



## Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications

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### ABSTRACT

Nanocellulose is the crystalline domains obtained from renewable cellulosic sources, used to increase mechanical properties and biodegradability in polymer composites. This work has been to study how high pressure defibrillation and chemical purification affect the PALF fibre morphology from micro to nanoscale. Microscopy techniques and X-ray diffraction were used to study the structure and properties of the prepared nanofibers and composites. Microscopy studies showed that the used individualization processes lead to a unique morphology of interconnected web-like structure of PALF fibers. The produced nanofibers were bundles of cellulose fibers of widths ranging between 5 and 15 nm and estimated lengths of several micrometers. Percentage yield and aspect ratio of the nanofiber obtained by this technique is found to be very high in comparison with other conventional methods. The nanocomposites were prepared by means of compression moulding, by stacking the nanocellulose fibre mats between polyurethane films. The results showed that the nanofibrils reinforced the polyurethane efficiently. The addition of 5 wt% of cellulose nanofibrils to PU increased the strength nearly 300% and the stiffness by 2600%. The developed composites were utilized to fabricate various versatile medical implants.

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### 1. Introduction

Research for development of biodegradable materials from renewable sources is increasing. The availability of biopolymers, relatively cheaper, which occur in abundance in nature, can be cited as an important reason. An example of biopolymers presenting these advantages is cellulose. The recent interest in using stiff nanometric particles as reinforcement materials in polymeric

matrixes, composites or nanocomposites, has been increasing. Two good examples of these types of particles are carbon nanotubes and cellulose nanocrystals. Cellulose nanocrystals, also reported in the literature as whiskers, nanofibers, cellulose crystallites or crystals, are the crystalline domains of cellulosic fibers, isolated by means of acid hydrolysis, and are called in this way due to their physical characteristics of stiffness, thickness, and length (De Souza Lima & Borsali, 2004).

Samir, Alloin, and Dufresne (2005) report that cellulose whiskers are regions growing under controlled conditions, which allows individual high-purity crystals to form. Their highly ordered structure may not only impart high resistance, but also make significant changes to some important properties of materials, such as electrical, optical, magnetic, ferromagnetic, and dielectric nature, as well as concerning conductivity.

Since cellulose is classed as a carbohydrate (a substance containing carbon, hydrogen and oxygen), it is necessary to point out that although this term applies to a large number of organic compounds, cellulose is unique in that it can be either synthesized from, or hydrolyzed to, monosaccharides (Khadem, 1988). The repeating unit of the cellulose polymer is known to comprise two anhydroglucose rings joined via a  $\beta$ -1,4 glycosidic linkage from

**Abbreviations:** PALF, Pineapple leaf; NC, Nanocellulose; PU, Polyurethane; min, Minutes; DP, Degree of polymerization; BC, Bacterial cellulose; NaOH, Sodium hydroxide; CH<sub>3</sub>COOH, Acetic acid; NaClO, Sodium hypochlorite; H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Oxalic acid; MDI, Methylene di-*p*-phenyl-diisocyanate; BD, 1,4-Butanediol; MIDE, 2,2'-(Methylimino)diethanol; DMF, *N,N*-dimethylformamide; PCL-diol, Polycaprolactone diol; *M<sub>n</sub>*, Molecular weight; kPa, Kilopascal; MPa, Megapascal; rpm, Revolutions per minute; XRD, X-ray diffraction; SEM, Scanning Electron Microscopy; ESEM, Environmental Scanning Electron Microscopy; AFM, Atomic Force Microscopy; *A*<sub>0</sub>, Free amplitude; *r*<sub>sp</sub>, Set-point ratio; *A*<sub>sp</sub>, Setpoint amplitude; THF, Tetrahydrofuran; PTFE, Polytetrafluoroethylene; mm, Millimetre;  $\mu$ m, Micrometre; nm, Nanometre.

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this unit (called cellobiose) (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998).

In its native form cellulose is typically called cellulose-I. This cellulose-I crystal form, or native cellulose, also comprises two allomorphs, namely cellulose I $\alpha$  and I $\beta$  (Atalla & Vanderhart, 1984). The ratio of these allomorphs is found to vary from plant species to species, but bacterial and tunicate forms are I $\alpha$  and I $\beta$  rich, respectively. The crystal structures of cellulose allomorphs I $\alpha$  and I $\beta$  have been determined with great accuracy, particularly the complex hydrogen bonding system (Nishiyama, Langan, & Chanzy, 2002; Nishiyama, Sugiyama, Chanzy, & Langan, 2003). The hydrogen bond network makes cellulose a relatively stable polymer, which does not readily dissolve in typical aqueous solvents and has no melting point. This network also gives the cellulose chains a high axial stiffness (Kroonbatenburg, Kroon, & Northolt, 1986).

Generally, cellulose-based biofibers, counting PALF, banana, cotton, flax, hemp, jute and sisal, and wood fibers are used to reinforce plastics due to their relative high-strength, high stiffness and low density (Alves et al., 2010; Arib, Sapuan, Ahmad, Paridah, & Zaman, 2006; Jacob, Francis, Varughese, & Thomas, 2006; Jacob, Varughese, & Thomas, 2006; John & Anandjiwala, 2009; Kim, Moon, Kim, & Ha, 2008; Placet, 2009; Pothan, Cherian, Anandakutty, & Thomas, 2007). Because of their annual renewability, agricultural crop-residues can be a valuable source of natural fibers. Biocomposites have future commercial application that would unlock the potential of these underutilized renewable materials and provide a non-food based market for agricultural industry (John & Thomas, 2008). In addition, they are biodegradable and offer potential advantages over unmanageable synthetic plastics in disposable applications (Jacob, Jose, Jose, Varughese, & Thomas, 2010; John, Anandjiwala, Pothan, & Thomas, 2007). Recent advances in producing bio-fibers, microfibrillated or nano-size fibers with the high-strength and surface area offer manufacturing high-performance composites from these bio-fibers (Chakraborty et al., 2006; Dufresne & Vignon, 1998; Nakagaito & Yano, 2005).

The reinforcing cellulosic nanofibers obtained from PALF fibers used for the preparation of nanocomposites are developed by the process of steam treatment correlated with acid treatment. Steam treatment is a hydrothermal process of biomass treatment, involving the application of steam at high pressure, and, which can be performed by batch or continuous reactor. The biomass is exposed to saturated steam (180–230 °C) for 20–40 min; during this time, hemicellulose is hydrolysed and solubilized. Pressure is then suddenly lowered to the atmospheric value. In doing so, the biomass undergoes an explosive decompression which induces disruption of the plant cells. Among the alternative separation processes for biomass components, the research team adopted steam treatment due to its attractiveness. The attractive features of steam treatment in comparison to autohydrolysis, pulping and other methods include the potential for significantly reducing the environmental impact, the investment costs and the energy consumption. Furthermore, less hazardous chemicals are used and a more complete recovery of all plant biopolymers in a useful form is possible (Avellar & Glasser, 1998). Generally, the steaming process results in a hydrolysis of glycosidic bonds in the hemicelluloses and, to a lesser extent in the cellulose. It also leads to a cleavage of hemicellulose–lignin bonds. The reactions result in an increased water solubilization of hemicelluloses and in an increased solubility of lignin in alkaline or organic solvents, leaving the cellulose as a solid residue with a reduced degree of polymerization (DP). PALF fibre bundles were employed for the production of nanofibrils, which at present is the waste product of pineapple cultivation. Tones of unused PALF fibre residues are generated every year, with only a small percentage being used in applications such as feedstock and energy production. The development of biocomposites has increased commercial application that would unlock the potential

of these underutilized renewable materials and provide a non-food based market for agricultural industry.

Pineapple leaf fibre (PALF) is an important natural fibre that exhibits high specific strength and stiffness. The fibers have a ribbon-like structure and consist of a vascular bundle system present in the form of bunches of fibrous cells, which are obtained after mechanical removal of all the epidermal tissues. PALF is of fine quality, and its structure is without mesh and can be extracted into nanofibers thinner than fibers from bacterial cellulose (BC) and tunicates. The fibre is very hygroscopic, relatively inexpensive and abundantly available. The PALF observed to have the high percentage of  $\alpha$ -cellulose content (81.27%) and low percentage of hemicellulose (12.31%) and lignin (3.46%) content (Cherian et al., 2010). The  $\alpha$ -cellulose is purified with steam treatment correlated with acid treatment processes. The superior mechanical properties of PALF are associated with its high  $\alpha$ -cellulose content and comparatively low microfibrillar angle (14°). Due to the unique properties exhibited by pineapple leaf fibre (PALF) they can be used as excellent potential reinforcement in composite matrices (Lopattananon, Panawarangkul, Sahakaro, & Ellis, 2006).

The cellulose or wood polymer composites always face the interfacial problem due to the cellulose being hydrophilic and polar and the polyolefins being hydrophobic (Bengtsson, Gatenholm, & Oksman, 2005). In this study hydrophilic polyurethane has been used as the matrix polymer. When the polyurethane is used as matrix, it is believed that no adhesion problem would occur and the dispersion would be much better.

Polyurethanes are an interesting family of polymers which have been used in many different applications such as biomedical, coatings, adhesives and composites (Gorrasi, Tortora, & Vittoria, 2005; Moon, Kim, Nah, & Lee, 2004). Polyurethanes form a copolymer structure with the isocyanates as hard domains and polyols as soft domains. The properties of the polyurethanes can be adjusted mainly by two routes. The first route is based on the chemistry of polyurethanes formulating the polyurethane based on different isocyanate/polyol ratio and using different amounts of chain extender. The second route is altering the properties of the polyurethanes with different fillers and reinforcements (Gorrasi et al., 2005). Polyurethanes have been reinforced with certain fillers such as talc, mica and glass fibre in the form of polymer matrix composite material (Gorrasi et al., 2005). These materials increase the tensile strength but decrease the elongation to break and discolour the polymer (Sternitzke, Derby, & Brook, 1998; Vaia, 2002). The aim of this study was to examine the effect of fibrillation of cellulose fibers from PALF using a high pressure steam treatment and investigate the reinforcing effect of nano sized cellulose fibrils in the polyurethane matrix especially for medical implants. Earlier studies made on polyurethane and cellulose both as micro and nanocomposites have been reported by Auad, Contos, Nutt, Aranguren, and Marcovich (2005) and Rials, Wolcott, and Nassar (2001) but high crystalline nanofibrils of PALF prepared by steam explosion process, reinforced in a polyurethane matrix particularly used for medical application has not been reported before.

## 2. Experimental

### 2.1. Materials

The materials used for the study includes PALF fibers were supplied by the company Superpolpa from Iaras – SP, Brazil, Sodium hydroxide (NaOH), Acetic acid (CH<sub>3</sub>COOH), Sodium hypochlorite (NaClO) and Oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) of analytical purity grade were purchased from Merck and Co., Inc., Methylene di-*p*-phenyl-diisocyanate (MDI, 99%, Sigma–Aldrich), 1,4-butanediol (BD, 99%, Sigma–Aldrich), 2,2'-(methylimino)diethanol (MIDE,

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