



New and improved method of investigation using thermal tools for characterization of cellulose from eucalypts pulp



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ABSTRACT

Despite cellulose being the most abundant biopolymer on earth and an important commodity, there is a lack of deeper knowledge about its structure as well as faster and more efficient characterization techniques. This paper presents preparation of nanocellulose from bleached cellulose pulp of Eucalyptus by chemical and mechanical pre-treatments, while the cellulose was given treatment to obtain a great range of crystallinity index. The nanocellulose is characterized by X-ray diffraction to evaluate Segal's index while chemometric tools by TGA and DTA were used to predict Segal's index. DTA curves, along with multivariate statistical model, presented better result than TGA. The coefficient of variation and standard error of prediction for the proposed models using external validation samples were in the range of 0.91–0.96 and 4.18–8.71, respectively. These successful mathematical models are discussed by correlating them with the observed characteristics of cellulose.

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1. Introduction

Cellulose is the most abundant organic polymer in the planet and the largest component of biomass. It is commonly found associated with hemicelluloses and lignin in the cell wall of lignocellulosic materials, though it can also be found in its pure form, such as in cotton. Cellulose possesses a relatively simple structure, being formed of monomers of D-glucose linked by glycosides bonding β -1,4 [1,2].

Cellulose is a renewable biopolymer used widely, be it in its natural or derived form, in various technological areas including medical, textiles, and nutrition. In the last decade or so, cellulose has been very much studied with a view to find out and to improve its properties [3]. Several industrial sectors also use cellulose, such as paper manufacturing [4]. Other applications are as emulsifier in pharmaceuticals [5], light products [6,7], cosmetics [8], lithium

batteries [9], as reinforcement in paper [10,11], and in composite materials [12–14]. It has also been researched widely as source for ethanol second-generation production [15,16].

Coming to the study of structure of cellulose, Hermann Staudinger did pioneering work for the elucidation of the polymer structure of cellulose [17]. Through acetylation and deacetylation, he discovered the covalent bonding along cellulose molecular chains. Today, researchers know that the hydrogen bonds among hydroxyl groups are responsible for the hierarchical structure of cellulose. These may occur in the same molecule, called as 'intramolecular' bonding, or in inter adjacent molecules, called as 'intermolecular' bonding. Intramolecular hydrogen bonds are responsible for the rigidity of the chains, while the intermolecular hydrogen bonds are responsible for the formation of the supra molecular structure [1]. Because of this structure, cellulose exhibits highly ordered crystalline areas along with intermediate as well as less ordered amorphous areas along with insolubility in common solvents, and lack of glass temperature transition.

The amorphous area of cellulose is more accessible to attack by reagents, enzymes or even for the absorption of water [18]. However, much of the research is focused on understanding of thermal,

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chemical, and even mechanical behaviours of the crystalline part [3,19–21].

The hydrogen bonds will lead to the generation of distinct cellulose allomorphs. These are named as I, II, III, and IV, having different crystalline, and even amorphous, structures [18,22].

Both crystallinity and the orientation of the crystalline domains and amorphous regions in the fibers affect the mechanical properties of the cellulose fibers [23,24]. The standard technique used for crystallinity index measurement is X-ray diffraction [21,25]. The ratio between the crystalline and the amorphous intensities in the diffractograms determines the Segal's index (SI) of the cellulose [26]. Other faster, and in some cases cheaper, techniques have been studied to predict crystallinity index, such as Fourier-transform infrared spectroscopy [25,27–29], ^{13}C nuclear magnetic resonance [30–32] and Raman spectroscopy [33]. However, there is still certain reluctance on the part of the research community over the possibility of using those techniques to predict and characterize the crystallinity of the cellulose.

Despite Segal's method receiving a lot of criticism [34–36], still it is being used by many researchers because of its feasibility and reproducibility [37,25].

Avolio et al. [38] used wide angle X-ray diffraction (WAXD), attenuated total reflection-Fourier transform infrared (ATR-FTIR), cross-polarization and magic angle spinning-nuclear magnetic resonance (CP-MAS-NMR) techniques to assess the crystallinity of cellulose type I after ball milling [38]. Nevertheless, the authors showed qualitatively the possibility of correlation among all techniques tested but did not construct a mathematical model. Schultz et al. [39] correlated cellulose XRD crystallinity with FT-IR and TGA techniques; however, similar to O'Connor's work [40] with FT-IR just one peak ratio was employed, and for TGA just the maximum rate of weight loss was correlated. The correlation presented by those authors could not predict crystallinity for nanocellulose or alkali treated cellulose. It is well known that cellulose thermal degradation is dependent on its polymorphism [41,42] and never be thought before as a useful technique to predict its crystallinity.

Due to the wide range of applications, both present and in the future with the possibility of even more applications, it has become highly necessary to gain deeper knowledge about the structure of cellulose, along with faster and more efficient techniques to apply in research as well as at an industrial scale, for instance, in controlling processes.

With the above mentioned various aspects about cellulose, this research was undertaken with the following objectives: (i) to prepare nanocellulose from bleached cellulose pulp of *Eucalyptus* by mechanical defibrillation and chemical treatment as well as ball milling to obtain cellulose with great range of Segal's index; (ii) to propose chemometric models for the prediction of Segal's index through TGA and DTA, and finally, (iii) to discuss these models through chemical or physical meanings.

2. Material and methods

2.1. Raw material and preparation of the cellulose samples

Dry sheets of commercial bleached Kraft cellulose pulp of *Eucalyptus* sp. was purchased from Klabin SA. This was used to prepare fluffy cellulose through a process of blending. A white liquor used in the digestion of cellulose was supplied by a Brazilian Pulp Mill (Iguaçu Celulose e Papel) had concentration of 14.13 g L^{-1} of total alkali consisting of 2.26 g L^{-1} of sodium sulphate, 7.29 g L^{-1} of sodium sulphite and 4.58 g L^{-1} of sodium thiosulphate.

Seven samples were acid hydrolyzed using sulphuric acid solution in a ratio of 10 mL g^{-1} of solid. Six samples were alkaline treated using a ratio of 2.2 mL of white liquor per g of fluffy cellulose in a

50 mL capacity stainless steel reactor (Paar Inc.) that was tightly closed. Six samples were mechanically defibrillated in an ultra-fine grinder (Super Masscolloider, Masuko Sangyo) with nonporous SiC mill. Nine samples were placed in zirconia and porcelain bowls and subjected to grinding in a ball mill (Serviteck, Brazil) with horizontal rotation. Some of the above samples with different treatments are tabulated in Table 1 with appropriate designations.

2.2. Measurement of the XRD Segal's index (SI)

Powder X-ray diffraction (PXRD) patterns were recorded in an X-ray diffractometer (Shimadzu XRD-7000) having a monochromator with slits (1, 1, 0.3). A speed of 1° min^{-1} , Cu-K α radiation wavelength of 1.541 \AA and settings of 40 kV and 20 mA were used for all the measurements. The diffractograms were normalized by dividing each curve by its area, therefore the normalized curves present area equal to 1. Segal's index was calculated (see Table 1) for the original and treated cellulose, following the method proposed by Segal [26] using OriginPro 2015 software to smoothen signals with a treatment using 15 percentile filtering from Fast Fourier Transform to remove noise. The peak intensities of the crystalline and amorphous regions used for SI calculations were collected after smoothing.

The SI was calculated using the maximum height around 23.6° (due to 002 crystal plane) and the minimum valley around 18.6° (due to amorphous cellulose) $\text{SI} = 100 \cdot (1 - h_{002}/h_{\text{amorphous}})$.

Part of the sample treated by alkali transformed into cellulose type II. Therefore, the SI calculation for these samples are influenced by the intensity diffraction of the 10 from cellulose type II. This is the reason why we are calling SI index instead of crystallinity index. However, chemometric techniques are most useful for multi-component mixtures [43] for many reasons including can deal with error on the reference measurement and discriminate components.

2.3. Thermogravimetric analysis (TGA and DTA)

The simultaneous TGA-DTA curves were obtained in a DTG-60 equipment from Shimadzu using an inert atmosphere with nitrogen gas flow of 20 mL min^{-1} , temperature range between 25 and 600°C , and heating rate of $10^\circ\text{C min}^{-1}$. Samples weighing 1.2–7.5 mg were put inside a platinum pan to perform the tests. The instrument was preliminarily calibrated with standard mass and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software.

2.4. Calibration, validation and selection of model

Partial Least Squares (PLS) regression analyses were developed to describe the relationship between the TGA and DTA curves and the cellulose Segal's index using Unscrambler[®]. The data set was divided into two parts: 2/3 (20 samples) were used for calibration (model construction) and the remaining 1/3 (9 samples) for external validation (prediction). The selection of the samples for the calibration subset was done by ranking in ascending order of cellulose Segal's index and selecting uniformly distributed subsets (two out of three samples). The validation subset used the complementary one-third samples. This procedure allowed higher control of the variability within each subset.

After comparing the performance of the models the best pretreatment method for the whole sample set was weighted smoothing (51-point filter and second order polynomial) [44] and Max Normalization were applied on the TGA dataset. The DTA data was presented as mV mg^{-1} . In this case, the best treatment method for the whole sample set was weighted Smoothing (21-point filter and second order polynomial) [44] and Standard Normal Variate (SNV) [45]. The Martens' uncertainty test [46] was used to select the

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