), and acid concentration (55% v/v). The acid/cellulose ratio was 1:20 (g/mL); (2) Dilution with distilled water to stop the reaction and repeated washing by successive centrifugation; (3) Extensive dialysis to eliminate completely any free acid molecules (72 h with constant change of distilled water); (4) Mechanical sonication (20 min) to disperse the nanocrystals as a stable, uniform suspension; (5) Ultra-centrifugation to obtain a concentrated solution with nanocrystals. The diameters of the nanocrystals were between 10 and 20 nm and the crystallinity index (CI) was 92%.

2.2. Preparation of the solution for electrospinning

The method used was based on Liu and Tang [29]. The polymer matrix was prepared with cellulose acetate (39.8% acetyl content, molecular weight 50,000 daltons, CAS-9004357, Sigma-Aldrich) and solvents at a concentration of 1.5% w/v. The solvents used were acetone (Sigma-Aldrich) and N,N-dimethylacetamide (DMAc, Sigma-Aldrich). The binary mixture consisted of 60% v/v acetone and 40% v/v DMAc.

The nanocrystalline quila cellulose was previously subjected to 5 cycles of washing and centrifugation (10,000 rpm) with acetone, in order to eliminate the water (polar compound) and improve the solubility of the cellulose in acetate (apolar compound). The quantities of NCC used to prepare the emulsions were 0.015 g, 0.075 g and 0.15 g, corresponding to 1% (BioT1), 5% (BioT5) and 10% (BioT10) as a dry weight proportion of the dry weight of cellulose acetate, 1.5 g.

A polymer solution with 10 mL of the binary mixture of solvents and 1.5 g of CA was prepared under constant shaking; then the NCC precipitate obtained from acetone washing was introduced into the polymer mixture and kept under axial shaking at ambient temperature for 12 h. The viscosity and conductivity of the emulsions were determined using a Brookfield digital viscosimeter (Model-DV-premium) and a conductivity metre (Model Isteck) at 19 °C respectively. The CA/NCC (cellulose acetate/nanocrystalline cellulose) emulsion was placed in a glass syringe (15 mL) in the electrospinning equipment and connected to a piston pump, allowing a constant flow to be generated through the syringe.



Fig. 2. Electrospinning equipment with rotating cylindrical collector.

2.3. Configuration of electrospinning

Previous conditioning and adaptation tests of the emulsions allowed better configuration of the electrospinning equipment parameters (Model Ne300, Inovenso, Turkey). Fig. 2 shows the equipment. The following parameters were adopted: flow velocity through the syringe, 0.2 mL h⁻¹; distance from the ejector to the collector 15 cm; voltage, 27 kV; interior temperature, 25 °C and continuous production time 5 to 6 h.

2.4. Characterisation of bio-tissues

The thicknesses were measured by micrometre (Mitutoyo, model IDC 112, Kawasaki, Japan), precision 0.01 mm. All the bio-tissues were pre-conditioned in a constant temperature humidity chamber at 25 °C and 50% relative humidity (RH) for at least 48 h. The results reported are the mean of 10 measurements taken from different positions in the bio-tissue.

Sweep electronic microscopy (SEM) was used to determine the morphology of the bio-tissues (15 kV and 20 to 25 mm working

distance; JEOL Model LV6610, JEOL USA, Inc.). To prepare the sample a small portion of the fibre bands was fixed to the carbon transporter belt and mounted on a solid support; each sample was then coated with gold using a sputter coater [30].

Thermal degradation profile of the nanofibers obtained was characterised by TGA (TGA Q 500, TA Instruments) at a heating rate of 10 °C/min with purged nitrogen gas at 100 ml/min.

Traction was measured with a Zwick Roell Universal Testing Machine (Model Z202, 2000 kg Zwick Roell – Germany) according to ASTM D882-1991 with traction strips 100 mm long and 25 mm wide. The initial length between pincers was 50 mm at a deformation rate of 10 mm/s.

Water vapour permeability tests were carried out using the ASTM F1249-13 method with some modifications. Each bio-tissue sample was sealed over a circular aperture of 0.00185 m² on a permeation cell and stored in a desiccator at 20 °C. To maintain a relative humidity (RH) gradient of 75% across the bio-tissue, a saturated NaCl solution (75% RH) was used in the desiccator. The RH inside the cell was always lower than outside, and the water vapour transport was determined by the weight gain of the permeation cell.

Permeability of the bio-tissues to oxygen and carbon dioxide was assessed by the accumulation method, in a specially designed stainless-steel cell formed of two chambers of volume 89.10 cm³, separated by the bio-tissue to be tested, with a transmission area of 0.0012 m² [31]. The gas permeability was measured by placing the bio-tissue to be tested between these chambers after closing the cell firmly. The total pressure difference across the bio-tissue should be zero and the partial pressure difference for the gas was approximately 1 atm. The quasi-isostatic method used was based on measuring the amount of gas diffused across the bio-tissue. To measure the concentration, 100 µmL O₂ or 50 µmL CO₂ were extracted from the samples in the test chambers, originally filled with air, with a Pressure-Lok[®] syringe (Supelco, USA). The gas concentration was measured in a Clarus 500 gas chromatograph (Perkin Elmer) with a thermal conductivity detector with a Carboxen 1000 column for oxygen permeability and a flame ionisation detector with a Carboxen 1006 column for carbon dioxide. The gas permeability was measured under 25 °C and 100% RH and expressed in cm³ m⁻¹ s⁻¹ Pa⁻¹.

3. Results and discussion

Table 1 shows the conductivity electrolytic and apparent viscosity results of the emulsions prepared (BioT1, BioT5 and BioT10), with a control consisting of cellulose acetate prepared without addition of nanocrystalline cellulose. Likewise, it was found that the viscosity and conductivity values of the solutions increased with the CA concentration. There are prior reports of this behaviour in the literature. When the NCC concentration in the solution is low, the polymer chains are sufficiently separated, so interaction between the polymer and the nanoparticles is minimised; in these cases, the only variable influencing the electrospinning process is the surface tension [32]. Furthermore, the increase in conductivity and viscosity in an emulsion may be attributed to the solution of residual electrolytes in the CA during preparation of the solution.

The electrospinning equipment used in this study had a rotating cylindrical collector, giving a final result of a bio-tissue with approximate dimensions 30 cm long by 20 cm wide. The bio-tissue samples were cut into 70 mm diameter circles for the thickness measurements and the permeability tests for water vapour, oxygen and carbon dioxide. The thickness values presented a uniform range from 60 µm and 80 µm, concentrated around 70 µm. Fig. 3 shows the measurement points.

Fig. 4 shows SEM images of the electrospinning fibre bands produced from CA using NCC: BioT1 (B), BioT5 (C) and BioT10 (D).

Table 1
Result of conductivity and apparent viscosity in prepared emulsions.

	Conductivity electrolytic (µS cm ⁻¹)	Viscosity (mPa s)
Pure cellulose acetate	3.92	69.4
BioT1	3.50	66.5
BioT5	2.94	60.1
BioT10	2.65	58.7

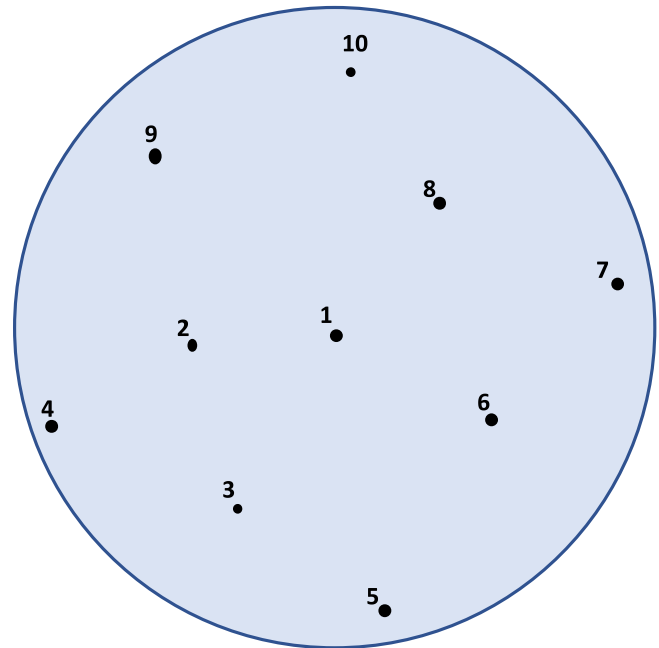


Fig. 3. Diagram of bio-tissue samples for the thickness measurements and the permeability tests for water vapour, oxygen and carbon dioxide.

An image of a sample of pure cellulose acetate is also included for reference (A). It can be seen that the CA nanofibers containing NCC were of better quality and more uniform diameter (and diameter distribution) than the pure CA. This suggests that NCC give CA solutions better 'electrospinnability' [33]. This may possibly be due to certain molecular interactions which improve the miscibility of the polymer and provide a more uniform flow, leading to the formation of fibres free of solidification or crystallisation [34].

Another important aspect is the reticulation effect. The improvement observed in the structural integrity of the fibres with NCC may be explained by the interactions and the hydrogen bonding network formed between the CA chains of the matrix and the NCC reinforcements [35].

Fig. 5 shows the TGA curves of the BioT1, BioT5 and BioT10 composite nanofibers. BioT1 and BioT5 started to decompose at 340 °C and decomposition peaks are found between 360 and 380 °C. The maximum decomposition temperatures were 405 °C and 390 °C respectively. The nanofiber residues after thermal decomposition at 550 °C were 23% for BioT1 and 29% for BioT5. These results coincide with the range of values reported in the literature for cellulose acetate compounds reinforced with nanoparticles [36].

The BioT10 sample presented a lower temperature for the start of decomposition (225 °C), followed by an irregular degradation stage and leaving 38% waste at 700 °C. This may be explained by the quantity of nanocrystals present in the compositions. The presence of NCC altered the crystallinity of the polymer matrix, making it more vulnerable to temperature [37].

Fig. 6(A) shows the traction studies of the BioT1, BioT5 and BioT10 bio-tissues, and a control sample of CA. The resistance

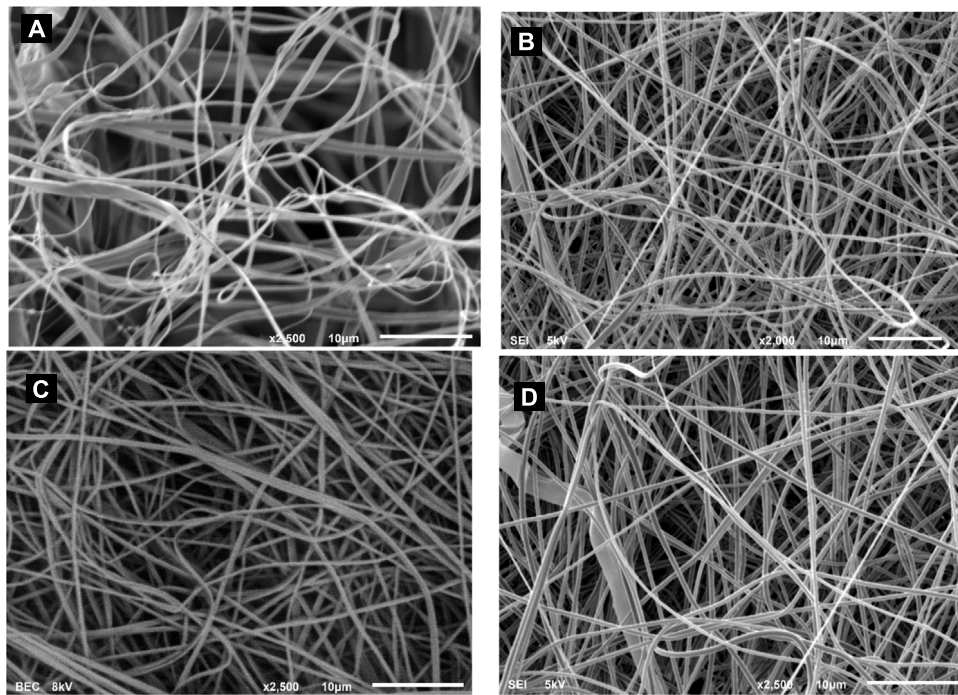


Fig. 4. SEM micrography of electrospinning fibres produced from (A) pure cellulose acetate; (B) BioT1; (C) BioT5; (D) BioT10.

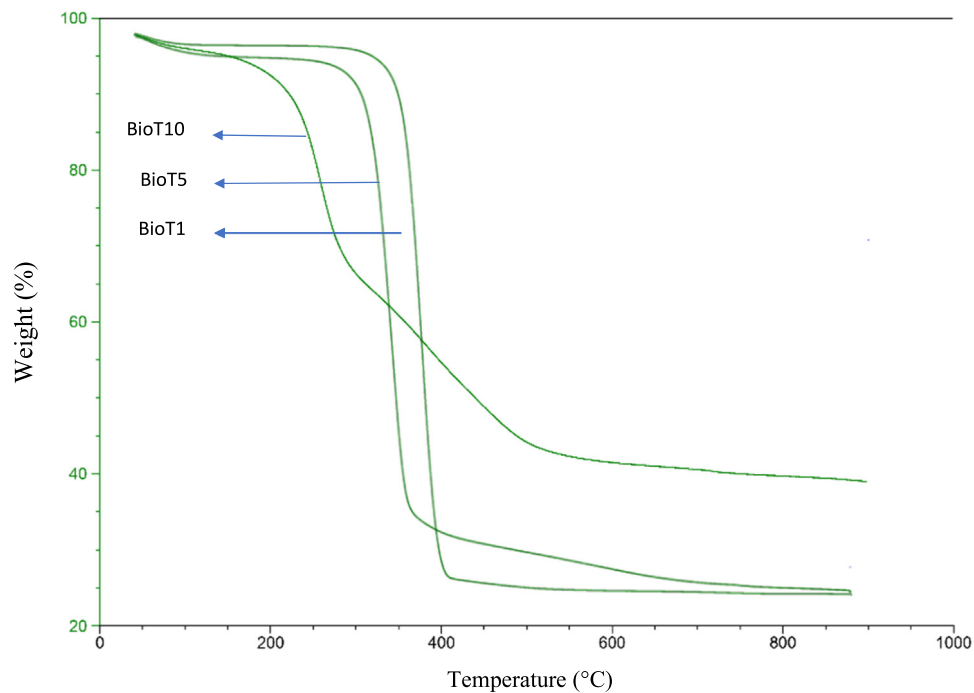


Fig. 5. TGA curves of the BioT1, BioT5 and BioT10 composite nanofibers.

to traction increased with the increase in the NCC concentration from BioT1 to BioT5. The highest resistance to traction was 30.67 MPa, approximately 15 times higher than the resistance of the CA control. However, at the highest concentration of NCC (BioT10), the resistance to traction fell to 27.44 MPa. The improvement in resistance to traction may be related with the “reinforcement of the polymer matrix” effect explained by good dispersion of the cellulose crystals at a concentration of 5% as a dry weight proportion of the dry weight of CA polymer; however when

this concentration is doubled, the phases may have separated, resulting in poor dispersion of the nanofibers [38].

The maximum elasticity module of 1.59 MPa was found in the BioT5 sample, while the value for the control sample was 0.85 MPa. The bibliography suggests that the nanofibers in pure cellulose acetate tissue are very short, with maximum length of a few centimetres at most; moreover, the fibres are slightly bunched, with no point of chemical reticulation between them. Consequently, their resistance to traction and their elasticity module

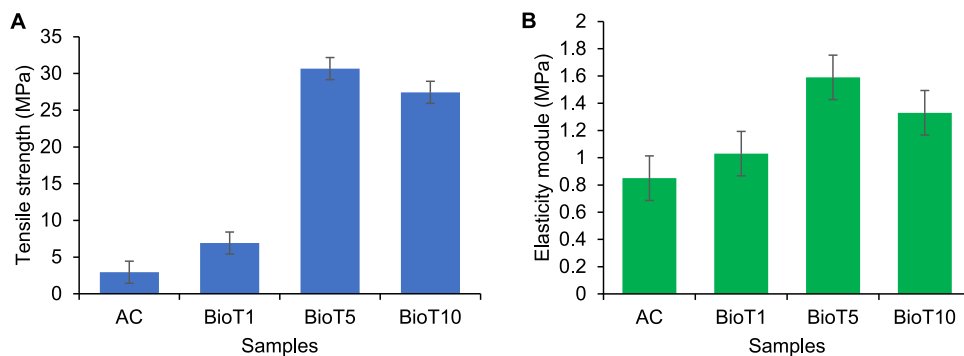


Fig. 6. Traction studies (A) and Elasticity module tests (B) of the nanofiber composites BioT1, BioT5 and BioT10.

are low [29]. This theory is supported by the results of the present study.

The permeability to water vapour is a very important test for natural nanoparticles and reinforced fibres, since it defines their potential as a coating and a barrier in the construction industry. The performance of these nanocompounds may suffer when exposed to environmental conditions for a long period. The water vapour permeability test provides information on the adhesion between the particles and the matrix in the interface region, since the better the adhesion between the matrix and the particles, the fewer will be the sites where water can be stored and thus the lower the water absorption [39]. Fig. 7 shows the percentage of water absorbed at different time intervals.

Cellulose acetate is a hydrophobic polymer by nature and insoluble in water; thus, the values given below show a tendency for water absorption to increase with the quantity of cellulose nanocrystals in the composition of the bio-tissue. The graph shows that the increase in the water absorption rate is almost linear for nanofibers of BioT1 and BioT10. The water absorption rate is lower in the BioT5 composition as shown by the smaller percentage increase in weight, with only 1.8% water absorption after 7 h. This may be explained by the fact that the concentration of 5% cellulose nanocrystals allows uniform adhesion between the polymer matrix and the nanoparticles.

The positive impact of polymer biocompounds reinforced with cellulose nanoparticles on barrier properties is very varied, since it depends on several very important parameters. One of these parameters is the nature of the polymer matrix (polar or apolar, hydrophilous or hydrophobic). The thickness of the compound studied, and the composition/quantity of the nanoparticles inserted are also important [40].

One study showed that the presence of cellulose nanoparticles modified strongly the diffusion properties of starch. It was observed that in nanocompounds plastified with glycerol and filled with cellulose nanoparticles to 70% weight, the humidity absorption of the compound material was reduced to half the value obtained with a film of pure plastified starch. Nevertheless, the mean and initial diffusion coefficients diminished with the increase in the content of cellulose nanoparticles and increased with the increase in the glycerol content [41]. In another study, the gas (oxygen) permeability of samples with cellulose nanocrystals in PVA (polyvinyl alcohol) was measured, showing that the oxygen transmission rate (OTR) was quite low. The values for pure films were 17.0 and 17.8 ml m⁻² day⁻¹. These values are within the recommended range for packing in a modified atmosphere. The good barrier properties of films with cellulose nanoparticles were attributed to the low permeability of improved cellulose (generally with crystalline fibril structure) [42].

The water and air barrier in buildings requires a structure designed to create millions of microscopic pores to regulate the

passage of air and liquid water, while allowing water in the gas phase to pass. A polyethylene coating is impermeable to air and water, but it is also impermeable to water vapour; thus, walls cannot breathe and any water which penetrates them remains trapped inside indefinitely. With time, these permanently damp materials may start to rot or rust, and fungi and mould may develop. An intelligent product should offer a strong, resistant, selective barrier, permeable to water vapour and with regulated impermeability to air [43].

The improvement in the barrier properties of the bio-tissues in this study may be attributed to the crystallinity and uniform thickness of the nanocrystalline quila cellulose used, although moderate increases in the values recorded were observed. One possible explanation is that the O₂ and CO₂ molecules tend to react chemically with the surface of the nanofibers; the best permeability properties were observed in the BioT1 and BioT5 bio-tissues.

As might have been expected, the quantity of nanocrystalline cellulose is an important factor which governs the performance of the biocompound (Fig. 8). Bio-tissues have a potential for use in barrier applications, while water absorption and high humidity can be mitigated with hydrophobic polymer matrices. We found that the two bio-tissue sample compositions BioT1 and BioT5 offer potential for further research into new parameters which will allow them to be applied as a coating in the construction industry in small buildings.

4. Conclusions

1. This study is the final part of a doctoral thesis project which culminated with the last specific object proposed: to make a bio-tissue composed of nanocrystalline *Chusquea quila* cellulose inserted into a cellulose acetate polymer matrix made by electrospinning.

2. Cellulose acetate bio-tissues were made with three concentrations of nanocrystalline cellulose, BioT1, BioT5 and BioT10 (1, 5 and 10% as a dry weight proportion of the acetate). Morphological analysis showed that the CA nanofibers containing NCC present better quality and more uniform diameter. The thermal profile showed that a higher concentration of NCC produced a more thermally unstable product which decomposed at lower temperatures. The BioT5 bio-tissue showed the greatest resistance to traction with a break-point of 30 MPa and an elasticity module of 1.597 MPa. The permeability to water vapour, oxygen and carbon dioxide was shown to be low, allowing regulated passage to these molecules.

3. These results show the feasibility of developing polymer fibres with cellulose nanostructures to reinforce their properties; this could have various applications in fields ranging from the construction industry to food packaging.

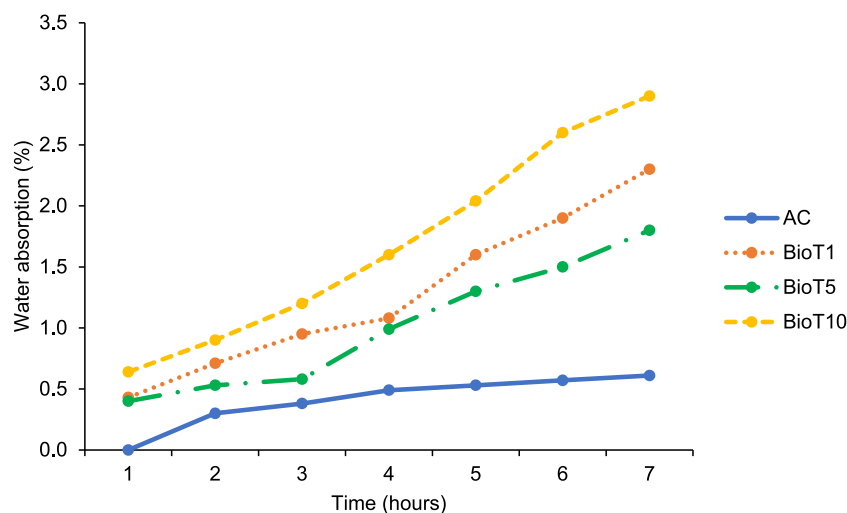


Fig. 7. Results of the water vapour permeability test in bio-tissues.

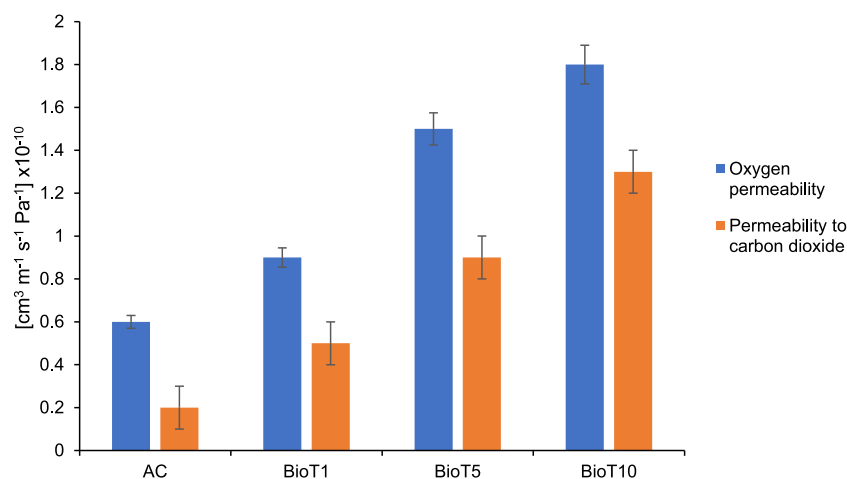


Fig. 8. Results of the oxygen and carbon dioxide permeability tests.

CRediT authorship contribution statement

Patricia E. Oliveira: Conceptualization, Methodology, Validation, Formal analysis, Writing - original draft, Visualization. **Ximena Petit-Breuilh:** Writing - review & editing, Supervision. **Paola E. Díaz:** Investigation, Data curation. **William Gacitúa:** Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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