Surface properties of distinct nanofibrillated celluloses assessed by inverse gas chromatography

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HIGHLIGHTS

- Nanocelluloses were distinguished from each other for their surface properties.
- Dispersion component of the surface energy (γ_s^d) at 40 °C was of 42–52 mJ m^{-2}.
- Higher γ_s^d value was found for enzymatic nanocellulose than for TEMPO-oxidised ones.
- For TEMPO-nanocelluloses acidity/basicity ratio increased with the fibrillation.
- Results may have interest in the composites production area/coatings applications.

GRAPHICAL ABSTRACT
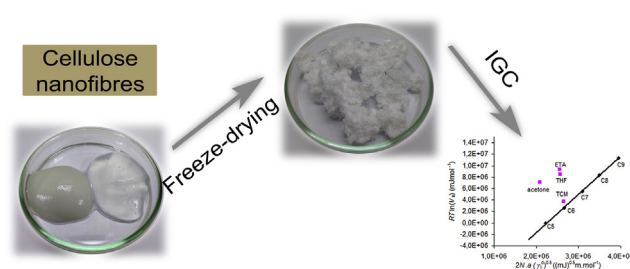
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ABSTRACT

The adhesion and surface properties of nanocelluloses are an important issue to consider when using this material for composites production, in food packaging or coatings, as well as for determining the influence of added functional groups. In the present work, the surface properties of two nanofibrillated celluloses obtained by mild 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation with distinct mechanical treatment intensity in a homogenizer (5 and 15 passes), and one nanofibrillated cellulose obtained by enzymatic process, were thoroughly assessed by inverse chromatography, at infinite dilution conditions. The dispersion component of the surface energy (γ_s^d) was 42–46 mJ m^{-2} at 40 °C for the TEMPO nanofibres and 52 mJ m^{-2} for the enzymatic nanocellulose. It was confirmed, based on the determination of the specific components of the works of adhesion and enthalpies of adsorption with polar probes, that the surfaces of the materials have a more Lewis acidic than Lewis basic character. Regarding TEMPO nanofibres, a slight increase of Lewis acidity/basicity ratio seemed to occur for the more nanofibrillated material (15-passes). Higher specific interactions with polar probes were found for enzymatic nanocellulose. The higher values of γ_s^d and specific interactions observed for the enzymatic nanocellulose could partly be due to the higher crystallinity of this sample. On the other hand, the increase of the acidity/basicity ratio (as well as of the γ_s^d value) for the 15-passes versus 5-passes TEMPO nanofibres was attributed to a higher exposition of the hydroxyl groups of cellulose at the surface of the former material.

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1. Introduction

Nanofibrillated cellulose (NFC) is a type of cellulose fibres with nanosized diameters (typically in the range of 5–50 nm) and

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lengths up to several micrometres, being sometimes also referred to as microfibrillated cellulose (MFC). It is usually obtained from bleached kraft pulp or non-woody materials by a homogenization process under high pressure, which may be preceded by a chemical pre-treatment. The chemical pre-treatments are used to decrease the energy needed for fibrillation and can be of several types, namely enzymatic, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation pre-treatment, carboxymethylation and acetylation processes. The chemical pre-treatment with NaClO (oxidant) and TEMPO and NaBr as catalysts at pH 10–11 is by far the most commonly employed. Using this pre-treatment, the C6 hydroxyl groups of cellulose are converted to aldehyde and carboxylate groups, which enable the nanofibrils within the fibres to separate better from each other due to the repulsive forces between the ionized carboxylic acids [1].

NFC possesses several properties that make it a potential interesting material for a wide range of applications. Amongst its more relevant properties are the relatively high specific surface area in comparison to that of the pristine cellulose fibres (values can be higher than $100 \, m^2/g$), the viscosity (rheological) properties of the NFC gel, the high tensile strength and the high light transmittance of the corresponding NFC films. Its barrier properties namely for the water vapour and molecular oxygen have also been highlighted [1]. NFC has thus been used in formulations as a viscosity modifier, as gel for biomedical applications, as a mechanical reinforcement material in (nano)composites, including (nano)paper, for paper coating, in films for food packaging and for electronic devices [1–8].

The adhesion and surface properties of nanocellulose are key points that have to be considered regarding the aforementioned uses, for instance, in composites or in barrier materials [1,9,10]. Studies on the surface properties of cellulose nanofibres have been generally focused on (i) the determination of "surface" charge by zeta potential measurements or by polyelectrolyte titration, (ii) the determination of the amount of carboxylate and aldehyde groups formed during chemical pre-treatments, by conductometric and potentiometric titrations and, (iii), the assessment of the chemical composition and reactivity of the nanocellulose surface in the course of chemical pre-treatments/surface modification, by using X-ray photoelectron spectroscopy [1,10].

One powerful tool to assess the surface properties of solid materials is inverse gas chromatography (IGC). It enables to obtain the dispersion component of the surface energy, adsorption thermodynamic parameters with a wide range of polar substances (specific components of the free energy of adsorption, enthalpy and entropy of adsorption), Lewis acid–base character of the surface, surface nanoroughness parameter, etc. [11–14]. Thus, using IGC, a cellulosic fibrous material can be thoroughly characterized with respect to its surface chemical properties. Besides, this technique is advantageous over the classical contact angle measurements for the analysis of porous, rough, heterogeneous and hydrophilic surfaces. Not many papers reported the use of IGC to analyze nanocellulose [15–19]. In particular, under infinite dilution conditions, the dispersion component of the surface energy was determined for cellulose nanofibres obtained by enzymatic pre-treatments [15] and cellulose nanofibres extracted from hemp fibre by acid hydrolysis and mechanical treatment [16]. For the latter, the Lewis acid–base characteristics were also assessed. The influence of the drying method on the surface energy of cellulose nanofibrils was also evaluated [18].

In the present work, two nanofibrillated celluloses obtained from an eucalypt bleached kraft pulp by NaClO/TEMPO/NaBr pre-oxidation with distinct mechanical treatment intensity, and one nanofibrillated cellulose obtained by enzymatic process, were thoroughly analyzed for their surface properties by inverse chromatography. The results of these analyses with regard to a wide range of assessed parameters will be presented and discussed.

2. Experimental

TEMPO-oxidised cellulose nanofibres were obtained by firstly treating a bleached eucalypt pulp with NaClO (4 mmol/g of pulp) and catalytic amounts of TEMPO and NaBr, accordingly to a previously reported methodology [20]. The fibres were then passed through a homogenizer (GEA Niro Soavi Panda Plus 2000) 5 times at 300 bar or 15 times (five passes at 300 bar and 10 passes at 600 bar), affording NFC-5p and NFC-15p, respectively. The enzymatic nanocellulose was purchased from Grenoble INP-Pagora. This sample was obtained from a softwood bisulfite pulp by treatment with endoglucanases followed by homogenization with 1 pass at 1000 bar and 4 passes at 1500 bar. The nanofibres suspensions were characterized for their general properties, as described below.

The suspensions were then freeze-dried in order to obtain a solid material that was then packed into the IGC column for the physicochemical surface analysis.

In order to evaluate the relative amount of nanofibrillar material in each original sample, the transmittance of NFC suspensions (diluted to 0.1%, w/w) in the 400–800 nm visible range was measured using a Jascow V550 spectrophotometer. Besides, 40 ml of each NFC suspension, previously diluted up to 0.2% (w/w), was centrifuged at 9000 rpm for 30 min, and the retained fraction was analyzed for its solid content and compared to the original to obtain by difference the percentage (w/w) of supernatant material. The results were an average of three replicated measurements. To evaluate the nanofibres "surface" charge, zeta potential measurements were carried out in triplicate in a Zetasizer Nano ZS from Malvern Instruments.

The inverse gas chromatography analysis was performed using a DANI GC 1000 digital pressure control gas chromatograph equipped with a hydrogen flame ionization detector. Stainless-steel columns, 0.5 m long and 0.4 cm inside diameter were washed with acetone and dried before packing. For each analysis, approximately 1 g of nanocellulose was packed into the gas chromatograph column. The columns were shaped in a smooth "U" to fit the detector/injector geometry of the instrument. The packed columns were conditioned overnight at 105 °C, under a helium flow ($P = 0.1$ bar), before any measurements were made. Measurements were carried out at four different temperatures (40, 45, 50 and 55 °C) with the injector and detector kept at 180 °C and 200 °C, respectively. Helium was used as carrier gas. Small quantities of probe vapor (<1 μL) were injected into the carrier gas, allowing work under infinite dilution conditions. The probes used for the IGC data collection were *n*-pentane (C5), *n*-hexane (C6), *n*-heptane (C7), *n*-octane (C8), *n*-nonane (C9), trichloromethane (TCM, Lewis acidic probe), tetrahydrofurane (THF, basic), ethyl acetate (ETA, amphoteric) and acetone (amphoteric). It should be noted that polar probes with similar molecular surface area values and different electron donating/acceptor properties were chosen, in order to assess only the effect of Lewis acid–base interactions with the materials surface. All probes were of chromatographic grade and were used as received (Sigma–Aldrich). Methane was used as the reference probe. The retention times were the average of three injections and were determined by the peak maximum for the *n*-alkanes and TCM or by the Conder and Young method for THF, ETA and acetone, which provided less symmetrical chromatograms [21]. The coefficient of variation between runs was typically lower than 3%. Two columns were prepared for each material with the final results being the average of two separate measurement series. The theoretical aspects of inverse gas chromatography have been previously described [11–13]. Using this technique, the dispersion component of the surface energy, and the specific components of the work of adhesion, enthalpy