A common strategy to extracting cellulose nanoentities from different plants

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ABSTRACT

In order to obtain cellulose nanoentities like nanofibres (CNF) and nanocrystals (CNC) from sisal (S), hemp (He) and flax (F) fibres, a new succession of specific chemical treatments including extractives (E), prealkalization (PA), alkalization (A), acetylation (Ac) and acid hydrolysis (H) treatments have been developed. Cellulose nanoentities obtained have been characterized by different techniques. FTIR spectra confirmed the removal of non-cellulosic components after chemical treatments. XRD results showed that all samples exhibited cellulose I crystalline structure and the crystallinity index of cellulose nanoentities was increased about 30% relative to raw fibres owing to removal of non-cellulosic components. The thermal stability of samples decreased after using an acid medium. AFM images confirmed that cellulose nanofibres and nanocrystals were obtained.

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1. Introduction

Long and ongoing discussion about the preservation of natural resources and recycling has raised a renewed interest concerning natural materials with the focus on renewable raw materials. More recently, with an increase in environmental conscience (Fan et al., 2013), lignocellulosic materials and industrial solid wastes with high cellulose content (Jonoobi et al., 2012) have gained considerable attention. Cellulose, the main component and the most abundant organic compound derived from lignocellulosic biomass and also the oldest used on earth, is the most widespread natural polysaccharide, which perform structure-forming functions in flora. Cellulose, presents unique advantages and properties, such as biodegradability, recyclability, renewability, biocompatibility, relatively high resistance and stiffness, among others (Arbelaiz et al., 2005, 2006; Chen et al., 2011a; Eichhorn et al., 2010; Johar et al., 2012). In nature, cellulose does not occur as an isolated individual molecule, but it is found as assemblies of individual cellulose chains into the repeated semicrystalline structure forming microfibrils in the plant cell wall. This is because cellulose is synthesized as individual molecules, which undergo spinning in a hierarchical order at the site of biosynthesis. Typically, approximately 36 individual cellulose molecules assemblies are brought together by

hydrogen bond network into large units known as elementary fibrils. The elementary fibril itself consists of highly ordered crystalline regions with diameters of 5–20 nm and lengths of 100–400 nm. These ordered regions are bridged by amorphous phases packing into large units with diameters of 20–60 nm and lengths of several micrometres (Habibi et al., 2010; Roya et al., 2010). In order to isolate individualized cellulose nanoentities with high crystallinity from plants, the hierarchical structure of macroscopic fibres has to be broken, therefore reducing the amount of non-crystalline domains located at the surface and along their main axis, exploiting in this way the high stiffness of cellulosic crystalline structure for reinforcements. The modulus, depending on the method followed for their determination, ranges between 100 and 170 GPa and taking into account their low density, is quite superior than commonly used engineering materials (Eichhorn et al., 2010; Habibi et al., 2010). Due to the intrinsic higher performance of nano-sized fillers, cellulose nanoentities are predicted to enhance mechanical properties when compared with traditional micron-sized cellulose fibres. A high aspect ratio of the nanoentities is desirable for stress transfer from the matrix to the reinforcing phase. The exploitation of nano-sized cellulose could become a bridge between nanoscience and natural resource products, which could play a major role in reviving biomass based industries on the world (Habibi et al., 2010; Peng et al., 2011). The isolation of nano-sized cellulose from lignocellulosic fibres can be achieved using a purely chemical treatment of strong acid hydrolysis resulting in colloidal suspension of aggregates, highly crystalline and with low aspect ratio fibril bundles

(Pääkkö et al., 2007; Fleming et al., 2001). Combining specific chemical treatments non-cellulosic components can be removed from natural fibres maintaining their crystalline structure (Frone et al., 2011; Retegi, 2009). The subsequent acid hydrolysis gives rigid rod-like crystals with several values of diameter and length depending on origin and source of biomass (Kristiina and Mohini, 2006), having high specific strength, aspect ratio and modulus, unique optical properties and low density, focusing much attention from materials scientists (Wu et al., 2013). In the literature different terminologies are used to describe cellulose nanoentities, leading to some misunderstanding and ambiguities. This wide terminology include: nanowhiskers, whiskers, nanocrystals, nanocrystalline cellulose, microfibrils, microfibrillated cellulose, nanofibers, etc. In this work, cellulose nanofibres and cellulose nanocrystals terminologies are used. These nanoentities have nanometric diameters and differ in their length.

The aim of this work is to set a common strategy to obtain CNF and CNC from sisal, hemp and flax lignocellulosic fibres using a succession of specific chemical treatments, firstly removing the most of the non-cellulosic constituents of the surface of the cellulosic fibres giving CNF and then by acid hydrolysis treatment, which dissolves the amorphous regions along nanofibres, obtaining CNC. The chemical constitution and thermal stability of the obtained samples along the successive chemical treatments has been characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. The effect of chemical treatments on the structure and morphology were observed by using X-ray diffraction and different microscopies, respectively.

2. Experimental

2.1. Materials

Sisal fibres (S) used in this work were provided by Celulosa de Levante, S.A. from Spain and Flax (F) and Hemp (He) fibres were supplied by Arctic Fiber Company from Finland. The reagents employed for the specific chemical treatments were sodium hydroxide pellets PA-ACS-ISO, glacial acetic acid QP, nitric acid PA-ISO (65% purity), sulphuric acid PA-ISO (96% purity), ethanol PA-ACS (96%, v/v purity) and toluene HPLC grade supplied by Panreac. All reagents were used as received without further purification.

2.2. Chemical composition characterization

Based on Technical Association of Pulp and Paper Industry (TAPPI) standards (T257 cm-85, T264 cm-97, T211 om-93, T207 om-93, T212 om-98, T204 cm-97, T222 om-98) the chemical composition of each raw fibre was determined. The α-cellulose, lignin, moisture content, ashes, hot water solubility, sodium hydroxide solution solubility and ethanol-toluene extractable contents were obtained based on the corresponding TAPPI standards. The holocellulose content in the raw materials was determined by using the method of Wise et al. (1946). The difference between the values of holocellulose and α-cellulose gives the hemicellulose content of the fibres. A minimum of three samples of each material were tested, and the obtained average values are shown in Table 1.

2.3. Isolation of cellulose nanoentities from different plants

The specific chemical treatments employed for extraction of CNF and CNC were made in the following order: extractives, prealkalization, alkalization, acetylation and acid hydrolysis. For removing the extractives (waxes and oils) (E), using the standard method TAPPI T204 cm-97, fibres were subjected to a solvent mixture of ethanol/toluene (1:2, v/v). In order to swell raw fibres, prealkalinization (PA) treatment was applied. Fibres were treated with 2 wt%

NaOH solution into a round bottom flask for 12 h at 40 °C. After this step, fibres were subjected to an alkali treatment (A) with 7.5 wt% NaOH solution into a round bottom flask under reflux for 90 min to remove hemicelluloses and lignins. Lignocellulosic fibres derived from this chemical treatment were washed until pH 6. In order to extract CNF, the acetylation treatment (Ac) was made under reflux for 30 min and thereafter these fibres were washed with distilled water to neutralize. Acetylation treatment was carried out with an acid solution of acetic and nitric acids (6:1 v/v) and the ratio fibre/acid was of 0.6:14 (w/v). Finally, acetylated nanofibres were treated with 32 wt% sulphuric acid (H) at 45 °C for 45 min under continuous stirring to isolate CNC. Afterwards, the reaction was stopped adding deionized water and suspension was washed using repeated centrifuge cycles until the supernatant became turbid. The solid part was dialysed in deionized water for 4 days to pH 4–5, and then the suspension was sonicated during 5 min, poured in containers, frozen and finally lyophilized. Fig. 1 shows a scheme describing the procedures to extract cellulose nanoentities from lignocellulosic fibres.

3. Characterization techniques

3.1. Fourier transform infrared spectroscopy

The Fourier transform infrared spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer in the 4000–400 cm^{-1} range using KBr. Spectra were taken with a resolution of 2 cm^{-1} with a total of 40 scans for each sample.

3.2. X-ray diffraction

X-ray diffraction patterns of each sample were collected using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu-Kα radiation (λ = 1.5418 Å) and a PIXcel solid state detector. Data were collected at 2θ from 6 to 50°. The crystallinity index (CI) of cellulose samples has been calculated from the diffracted peak intensity data using Segal et al. method (1959), Eq. (1):

$$CI = \left(\frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \qquad (1)$$

where I_{002} is the maximum intensity of the (0 0 2) lattice diffraction peak (diffraction angle at around 2θ of 23° representing the crystalline material) and I_{am} is the intensity scattered by the amorphous part of the sample (the location of the amorphous material intensity considered in this work was at around 2θ of 18°).

3.3. Thermogravimetric analysis

Dynamic thermogravimetric measurements were performed by using a TGA/SDTA 851 Mettler Toledo instrument. Dynamic tests were run from 25 to 600 °C at a heating rate of 10 °C/min. These tests were carried out under nitrogen atmosphere (10 mL/min) in order to prevent any thermoxidative degradation.

3.4. Morphological analysis

The morphological and structural characteristics of untreated and treated fibres were observed using a Nikon Eclipse E600 optical microscopy (OM) and a JEOL JSM-6400 scanning electronic microscopic (SEM). Samples for SEM were prepared placing fibres on an aluminium plate and coated with carbon using a vacuum sputter coater under given conditions (15 mA, 20 V, 100 min to encapsulate the sample). In order to examine nanoentities dimensions, an atomic force microscope (AFM) from Digital Instruments having