

Crystallinity of Nanocellulose Materials by Near-IR FT-Raman Spectroscopy

Abstract. Considering that crystallinity is one of the important properties that influence the end use of cellulose nanomaterials, it is important that the former be measured accurately. Recently, a new method based on near-IR FT-Raman spectroscopy was proposed to determine cellulose I crystallinity. It was reported that in the Raman spectrum of cellulose materials, the peak intensity ratio of 380 and 1,096 cm^{-1} bands can be used to determine cellulose crystallinity. Raman crystallinities of the calibration-set Whatman CC31 samples were correlated with the WAXS data (Segal-WAXS-21°; coefficient of determination $R^2 = 0.98$). Average standard error calculated from replicate Raman acquisitions indicated that the Raman crystallinity model was highly reliable. In ongoing investigations, the Raman method is being applied to determine crystallinity of nanocellulose materials.

Keywords. Nanocellulose, cellulose, crystallinity, Raman, spectroscopy

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Introduction. Cellulose crystallinity is defined as the mass fraction of crystalline domains in cellulose materials. This mass fraction can vary significantly in various materials. Crystallinity has an important effect on the physical, mechanical, and chemical properties of cellulose.

Among the techniques used for estimating cellulose crystallinity, WAXS is the most extensively used method. The X-ray method involves isolation of amorphous background from the diffraction pattern, which in the case of cellulose materials is not always easy for reasons that have to do with cellulose crystallites being small and the diffraction pattern being poorly defined (weak broad features) at lower crystallinities. Similarly, other techniques have limitations, which have been discussed in the literature [1,2].

Raman spectroscopy has proven to be a useful technique in the field of cellulose and lignocelluloses [3,4]. The near-IR FT-Raman technique has an added advantage because of its ability to deal successfully with the

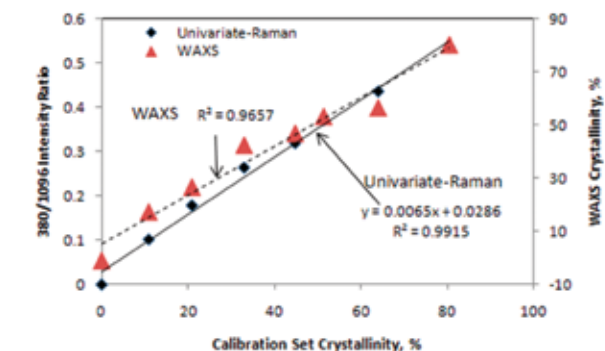


Figure 1. Univariate analysis of the calibration set samples showing the correlation between calibration set crystallinity versus 380/1,096 Raman intensity ratio or WAXS crystallinity [2].

issue of laser-induced fluorescence, which appears when samples are excited with visible lasers. Crystallinity measurements, using Raman, of semicrystalline polymers, including cellulose [2, 5–7], have been performed. Here, a summary of the work focused on estimation of the crystallinity of CNCs and CNFs is provided.

Methodology. CNCs and CNFs, along with other cellulose samples, were analyzed with a near-IR FT-Raman instrument. The Raman system is equipped with a 1,064-nm 1,000-mW continuous wave (CW) diode-pumped Nd:YAG laser. About 20–30 mg of dry CNCs and CNFs were sampled in an “aluminum well” (a Raman sampling accessory) or alternatively, a pellet was made with ~100 mg of the sample. For the rest of the cellulose samples, approximately 250 mg of each sample was pressed into a pellet. The laser power used for sample excitation was 600 mW, and 1,024 scans were accumulated. Bruker’s OPUS software program was used to find peak positions and to process the spectral data. From the Raman spectra, amorphous contributions in the frequency region 250–700 cm^{-1} were removed by first normalizing the spectra on the 897 cm^{-1} band and then subtracting the corresponding spectrum of a 120-min milled sample [2]. This was necessary because Raman spectroscopy is a semi-quantitative technique. The 897 cm^{-1} spectral band was chosen because its peak height was minimally impacted by changes in crystallinity. Raman crystallinity was determined using the univariate method of Agarwal *et al.* [2], which consists of calculating the peak height ratio I_{380}/I_{1096} from the spectra

1.1 Preparation and Characterization

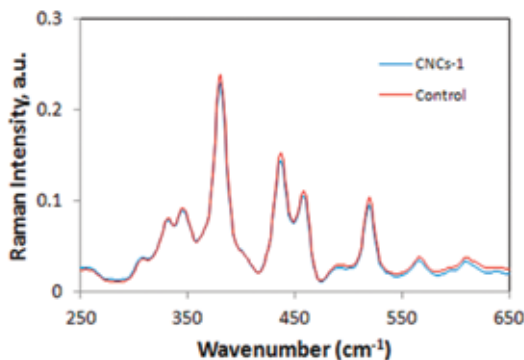


Figure 2. CNCs-1 and control Raman spectra in 380 cm^{-1} region after being normalized at 1096 cm^{-1} .

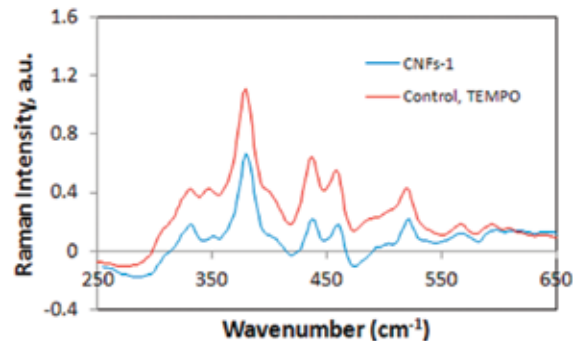


Figure 3. CNFs-1 and control Raman spectra in the 380 cm^{-1} region after being normalized at 1096 cm^{-1} .

of samples from which the spectrum of amorphous cellulose had been subtracted.

Results. As shown in Figure 1, for the calibration-set cellulose samples, the Raman ratio plot for 380/1,096 (Fig. 1, Raman-Univariate) generated excellent regression results ($R^2 = 0.992$) and showed good sensitivity to changes in crystallinity. The correlation of the calibration-set crystallinities with Segal-WAXS-21° is also shown in Figure 1 (WAXS), but evidently, compared to Raman-Univariate, it is somewhat inferior. The calibration set consisted of control (80.5% crystalline) and 120-min milled (0% crystalline) Whatman CC31 and six cellulose mixtures produced with crystallinities in the range 10.9%–64% [2].

Univariate-Raman crystallinities of CNCs, CNFs, and selected cellulose samples are reported in Table 1. The spectra of CNCs-1 and CNFs-1 along with their controls are shown in Figs. 2 and 3 respectively. The Raman crystallinities of the CNCs were identical (Table 1) whereas the crystallinities of the CNFs were different. Although not shown here, the results were compared with those from the WAXS method, and in general, the Raman observations were supported.

Conclusions. The Raman method can reliably estimate the crystallinity of cellulose nanomaterials.

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Table 1:

Crystallinities of CNCs, CNFs, and other cellulose products.

Samples	Univariate-Raman
CNCs-1	66.0
Control-1, filter paper	70.7
CNCs-2	66.0
Control-2, wood pulp	69.6
CNFs-1, Bl. SWKP	40.4
TEMPO-CNFs-1	40.5
CNFs-2, Eucalyptus pulp	34.5
TEMPO-CNFs-2	54.4
Starting Pulp-CNFs-2	60.5
Other cellulose materials	
Whatman CC31	78.0
Whatman CC41	77.9
CF-11	72.0
Avicel PH-101	59.5
Whatman 541 paper	56.2

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Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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