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Rapid prediction of wood crystallinity in *Pinus elliotii* plantation wood by near-infrared spectroscopy

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Abstract Crystallinity is an important property of woody materials; it responds to tree growth traits, structure, and chemical composition, and has a significant effect on Young's modulus, dimensional stability, density, and hardness, etc. The ability of near-infrared (NIR) spectroscopy coupled with multivariate analysis to rapidly predict the crystallinity of slash pine (*Pinus elliotii*) plantation wood was investigated. The results showed that the NIR data could be correlated with the X-ray diffraction (XRD)-determined crystallinity of slash pine wood by use of partial least squares (PLS) regression, producing excellent coefficients of determination, r^2, and root mean square error of calibration, RMSEC. The use of either reduced spectral ranges or the selection of certain wavelengths consistent with known chemical absorptions did not have any detrimental effect on the quality of PLS models allowing the use of inexpensive, small, and portable spectrometers. These studies show that NIR spectroscopy can be used to rapidly predict the crystallinity of slash pine wood.

Key words Near-infrared (NIR) spectroscopy · X-Ray diffraction (XRD) · Partial least squares (PLS) regression · Slash pine · Crystallinity

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Introduction

The crystallinity of wood is defined as the weight fraction of crystalline material (crystalline cellulose) in wood. It has an important effect on the physical, mechanical, and chemical properties of cellulose fibers. For example, Young's modulus, tensile strength, alpha-cellulose content, dimensional stability, density, and hardness increase with increasing crystallinity, while moisture regain, dye sorption, chemical reactivity, swelling, and flexibility decrease.[1] Therefore, the study of wood crystallinity is important for understanding the ultrastructure and composition of woody materials. Previous studies on the crystallinity of wood have used a variety of techniques such as: X-ray diffraction (XRD),[1–5] infrared (IR) spectroscopy,[6,7] nuclear magnetic resonance (NMR) spectroscopy,[8] and dynamic mechanical spectroscopy (DMS).[9]

Near-infrared (NIR) spectroscopy has been widely used for the assessment of wood quality, pulp, paper, and wood composites in the forest products industry.[10–19] Extensive research has demonstrated that NIR spectroscopy can be used to estimate a wide variety of wood properties such as chemical composition,[11–15] density,[16,17] stiffness,[16–18] and microfibril angle (MFA).[12,19] This technique is nondestructive and has been successfully used to rapidly and accurately estimate wood properties from increment cores, clearwood, and wood powder. While there have been many NIR studies successfully predicting MFA, there are few with regards to crystallinity. A recent study by Kelley et al.[13] investigated the effects of refining pressure and age on the chemical composition and crystallinity of refined fibers using NIR and XRD techniques. Their results showed poor correlation between the crystallinity of wood fiber and NIR spectra, which the authors found somewhat surprising. Even though MFA and crystallinity are different properties, they are sufficiently similar that they anticipated the NIR spectra would contain some information about crystallinity.[13] The aims of this study were to investigate: (1) the ability of NIR spectroscopy to rapidly predict the crystallinity of slash pine specimens, and (2) the effect of using reduced wavelength

ranges and only selected wavelengths associated with cellulose on the quality of the models.

Materials and methods

Collection of wood samples

Six slash pine (*Pinus elliotii*) trees of 20 years of age were harvested from a plot in Jiangxi, China (27°22′29″N, 115°15′00″E, and altitude 188–233 m). Disks measuring 10 cm in length were cut from each tree at breast height, and were left to air-dry in an environment-controlled room for several months. Individual rings were sectioned from each disk between rings 4 and 20. These were further broken down into matchsticks prior to milling in a Wiley mill equipped with a No. 10 mesh screen. With 6 disks and 17 rings, a total of 102 powdered wood samples were prepared for analysis.

XRD analysis

X-Ray measurements were conducted on a PANalytical XRD diffractometer (Almelo, The Netherlands). The powdered specimens were pressed into the shape of a tablet with rectangular dimensions of 15 × 20 mm with a thickness of 1 mm. The X-ray diffractometer was operated at a voltage of 45 kV with a current density of 35 mA. The scanning range was from $2\theta = 5°$ to 40° at a scan speed of 0.071°/s. The data was collected using a continuous mode with angular intervals of 0.017°. Crystallinity was evaluated as a crystallinity index and determined from the ratio of the integral intensity of crystalline portions to the total intensity of the sample.[20] The formula for crystallinity index, *CrI*, is as follows:

$$CrI(\%) = (I_{002} - I_{am})/I_{002} \times 100$$

where I_{002} is the maximum intensity of the 002 diffraction peak at $2\theta = 20.002°$, and I_{am} is the minimum intensity of a peak near $2\theta = 18.000°$.

NIR spectroscopy

NIR measurements were collected with an ASD FieldSpec Pro FR spectrometer (Analytical Spectral Devices, Boulder, CO, USA) at 1-nm intervals between 780 and 2500 nm. The powdered samples were transferred to a bottle cap, leveled, and rotated at 45 rpm to minimize specular interference and surface heterogeneity. A fiber optic probe oriented perpendicular to the sample surface was used to collect the reflectance spectra. A piece of commercial microporous Teflon was used as the white reference material. The samples were illuminated with a DC lamp oriented at 30° above the sample surface. Thirty scans were collected and averaged to obtain a single spectrum.

Partial least squares analysis

Partial least squares (PLS) modeling of the data was performed using the Unscrambler (version 9.2) software (CAMO, Corvallis, OR, USA). Calibration models were constructed using PLS regression with full cross validation. First and second derivatives of the data were also analyzed. The performance of the models was assessed using several common statistical measures: the coefficient of determination, r^2; is a measure of the strength of the fit to the data, and the root mean square error of calibration or prediction (RMSEC or RMSEP) is a measure of the calibration or prediction error in the fit. Over two thirds of the samples (72 samples) were used for the calibration models while 30 samples were used for predictions.

Results and discussion

XRD analysis

2θ XRD patterns obtained from several of the slash pine samples are shown in Fig. 1. There are two major diffraction peaks at approximately 16° and 22° corresponding to the 101 and 002 crystal planes, respectively. The XRD plots show considerable variation at the 002 diffraction peak ($2\theta = 20.002°$), associated with the crystalline region of cellulose in slash pine. For each of the six slash pine trees, there was a general increase in crystallinity from rings 4 to 7, after which the values were fairly constant to ring 20. Andersson et al.[3] observed the same behavior in Norway spruce, in which the crystallinity increased from ring 4 to 10, remaining constant beyond ring 10. However, in a later study with Norway spruce and Scots pine,[4] they observed no change in the cellulose crystallinity or the thickness of the cellulose crystallites from the pith to the bark. This, they concluded was due to the degree of order of the cellulose microfibrils remaining constant from pith to bark. Nevertheless, the primary purpose of this study was to investigate any correla-

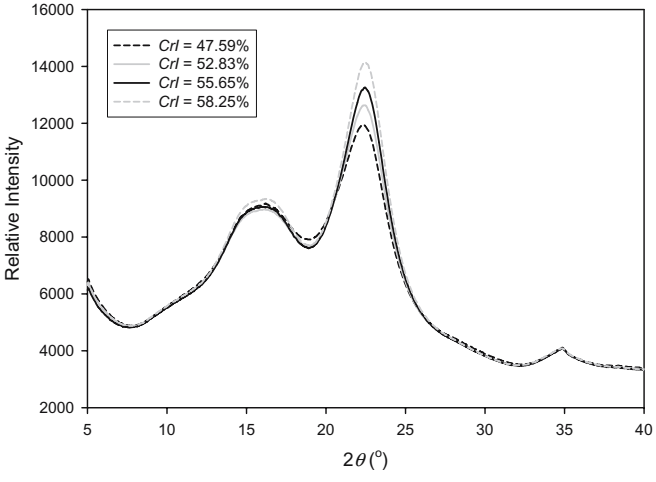

Fig. 1. Typical 2θ X-ray diffraction (XRD) patterns obtained for slash pine wood powder for 5°–40°

Table 1. The range of crystallinity for calibration and prediction sets

Sample set	No. of samples	Crystallinity (%)			
		Mean	Maximum	Minimum	SD
Calibration	72	52.91	61.04	35.01	4.88
Prediction	30	54.00	60.67	36.32	5.21

SD, standard deviation

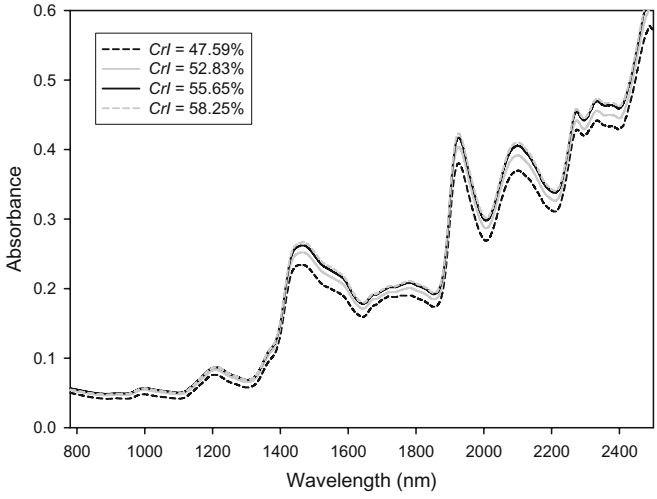

Fig. 2. Typical near-infrared (NIR) spectra obtained for slash pine wood powder between 780 and 2500 nm

tion between the NIR-predicted and XRD-determined crystallinity, and thus the samples were randomly divided into calibration and prediction sets with 72 and 30 samples, respectively, and a summary of their crystallinity values is shown in Table 1, ranging from 35.01% to 61.04% and from 36.32% to 60.67% for the calibration and prediction sets, respectively.

NIR spectra

NIR spectra collected from the same samples are shown in Fig. 2, with the greatest variation occurring in the regions of 1400–1600 and 2000–2500 nm. The bands between 1400 and 1660 nm arise from water[21] and the first overtone of cellulose and hemicellulose hydroxyl vibrations,[12] while the bands between 1890 and 2020 nm arise from the interactions between carbohydrate hydroxyls and water.[12,21]

PLS analysis

PLS regression was performed on the NIR spectra applying spectral pretreatments, as well as using different spectral ranges. The PLS regression model based on the raw spectra (780–2500 nm) is shown in Fig. 3 with the closed and open circles representing the calibration and prediction sets, respectively. These both gave r^2 values of 0.84 with RMSEC and RMSEP of mean values of 3.6% and 4.0%, respectively (Table 2). In addition, spectral pretreatments, such as de-

Table 2. Effect of different spectral pretreatments on the results of calibration and prediction of crystallinity on full near-infrared range of 780–2500 nm (calculated using five factors)

Math treatment	Calibration		Prediction	
	r^2_{calib}	RMSEC of mean (%)	r^2_{pred}	RMSEP of mean (%)
Raw	0.84	3.6	0.84	4.0
First derivative	0.95	2.0	0.86	3.9
Second derivative	0.76	4.5	0.11	9.9

RMSEC, root mean square error of calibration; RMSEP, root mean square error of prediction

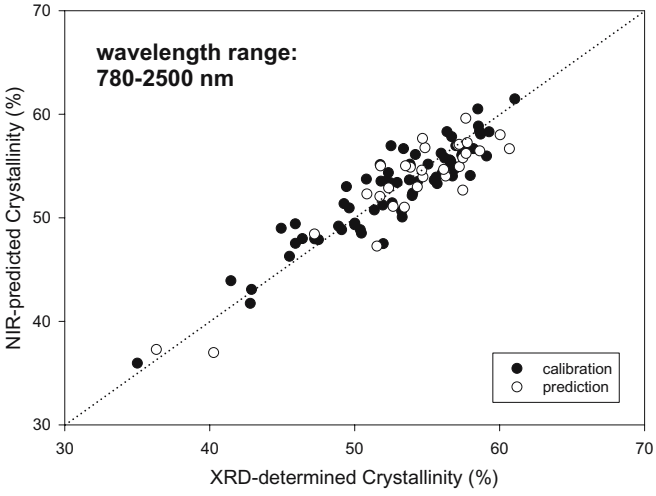

Fig. 3. Relationship between XRD-determined and NIR-predicted crystallinity of slash pine wood for the raw spectra between 780 and 2500 nm (calculated using five factors)

rivatives or multiplicative scatter correction, are often used for model improvement. The raw spectra and first and second derivative spectra were used in this study, and Table 2 summarizes the effect of these pretreatments on the performance of the calibrations and predictions. The calibration results show that PLS models based on the first derivative spectra yielded a high r^2_{calib} value of 0.95 and low RMSEC of mean value of 2.0%, while the second derivative spectra produced poorer results of 0.76 and 4.5%, respectively. The prediction result showed the same trends except that the second derivative values were much poorer with r^2_{pred} of 0.11 and a RMSEP of mean value of 9.9%. While these pretreatment methods are widely used to improve calibration performance, they can greatly complicate any chemical interpretation of the regression coefficients.[12] Therefore, because the raw spectra did not provide any significantly poorer results than the derivatives, the raw spectra were used for the remainder of the study.

Another aspect of particular interest is the effect of reduced spectral ranges, because this allows the use of inexpensive, lightweight spectrometers that can acquire spectra in fractions of a second.[12] Thus, two reduced wavelength ranges of 1400–1660 and 2020–2250 nm were employed; these were chosen based on the regression coefficients from the earlier models. Table 3 lists the results of the PLS mod-

Table 3. Calibration and prediction statistics for crystallinity from models based on wavelengths related with cellulose for raw spectra (calculated using five factors)

Wavelength range (nm)	Calibration		Prediction	
	r^2_{calib}	RMSEC of mean (%)	r^2_{pred}	RMSEP of mean (%)
1400–1660	0.88	3.2	0.86	3.8
2020–2250	0.91	2.7	0.92	2.9
1510, 1734, 1898,1935, 2045, 2120, 2236	0.87	3.4	0.86	3.6

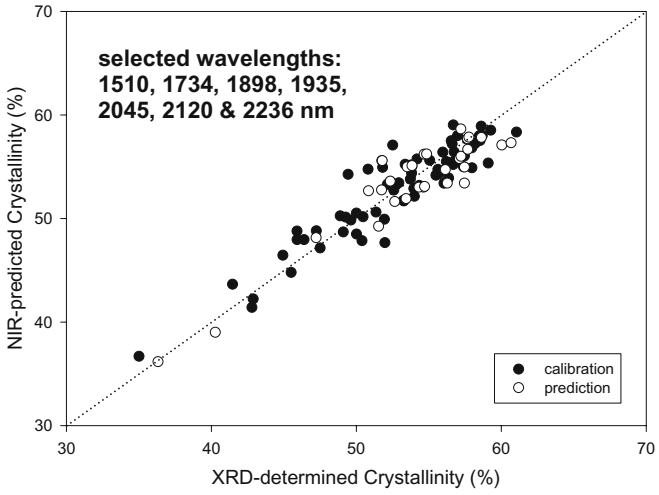

Fig. 4. Relationship between XRD-determined and NIR-predicted crystallinity of slash pine wood for the raw spectra using selected wavelengths of 1510, 1734, 1898, 1935, 2045, 2120, and 2236 nm (calculated using five factors)

eling with the reduced wavelength ranges; these yielded high r^2_{calib} and r^2_{pred} values of 0.88–0.91 and 0.86–0.92, respectively. Similarly, low RMSEC and RMSEP of mean values were also obtained. Modeling was further extended into the use of individual wavelengths; however, it is necessary to ensure that the selected wavelengths are consistent with known chemical absorptions. It has been previously reported that the NIR bands near: 1722, 1734, 2230, and 2310 nm are consistent with the cellulose in pine wood.[14] The selected wavelengths used in this model were: 1510, 1734, 1898, 1935, 2045, 2120, and 2236 nm. The relationship between NIR-predicted and XRD-determined crystallinity using only selected wavelengths is shown in Fig. 4. Strong correlations were obtained in calibration and prediction yielding comparable r^2_{calib} and r^2_{pred} values of 0.87 and 0.86 with low RMSEC and RMSEP of mean values of 3.4% and 3.6%, respectively. These results indicate that strong PLS models can be built for crystallinity using reduced wavelength ranges or selected individual wavelengths.

Conclusions

This study has successfully correlated crystallinity measurements of slash pine (*Pinus elliotii*) plantation wood using X-ray diffraction with those determined from near-infrared spectra with multivariate analysis. These correlations, using the raw NIR spectra, were strong in both calibration and prediction. Spectral preprocessing techniques were also employed with the first derivative spectra providing slightly improved results, while poorer correlations were obtained from the second derivative spectra. Another area of interest was to employ reduced wavelength ranges and similarly strong correlations were obtained. This was also achieved when using only selected individual wavelengths; however, it is important to ensure that the chosen wavelengths are consistent with known chemical absorptions of interest. The use of reduced wavelengths allows the possibility of utilizing low-cost, lightweight spectrometers for field applications.

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