



Bioplastic nano-reinforcement extracted from phormium leaf fibers

Debora Puglia, Elena Fortunati, Luigi Torre, José Maria Kenny, Marco Monti, and Carlo Santulli

Cellulose nanofibers from a native New Zealand plant are extracted for use as fillers for biodegradable polymers.

Biodegradable polymer resins, such as poly(lactic acid) (PLA), are increasingly being used for industrial applications because of growing environmental concerns. However, these plastics have several drawbacks—such as poor strength, stiffness, and toughness as well as high cost—that limit their use compared to petroleum-based plastics like polyethylene terephthalate. Combining PLA with a nanofiller, such as cellulose from plants fibers, to ameliorate its poor mechanical properties may provide a possible, cost-effective solution. For example, plant fibers can reinforce the polymer and render it more suitable for various applications. Here, we investigate the use of *Phormium tenax* fibers for this purpose.

P. tenax is a native New Zealand plant traditionally used to make ropes because of its characteristic stretchy fibers. Its aligned fibers can exceed 1m in length. Additionally, because the plant is a product of a declining traditional market, innovative technologies are eagerly being sought for its use. To that end, the plant fibers have been the subject of a number of recent studies that evaluated their mechanical, thermal, and morphological effects when introduced into polymeric matrices.¹ However, the material tends to form bundles of many fiber cells, with only a small portion contributing effectively to fiber-matrix adhesion. Insufficient adhesion is likely caused by the presence of lignin and all other non-structural materials from the plant, including waxes, hemicellulose, ashes, and pectin. While introducing up to 40% by weight of *P. tenax* fibers to PLA can increase composite stiffness, there is no improvement to tensile properties. This suggests that poor adhesion between the plant fibers and PLA matrix results in ineffective stress transfer across the interphase.² This can be overcome using highly crystalline fillers. For example, nanosized fibers (with diameters of 5–50nm and lengths of several millimeters) extracted from sisal plants^{3,4} have demonstrated improvements to the mechanical properties of polymers owing to their crystalline structures. Since sisal fibers are structurally

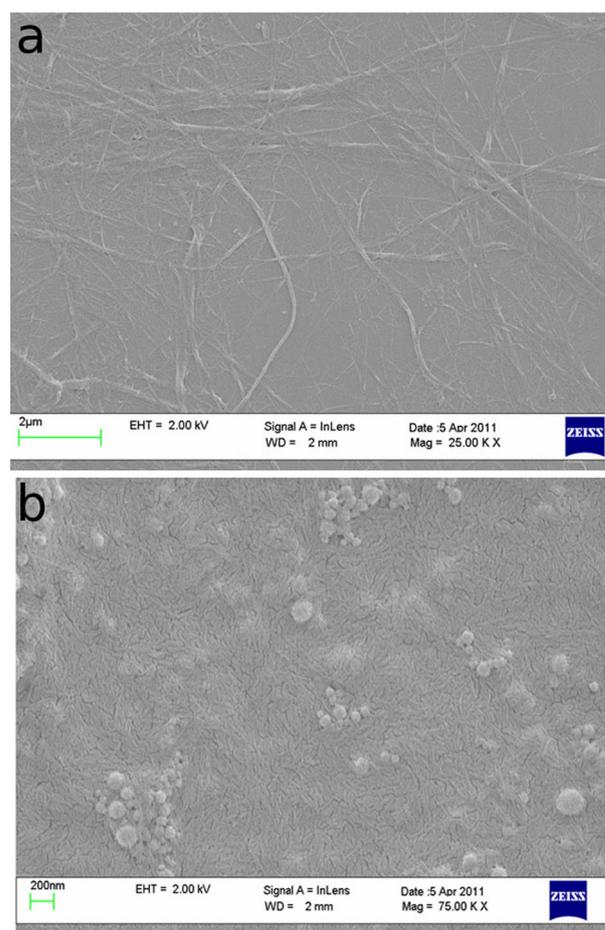


Figure 1. Field emission scanning electron micrographs of treated phormium fibers, (a) before and (b) after hydrolysis.

related to phormium fibers, we explored extraction methods to obtain nanocrystalline cellulose fibers from the latter.

We prepared cellulose nanocrystal (CNC) suspensions from phormium fibers by hydrolysis with sulfuric acid, using a known

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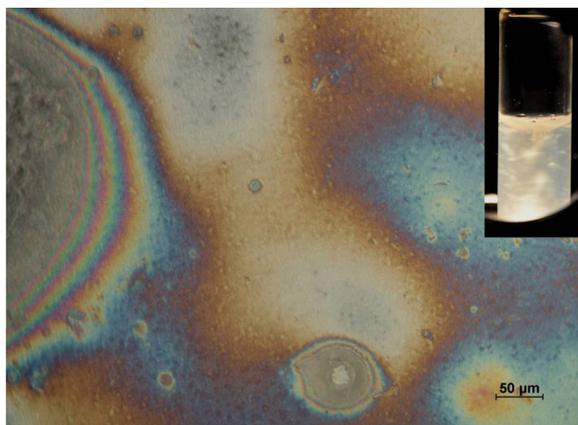


Figure 2. A polarized light microscope image of cellulose nanocrystal films prepared by evaporation of water and shear-induced polychromatic birefringence of an aqueous suspension (inset).

procedure.⁵ In detail, we carried out de-waxing by boiling the plant material in a 2:1 by volume mixture of toluene and ethanol for 6h. We then filtered the fibers, washed them with ethanol, and dried them. We then used a two-step treatment procedure to extract the cellulose. First, we removed the lignin gradually. We began by treating the phormium fibers with a 0.7% by weight to volume sodium chlorite solution. We boiled the fibers—at a liquor ratio of 1:50—for 2h, after which we lowered the pH of the solution to ~ 4 using acetic acid. We then treated the material with sodium bisulfate solution (5% by weight to volume), which provided a lignin-free holocellulose (composed of α -cellulose and hemicellulose) sample. After washing the holocellulose (with 17.5% by weight sodium hydroxide solution), filtering, and washing (with distilled water), the material was dried to a constant weight in a vacuum oven at 60°C.

In the second stage, we hydrolyzed the holocellulose with 64% by weight sulfuric acid at 45°C for 30min with vigorous stirring. Immediately following the acid hydrolysis, we diluted the suspension 20-fold with deionized water to quench the reaction. We then centrifuged the suspension to concentrate the cellulose crystals and remove excess aqueous acid. The resultant precipitate was rinsed, recentrifuged, and dialyzed against deionized water for 5 days until we achieved constant neutral pH. We finally sonicated the suspension repeatedly to create cellulose crystals with colloidal dimensions. Our resultant CNC aqueous suspension was $\sim 0.3\%$ by weight, with a hydrolysis yield of $\sim 35\%$.

Figure 1(a) shows a field emission scanning electron micrograph of the phormium fibers obtained after the acidic treatment, which revealed effective removal of the lignin to provide samples of holocellulose. The fibers appeared separated into individual micro-sized structures with variable dimensions, from bast fibers ($104.48 \pm 23.18 \mu\text{m}$)⁶

to micro-structured fibers ($10.90 \pm 3.01 \mu\text{m}$). Figure 1(b) shows the typical needle-like structures of our CNCs.

Having prepared CNC suspensions, we next investigated the flow birefringence properties (see Figure 2). The suspension exhibited strong shear birefringence between crossed polars. This confirms that ordered regions are present in the aqueous solution, which in turn indicates that high levels of crystallinity have been obtained. We also detected high levels of order in the samples in the solid phase, after we removed the water by evaporation. The method used to prepare the solid films determined their final structure, as indicated by their texture when viewed under crossed polars (see Figure 2). For example, the films obtained under vacuum exhibited a strongly birefringent texture resembling that of locally oriented anisotropic glass.

In summary, we extracted highly crystalline cellulose from *P. tenax* plant material by acidic hydrolysis. In future, we will use these structures in the production of biodegradable nanocomposites with enhanced mechanical properties. In doing so, we will introduce biodegradable plastics composed of low-cost, naturally occurring material and potentially revive a traditional market. This may also contribute to a growing trend of using local materials to reduce environmental impact in materials production.

Author Information

Debora Puglia, Elena Fortunati, Luigi Torre, José Maria Kenny, and Marco Monti

Civil and Environmental Engineering Department
University of Perugia
Terni, Italy

Debora Puglia obtained her PhD in industrial engineering in 2003. She is presently a postdoctoral researcher.

Carlo Santulli

Chemical Engineering, Materials, and Environment Department
The Sapienza University of Rome
Rome, Italy

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