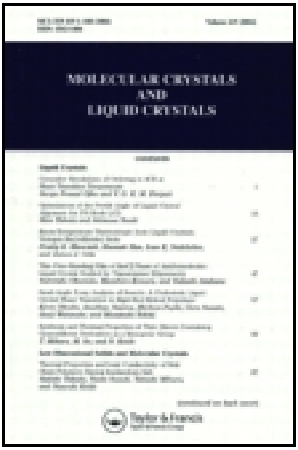

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NIR Study of Chemically Modified Cellulosic Biopolymers

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Near-infrared spectral analysis was useful to quantify the ester content of chemically modified cellulose and lignocellulosics. Two kinds of samples were studied, as long aliphatic-chain cellulose esters and wood sawdust chemically-modified either by anhydrides or by ethylene carbonate. It was possible to determine the degree of substitution (DS) of such samples through a correlation by partial least square (PLS) of second-order derivative of NIR spectra. This technique was efficient even when DS values were low, which is difficult to do by using FTIR. It was also possible to distinguish reagent molecules that were attached to the cellulosic substrate by hydrogen bonding from those linked by covalent bonding.

Keywords: cellulose fatty ester; degree of modification; degree of substitution determination analysis; wood chemical modification

INTRODUCTION

Near-infrared spectral analysis is a rapid technique that is being increasingly employed in industrial and academic laboratories. The

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reflectance data of solid samples at wavelengths between 750 and 2500 nm permit to determine the composition of complex substrates currently found in agro-food industry and other sectors such as wood [1]. This analytical technique presents numerous advantages, it is rapid, non-destructive and inexpensive. However it is very difficult or impossible to assign bands to a particular motion in the molecule, as it is done in the FTIR technique. The application of multi-variable statistical analysis (e.g., PLS) allows a fast treatment of the NIR spectra provided that a previous calibration be carried out.

The main objective of this study is to evaluate the possibility to determine the degree of substitution (DS) of cellulose fatty esters and the ester content (EC) of chemically modified lignocellulosics. Indeed, DS and EC values might be very difficult to be determined by other techniques under certain conditions. Moreover we expect to obtain information that allows to distinguish molecules that are attached to the cellulosic substrate by hydrogen bonding instead of covalent bonding. We have studied two kinds of samples, long aliphatic-chain esters of cellulose and wood sawdust after modification with stearate anhydride or ethylene carbonate.

EXPERIMENTAL

All the analyses were carried out on powdered samples with a UV-VIS-NIR spectrometer (UV-570, JASCO) with a device for diffuse reflectance in the 300–2500 nm domain. Cellulose stearates (C_{18} chains) with different DS were synthesized by the pyridine method [2]. α-Cellulose from Sigma (France) was the starting polysaccharide (DP = 960, 4% pentosans) for the synthesis of the cellulose esters. Stearoyl chloride, pyridine, and other chemicals were reagent-grade; they were purchased from Aldrich and used as received. Cellulose (10 g) was stirred in excess pyridine (250 mL) at 20°C for 30 min. Fatty acid chloride (2 eq/OH) was poured into the reactor, and reflux was conducted at 130°C with mechanical stirring for different reaction times to obtain several DS values. After cooling at 100°C, 250 mL of 50% aqueous ethanol was added to consume the remaining acid chloride. The powder product was recovered by filtration over sintered glass and then thoroughly washed with ethanol and acetone. After further purification by Soxhlet extraction with acetone for 16 hr, the cellulose ester was dried at 50°C to constant weight and stored in a desiccator at room temperature. Determination of the DS was done by elemental analysis according to an earlier study [3], six treated samples with variable DS, i.e., 0.3, 0.9, 1.6, 2.2, 2.4, 3 were obtained.

Wood esters were obtained by chemical treatment of Scots pine wood flour (10 g) with stearic anhydride (2 eq/OH) in the same batch reactor at 150°C. In order to obtain different ester contents, the duration of the reaction was varied (30, 60, and 120 min). All the samples were purified by Soxhlet extraction with acetone for 16 hr then dried at 50°C to constant weight.

Wood carbonates were synthesized by treating Scots pine wood flour (10 g) with ethylene carbonate (10 eq/OH) at 130°C during 8 hr with K_2CO_3 as catalyst (0,1%). The same step of purification as for wood esters was applied to the samples.

RESULTS AND DISCUSSION

Cellulose Esters

Near-infrared spectroscopy of these samples showed significant differences when compared to native cellulose (Fig. 1). The appearance of new absorption bands (1750 nm and 1200 nm) is accompanied by the disappearance of the 1450 nm absorption band. As reflectance is complementary to absorbance, negative changes in reflectance corresponding to new bands appeared in absorption. After calculation of the

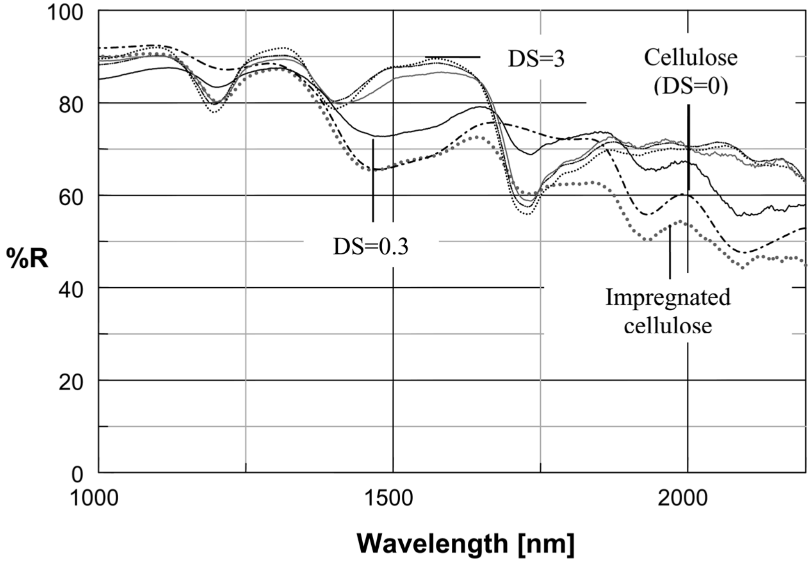


FIGURE 1 Near-infrared spectra of cellulose, cellulose stearate and impregnated cellulose with stearic acid.

second derivative (Fig. 2) it was possible to establish a correlation between the height of the calculated bands and the DS of the samples (cellulose stearates).

Partial Least Squares (PLS) calculations were done using the Unscrambler 9.0® software. It is clear that by using second derivatives of each spectrum there is no need to correct the baseline offset due to differences in samples geometry. Nevertheless, we tried to make samples as homogeneous as possible with a milling pre-processing step. Five acquisitions on different parts of each sample have been recorded and the average spectrum for the statistical treatment has been considered.

Due to the low number of samples, it was decided not to refine the model and to keep all the data, including the outliers. The model presented in Figure 3a is thus the result of a calibration made from raw data without any optimization, i.e., neglecting variables (wavelengths) that are potentially noisy. The predicted vs. measured plot demonstrates that this preliminary model can predict the response value for the calibration samples. These results are outstanding because a sample of cellulose impregnated with stearic acid, i.e., with no covalent bond to cellulose and therefore with DS = 0, is taken in account by the model and can be distinguished from real cellulose esters. In future research, our objective will be to develop this technique to distinguish mixtures of covalent and non-covalent bound samples.

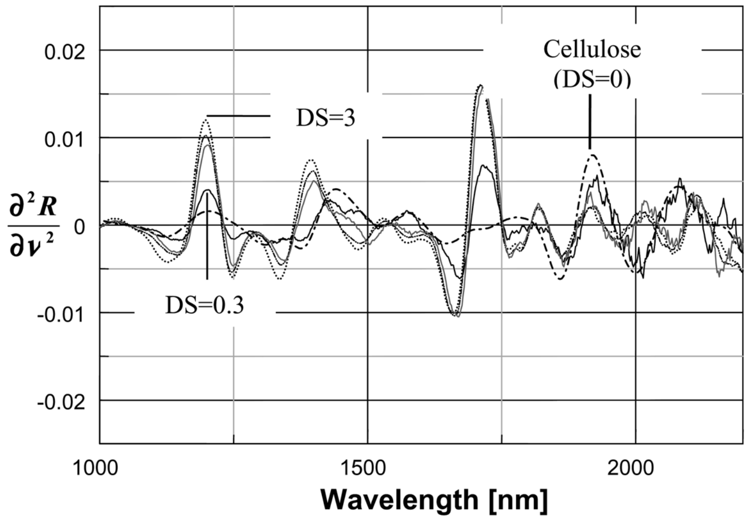
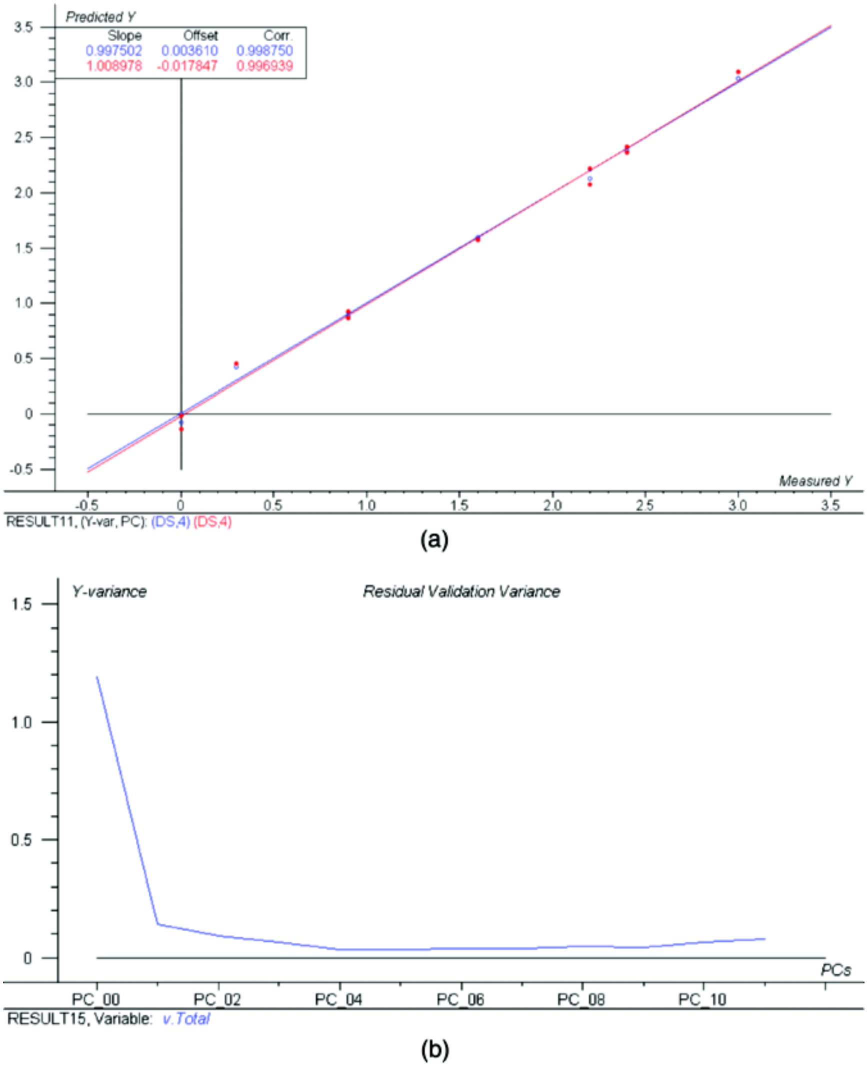


FIGURE 2 Second derivative spectra of cellulose stearates.



(a)

(b)

FIGURE 3 Results of the PLS statistical analysis.

By this procedure we might be able to simplify the determination of the degree of substitution without any complicated purification step. The plot of the residual validation variance (Fig. 3b) shows that four principal components (PC) were used to obtain the best model (that of Fig. 3a). When considering more than 8 PC the prediction variance increases significantly due to noise modeling.

Wood Esters

Five sets analysis of each sample were carried out in the same manner as for cellulose esters. We considered the average spectrum as the representative analysis.

If we compare the spectra of treated and raw wood (Fig. 4), significant differences appear such as a diminution of the intensity of the 1160–1170, 1410, and 1900 nm bands and the appearing of a new 1690 nm band. In spite of the lignocellulosic substrate complexity, finding a correlation between the degree of chemical modification of wood and NIR analyses seemed to be possible.

However, in order to perform a calibration with NIR spectroscopy it is important to define a reference technique. In the case of cellulose esters, many techniques exist: elemental analysis, NMR, etc. [3]. In the case of wood, there is no reliable and accurate method due to the natural heterogeneity of the substrate. Therefore, in order to obtain an accurate model, a large number of samples may be necessary to reduce the variance. In our case, only the qualitative approach was investigated.

Wood Carbonates

Some significant changes on the two bands of treated wood spectra at 1900 and 1400 nm have been observed, but contrarily to esterified

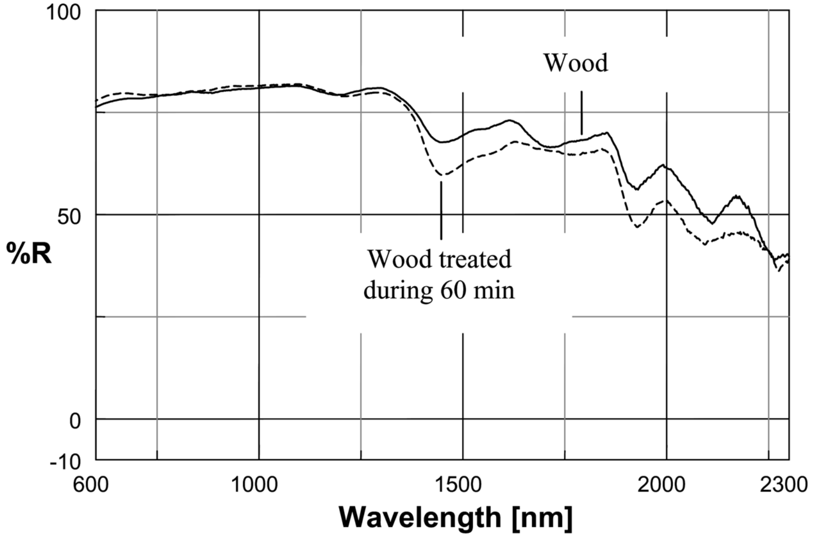


FIGURE 4 Near-infrared spectra of untreated wood and wood treated with stearic anhydride.

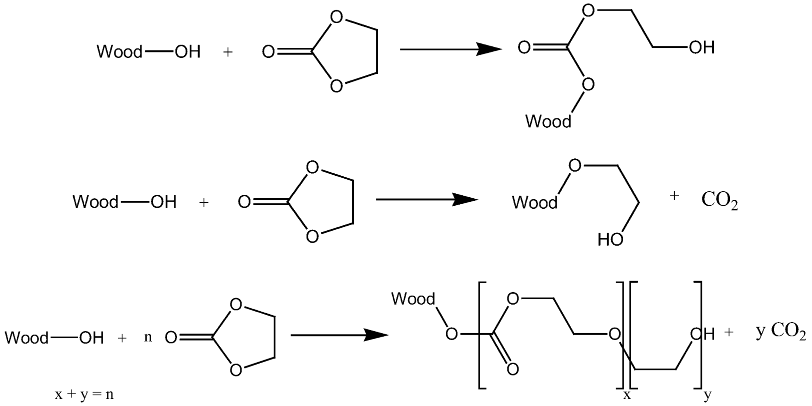


FIGURE 5 Schemes of possible reactions between wood and ethylene carbonate.

wood, NIR analyses of wood carbonates gave rise to extremely heterogeneous results. Grafting the reagent could however be demonstrated by the appearance of a characteristic band at $1750\,cm^{-1}$ in FTIR analysis.

Even though our approach was qualitative and limited to discriminate treated and non-treated wood, a correlation between the grafting of ethylene carbonate and the intensity of spectrum bands obtained by NIR spectroscopy was not possible to be demonstrated with certitude.

These results can be explained by the complexity of the reaction of EC with wood (Fig. 5). NIR spectra consist mainly of harmonics and combination bands of the fundamental stretching vibrations of O–H, N–H and C–H functional groups. This is the main reason why this kind of wood modifications is difficult to be observed.

CONCLUSION

NIR spectral technique offers a powerful tool to analyze the degree of substitution of cellulose long-chain esters such a stearate in the whole range of DS-values (0 to 3).

Reagent grafted to cellulose by covalent bonding can be distinguished from reagent retained only by non-covalent bonding such as hydrogen bonding.

This technique might be extended to wood derivatives provided that an accurate reference analysis technique is available and a high number of samples could be analyzed.

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