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The structure of different cellulosic fibres characterized by Raman spectroscopy

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ABSTRACT

Different samples of cellulosic materials were analyzed by Raman spectroscopy and wood chips from *Pinus elliottii*, treated with acidic and alkaline aqueous solutions, were used to evaluate diagnostic signatures of the chemical structure of the cellulosic fibres. Cotton and whiskers synthesized from cotton, ancient Egyptian linen from a mummy wrapping, and five different paper sheets used in museum handling were compared. The complementarity of the Raman spectroscopic and scanning electron microscopic data facilitated the evaluation of the crystallinity, the level of organization and chain sizes of the fibres and the identification of different oxidation products. Intensity ratios measured from pairs of key bands were used to characterize the crystallinity, chain lengths and presence of oxidative decomposition in the range of the studied samples. Finally, the Raman spectra of the ancient Egyptian linen specimen indicated a potential future application of the proposed analysis for the characterization of archaeological pieces composed of linen.

1. Introduction

Cellulose is a natural polymer which has played a major role in human history [1–4]. The large number of potential sources of cellulose from plants brings a challenge in the characterization of the botanical source of cellulosic samples especially due to the presence of contaminants in the fibre structures and the use of different processes applied historically for chemical treatment [5–7]. More recently, due to their unique properties, cellulosic materials have been used for the production of novel composite materials in a diverse range of applications in biology, biofuels manufacture and engineering [8–13].

Sheets of paper can be produced from cellulosic raw materials such as wood, cotton and linen fibres. The assessment of the state of paper-based works in museums and libraries involves working with books, paints, prints, documents and other art objects; the typical analyses using electron microscopy, infrared absorption and X-ray diffraction are fundamental but these techniques lead to the provision of only partial information about the structure of the fibres and usually require laborious preparation of the samples [14–16]. Hence, Raman spectroscopy can afford a suitable alternative for characterizing cellulosic materials for crystallinity, fibre structure and the sources of the raw materials as well as can inform changes that have been induced during the preparation or purification processes. The treatment of raw cellulosic materials using acid or alkalis (mercerization) is widespread [17–23], and Raman spectroscopy has been shown to be a valuable technique for analyzing structural changes in the fibres which arise from physical, chemical or mechanical processing [6,24–31].

In this work we report the Raman spectroscopic studies of the cellulose structure of *Pinus elliottii* wood after alkaline and acidic treatment and further evaluate these results for assessing the structural properties of other cellulosic materials: five commercial paper sheets, whiskers from cotton and ancient Egyptian linen samples. The vibrational spectroscopic conclusions were supported by data from scanning electron microscopy (SEM) analyses. The results permit an assessment to be made about the level of crystallinity of the cellulosic fibres, the interchain order and the presence of shortened polymer chains.

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2. Materials and methods

2.1. Reactants and papers

Sodium hydroxide and nitric acid were purchased from Sigma-Aldrich and used as received. The deionized water used in the solution preparation was of Milli-Q grade with an 18.2 MΩ cm resistivity.

Cellulose whiskers prepared from cotton were kindly supplied by the Brazilian Agricultural Research Corporation (EMBRAPA) [32]. The ancient Egyptian linen specimen was obtained from mummy wrappings from Nekht-Ankh taken from a XIIth Dynasty rock tomb burial (*ca.* 2100 BCE), The Tomb of the Two Brothers (Nekht-Ankh and Khnum-Nakht), excavated by Sir William Flinders Petrie in 1906 in the Nile Valley, Der Rifeh, near Assiut [3].

The paper samples were provided by the Museu de Arte Murilo Mendes, Juiz de Fora, Brazil. They are used in museum conservation for the manipulation of artistic objects and consist of i) Kozo Japanese low-acidity paper produced from *Broussonetia papyrifera*, with a density of 8 gm^{-2}, which is used for filling or masking in the restoration of degraded cellulosic artefacts; ii) paperboard and filiset papers, freed of acidity by the presence of an alkaline additive, which are used for both support and as archival mounting boards in technical storage; iii) filter paper used as a blotter during aqueous treatment of artefacts where the principal requirement is the absence of additives; iv) silicone-coated paper, with one face protected against humidity, which is used in the transport of artistic works and in this case the Raman spectra were recorded from the non-siliconed side of the paper.

2.2. Chemical modification of Pinus elliottii wood chips

Chips from *Pinus elliottii* wood were treated sequentially with aqueous solutions of nitric acid (volume fraction in%) followed by aqueous solutions of sodium hydroxide (mass fraction in%) using different H^+/OH^- concentration ratios: 5/5, 20/5, 30/5, 5/10, 5/20, and 5/30. The treatment consisted of the immersion of the wood chips in an aqueous solution of nitric acid, using 10.0 mL per gram of wood chips, keeping the mixture under reflux at 85–90 °C for 1 h. This was then followed by copious washing with deionized water to neutral pH and then the material was submitted to boiling with sodium hydroxide aqueous solution using also 10.0 mL per gram of wood chips, keeping the mixture under reflux at 95–100 °C for 1 h. After this procedure, a repeated washing was carried out to neutral pH and then the material was dried.

2.3. Equipment and methods

Raman spectra were recorded using a Bruker, RS-100, Fourier-Transform Raman Spectrometer with Nd-YAG laser source operating at a wavelength of 1064 nm with a germanium detector cooled by liquid nitrogen. The spectra were recorded from a coupled optical microscope and each spectrum presented is an average of those recorded from 3 different points on the sample using 50 mW laser power at source, 300 scans accumulated and 4 cm^{-1} spectral resolution. The fragments of paper used in museum handling, the ancient Egyptian linen and cellulosic whiskers were analyzed without any previous preparation being undertaken. The signal recorded at different points of the sample was very reproducible, which indicated the homogeneity of these samples, excepting that recorded from wood chips, where the estimated variability in the signal was 5–10%.

SEM micrographs were recorded using a Jeol, JSM-5310 microscope using 15 kV electron beam voltage, an ETD detector at a working distance at 15 mm. The samples were coated with a thin gold film prior to analysis.

3. Results and discussion

Fig. 1 presents the Raman spectra of *Pinus elliotti* wood with and without treatment using nitric acid solution followed subsequently with sodium hydroxide solutions at different concentrations. The Raman spectra were analyzed by measuring the intensity ratios of pairs of bands, without baseline correction being made, but accounting for the background emission. The values of these ratios are given in Table 1 and they are described as follows:

a) 1121/1096 cm^{-1} (I^{1121}/I^{1096}), assigned to symmetric and asymmetric β-(1,4)-glycosidic linkage stretching modes, respectively [6,33], which are characteristic monitors of the level of

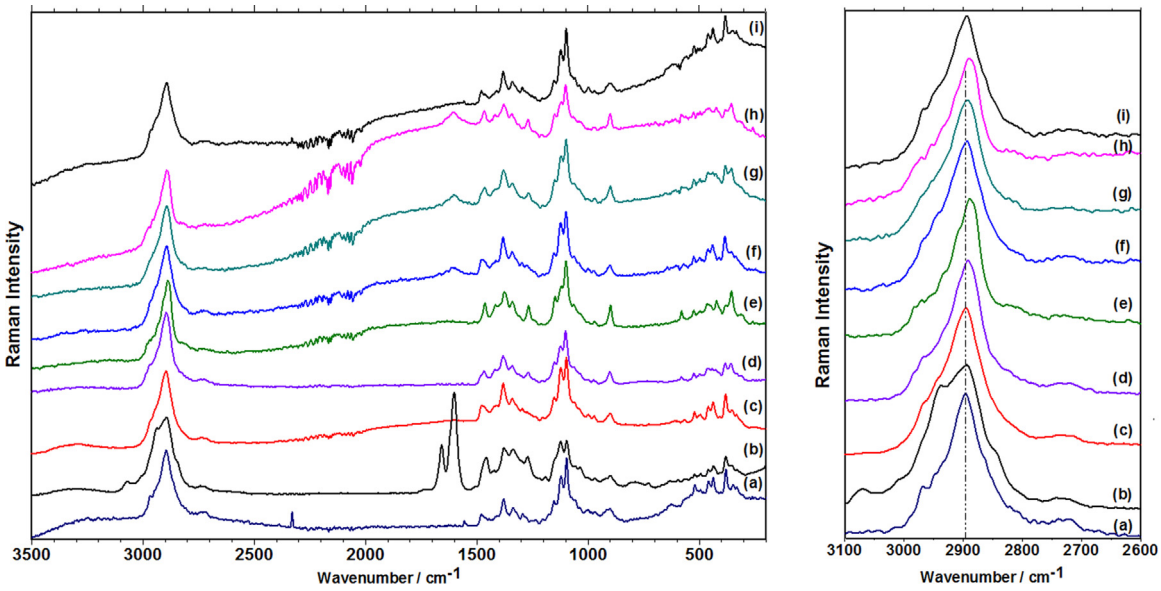

Fig. 1. Raman spectra of cellulose whiskers (a); *Pinus elliottii* wood chips without (b) and with treatment using H^+/OH^- ratios: 5/5 (c), 20/5 (d), 30/5 (e), 5/10 (f), 5/20 (g), 5/30 (h); and ancient linen (i). All spectra were normalized to the intensity of the band at 2896 cm^{-1}.