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Valorization of residual Empty Palm Fruit Bunch Fibers (EPFBF) by microfluidization: Production of nanofibrillated cellulose and EPFBF nanopaper

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HIGHLIGHTS

- ▶ Empty Palm Fruit Bunch Fibers (EPFBF) were subject to sulfur-free chemical treatments.
- ▶ Microfluidization of EPFBF yields nanofibrils comparable to those from wood fibers.
- ▶ Nanopaper with excellent properties was manufactured from nanofibrillar EPFBF.
- ▶ Valorization of EPFBF is attractive due its higher yields and lower costs.

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ABSTRACT

Different cellulose pulps were produced from sulfur-free chemical treatments of Empty Palm Fruit Bunch Fibers (EPFBF), a by-product from palm oil processing. The pulps were microfluidized for deconstruction into nanofibrillated cellulose (NFC) and nanopaper was manufactured by using an overpressure device. The morphological and structural features of the obtained NFCs were characterized via atomic force and scanning electron microscopies. The physical properties as well as the interactions with water of sheets from three different pulps were compared with those of nanopaper obtained from the corresponding NFC. Distinctive chemical and morphological characteristics and ensuing nanopaper properties were generated by the EPFBF fibers. The NFC grades obtained compared favorably with associated materials typically produced from bleached wood fibers. Lower water absorption, higher tensile strengths (107–137 MPa) and elastic modulus (12–18 GPa) were measured, which opens the possibility for valorization of such widely available bioresource.

1. Introduction

The marked increase in the use of alternative, non-wood fibers results from the need to cut costs and avoid negative environmental effects. In fact, non-wood raw materials constitute the sole useful source of cellulose fiber in some regions of the world (Rodríguez et al., 2008) and provide several interesting advantages (Rodríguez et al., 2008): (a) allows wood raw materials to be spared for uses where they are most required; (b) reduces wood and cellulose fiber imports in countries with a shortage of wood and, (c) satisfies the increasing demands for paper-grade fibers from green processes.

The use of Empty Palm Fruit Bunch Fibers (EPFBF), bagasse and rice straw for papermaking and production of composite panels is a common practice in several countries without large supplies of wood resources (English et al., 1997; Young, 1997). EPFBF, in particular, comprises residual fibers from the palm (*Elaeis guineensis*) oil processing. Malaysia is the largest palm oil producer (51% of the worldwide production), and constitutes an important economic resource for this country. Cultures are also extending to countries in Western Africa (Nigeria, Guinea, Ghana, etc.), South America (Ecuador, Colombia, Honduras, etc.) and Asia (Thailand). The global production of oil palm has risen from 16 million tons in 2007 to almost 21 million tons in 2010 (FAO, 2010). Palm plants start fruiting 4–5 years after planting. Fruit bunches usually weigh 15–25 kg and contain 1000–4000 oval-shaped, 3–5 cm long fruits. Fruit production peaks at 20–30 years, after which they decline and become unprofitable (especially because their fruits are too high to collect). Each hectare of oil palm produces an average of 10 tons fruits per year, which give about 3000 kg of palm oil as the main product (Malaysian Palm Oil Council, 2010). A significant amount of residual EPFBF can be used as a source of cellulosic fibers if separated by pulping processes. In this regard and owing

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to environmental pressures alternative, sulfur-free pulping methods can be considered (Rodríguez et al., 2008). Therefore, in this work soda-anthraquinone (NaOH-AQ) digestion was applied to yield high quality fibers from EPFBF (Ibrahim, 2002; Law and Jiang, 2001). Also, two organosolv processes (Formosolv and Milox) were used on the basis of expected advantages that include (Rodríguez et al., 2008): (a) reduced small- and mid-scale production costs relative to Kraft processes, (b) facile and efficient recovery of solvents and by-products; (c) relative low water, energy and chemicals usage.

Within the idea of harnessing the concept of biorefinery, fractionation of the byproducts of the palm oil industry may open a promising pathway for comprehensive use of residual biomass. It should be noted that cellulose is the most important component of EPFBF, which justify efforts to generate fermentable sugars (Kim et al., 2012). In the context of the present investigation, fibers from empty palm fruit bunches are proposed as a resource for obtaining nanofibrillated cellulose (NFC). Because of their wide abundance, their biodegradability and its renewable nature as well as their unique structural and physical aspects, NFC has recently garnered much attention for use as reinforcement in composites and in coatings, films, membranes, packaging materials, etc. It is also a natural nanomaterial that provides a large range of possibilities to obtain superior properties in different end-products. For example, it is known that NFC has unique properties and functionalities compared to macro-scale fibers. Moreover, environmental concerns drive the interest on sustainable and eco-friendly products, including NFC as an alternative to materials derived from petroleum or non-renewable sources.

Cellulose nano- and micro-fibers were isolated from banana rachis (Zuluaga et al., 2007) by using chemical and mechanical treatments; such agricultural residue, which is rich in cellulose, has attracted interest due to its potential use as a reinforcing component in composites (Faria et al., 2006; Gañán et al., 2004). It is worth noting that that NFC production has been primarily from bleached pulps. However, interest in the production of NFC from unbleached fibers has been reported (Ferrer et al., accepted for publication; Spence et al., 2010a,b). Some physical properties have been observed to improve with the presence of residual cell wall components (lignin and hemicelluloses). Of particular interest is the possibility of packaging films with high oxygen barrier capability as well as other gasses and vapors.

In this work EPFBF is proposed as a novel and suitable resource to produce NFC. Thus, different grades of cellulose nanofibrils were isolated from unbleached EPFBF and their properties as well as those of respective nanopaper were compared with those from conventional sources. The morphological and structural features of isolated nanofibrils and reference pulp handsheets were analyzed by atomic force microscopy (AFM) as well as scanning electron microscopy (SEM). The tensile index, elastic modulus and% elongation of handsheets and nanopaper with similar grammage were determined. Complementary examination of specific surface area, water absorbency and rates of capillary absorption are reported. The results are discussed in light of the properties of NFC from conventional sources, namely bleached wood pulps.

2. Methods

2.1. EPFBF, EPFBF pulps and handsheets

EPFBF from a Malaysian oil palm plant was supplied by Straw Pulping Engineering S.L. (Zaragoza, Spain). The chemical composition of EPFBF was determined following TAPPI standards T-222 for lignin, T-203 for α-cellulose, T-204 for ethanol–benzene extractives and T-211 for ash. Holocellulose content was determined by the Wise et al. method (1946). The analysis showed a composition that included 67% holocellulose, 41.9% α-cellulose, 24.5% lignin, 1.2% extractives and 3.2% ash. Average fiber length and thickness of microcooked EPFBF (10% soda, 80 °C, 1 h) were found to be 0.53 mm and 14 μm, respectively as determined from stainning (1% saffranin) and observation under a Visopan projection microscope (10× objective for 100× magnification) (Sánchez et al., 2010).

Three different EPFBF pulp grades were obtained after the following sulfur-free chemical treatments: (a) soda-anthraquinone (NaOH-AQ): 15% NaOH; 1% AQ; 30 min; 170 °C; H = 10; (b) formic and hydrochloric acid (FoOH, Formosolv): 92.5% FoOH; 0.075% HCl; 60 min; 100 °C; H = 10 and, (c) formic acid and hydroxide peroxide (Milox): 53% FoOH; 3% H_2O_2; 165 min; 80 °C; H = 10, where the H is the hydromodule (liquid–solid ratio). The short notation "N", "F" and "M" is used to refer to the respective process. The operation conditions used were selected based on results from previous work (Jiménez et al., 2009; Ferrer et al., 2011a,b). The pulps were obtained by using a 15 L rotating batch cylindrical reactor connected to a heater. The cooked, unbleached fibers were refined in a Sprout–Bauer device and the pulps obtained were screened (0.16 mm mesh size). Pulp chemical composition was determined using the standard methods mentioned above in the case of EPFBF fibers. Paper handsheets were produced with an ENJO-F-39.71 sheet machine according to the UNE-57-042 standard.

2.2. Isolation of cellulose nanofibrils (NFC)

2.2.1. Mechanical pre-treatment

The NaOH-AQ (N), FoOH-Formosolv (F) and Milox (M) pulps in their never-dried form were first dispersed in de-ionized water. Afterwards, they were treated (ion exchanged) under stirring for 20 min with a hydrochloric acid solution 1 M and washed with de-ionized water two times using a Büchner filter funnel. Following, the fibers were suspended in $NaHCO_3$ solution 1 M in order to convert the carboxyl groups to their sodium form. Finally, the fibers were washed with de-ionized water and drained on a Büchner filter funnel until a filtrate conductivity of less than 20 μS/cm was measured.

A refining treatment before microfluidization was necessary in order to enhanced fiber accessibility and processing efficiency. Therefore, the EPFBF pulps were refined for 20000 revolutions in a PFI-mill according to ISO 5264-2:2002. The drainability of the refined pulps was determined using the Schopper-Riegler method (°SR) according to ISO 5267-1:1999. The refining process resulted in fibers with enhanced internal and external fibrillation. In addition, fiber flow was improved and clogging avoided during fluidization. Noting that °SR was not used here as a parameter for property prediction but to control the fluidization process, it was determined that 90 °SR or above was suitable for an effective fluidization process.

2.2.2. Mechanical high-shear disintegration via microfluidization

Nanofibrillated cellulose from EPFBF pulps was obtained by microfluidization. Typically, 1.8% fiber suspension in water was processed in a high-pressure microfluidizer (Microfluidizer M-110 P, Microfluidics Corp., 2010). Samples were passed five times through an intensifier pump that increased the pressure, followed by an interaction chamber which defibrillated the fibers by shear forces and impacts against the channel walls and colliding streams. Through this process, fibers were broken up into nano-sized structures forming slurries of nanofibrillated cellulose. The microfluidizer operated at a constant shear rate and the operating pressure was maintained at 55 MPa. The temperature was not controlled but fluidization was temporarily ceased when the temperature of the stock reached approximately 90 °C, to prevent pump