

# USE OF ADVANCED SPECTROSCOPIC TECHNIQUES FOR PREDICTING THE MECHANICAL PROPERTIES OF WOOD COMPOSITES'

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(Received August 2001)

## ABSTRACT

Near infrared (NIR) spectroscopy was used to characterize a set of medium-density fiberboard (MDF) samples. This spectroscopic technique, in combination with projection to latent structures (PLS) modeling, effectively predicted the mechanical strength of MDF samples with a wide range of physical properties. The stiffness, strength, and internal bond properties of the MDF samples could be predicted from the NIR spectra of the MDF surface. The technique is very rapid and provides molecular level insight on subtle changes in the properties of the MDF panels. The results highlight the potential value of NIR spectroscopy for process monitoring and quality control applications.

Keywords: Near infrared spectroscopy, multivariate analysis, medium-density fiberboard, mechanical properties

## INTRODUCTION

As the variability of the wood raw material expands and the performance specifications for engineered wood composites become increasingly stringent, the need for information on manufactured composite wood products has never been greater. This demand has been addressed from a variety of fronts that take

advantage of numerous empirical correlations between some process (or experimental) variables and panel properties. Many of these research efforts have been concerned with on-line process monitoring, and have explored nondestructive mechanical tests (Lister 2000), acoustic emission methods (Chen and Beall 2000), and dielectric analysis (Wolcott and Rials 1995) to evaluate strength development during consolidation. Although each of these approaches provides some measure of the properties of wood composites, they provide

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This article was submitted while the senior author was a Project Leader at the USDA Forest Service, Southern Research Station.

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limited insight into the molecular processes that direct property development in composite wood products.

Chemical changes that occur during composite panel formation have not received extensive research attention for several reasons. The complexity of the wood/resin system accounts for much of this reticence, as does the expense associated with many of the analytical tests. Still, the value of understanding these chemical changes is apparent from recent progress using solid-state nuclear magnetic resonance spectroscopy (Schmidt and Frazier 2000; Marcinko et al. 1999), Fourier transform infrared spectroscopy (Rosthauser et al. 1997), and other spectroscopic tools. The persistent challenge has been the relatively long time frames required for these experiments and the requirements for controlled experimental conditions. The need for controlled environments, in particular, has limited the utility of these spectroscopic tools for process monitoring or routine analysis of wood composite properties.

Advances in both instrument technology and data analysis techniques have led to new opportunities for using several advanced spectroscopic techniques to study the origins of property development in these complex composite systems. Near infrared (NIR) spectroscopy is of particular interest since it is non-destructive and rapid and does not require extensive sample preparation. Research has shown that, through the use of multivariate analysis (MVA) techniques, NIR data can be used to accurately predict the chemical composition (Axrup et al. 2000; Raymond et al. 2000) and physical properties of wood (Schimleck et al. 1999; Meder et al. 1999).

This report presents preliminary results on the use of NIR spectroscopy to identify the source of property development in medium-density fiberboard (MDF) panels. The use of MVA techniques to model panel properties and explore relationships between NIR spectral data and MDF panel properties will be discussed.

TABLE 1. Summary of formulation and process variables used to produce the medium-density fiberboard panels.

Panel Number	Resin Content (Wt. %)	Resin Type	wax Content (Wt. %)	Internal Temp (°C)	Mat
1	5	UF	1	116	
2	10	UF	1	115	
3	15	UF	1	115	
4	10	UF	0	115	
5	10	MUF	0	114	
7	5	UF	0	83	
8	10	UF	0	77	
9	5	UF	0	118	
10	10	UF	0	115	
12	10	UF	0	118	

#### MATERIALS AND METHODS

The MDF panels were formulated to provide a wide range of physical and mechanical properties. The fiber furnish was a commercial loblolly pine, thermomechanical pulp (Temple-Inland Forest Products Corp., Diboll, TX). The required amount of adhesive (urea-formaldehyde or melamine-urea-formaldehyde from Borden, Inc., Diboll, TX) was applied by spraying in a rotary-drum applicator. Table I summarizes the formulation variables for the 10 MDF panels. Following the application of resin to the fiber, the fiber mat was immediately formed using standard vacuum lay-up procedure and pressed at 170° C for 3% min. The completed panel dimensions were 30.5 X 30.5 x 1.3 cm. The panels were cut to produce two samples for bending tests and five samples for IB tests. The panels' bending properties and internal bond (IB) were determined on an Instron testing machine according to standard procedures (ASTM 1999). The mechanical properties, e.g., modulus of elasticity (MOE), modulus of rupture (MOR), and IB, of the panels are presented in Table 2.

#### Near infrared spectroscopy

The NIR measurements were made in reflectance mode with an ASD Field Spec (Analytical Spectral Devices, Boulder, CO) spectrometer at wavelengths between 350 and 2500 nm. A fiber optic probe oriented perpendicular to the sample surface was used to col-

TABLE 2. *Descriptive statistics of property variation for all MDF panels.*

Panel Property	Average	Median	Minimum	Maximum
Density (g/cm <sup>3</sup> )	0.81	0.83	0.61	0.88
Modulus of Elasticity (MPa)	2,973	3,128	1,216	4,342
Modulus of Rupture (MPa)	29.1	29.9	12.9	48.1
Internal Bond (MPa)	0.39	0.40	0.09	0.74

lect the spectra. The samples were illuminated with a DC lamp oriented at 30 degrees above the surface, and rotated at 50 rpm to minimize specular interference and surface heterogeneity. Thirty individual scans were collected and averaged into a single spectrum. The sampling area was kept constant at approximately 5 mm<sup>2</sup>. Reflectance spectra measure only the surface properties of the samples and we estimate that these spectra are sensitive to the chemical composition of the top 100 pm. Two spectra were collected from different locations near the center of both the tension and compression surface of the bending samples, providing four spectra for each sample. For the internal bond test samples, two spectra were collected from different locations on each of the two failure surfaces. These four individual spectra were again averaged to provide a single spectrum for each sample, which was used to generate the models.

#### *Projection to latent structures (PLS) modeling*

While a complete description of MVA can be found elsewhere (Martens and Naes 1991; Vandeginste et al. 1998), the following summary describes the steps used to construct PLS models in this work. Multivariate analysis was performed using The Unscrambler@ version 7.1 (CAMO, Corvallis, OR). This software package has the capability to perform both principal component analysis (PCA) and PLS (also known as partial least squares) analysis. All of the NIR spectra are combined into a single data matrix (X-matrix) and then converted from reflectance to absorbance. To facilitate interpretation of the chemical changes that drive the models, no further spectral processing was used. Using the second derivative

of the NIR spectra will frequently improve the correlations, but will complicate interpretations of the loadings. The MDF panel property data are combined into a response matrix (Y-matrix). The PCA software is used to systematically extract (decompose) variation in the data matrix (X-matrix), while principal component regression is used to regress each response variable (Y-matrix) onto the decomposed spectra (X-matrix) and make a projection to latent structures. This process allows for the simultaneous and independent decomposition of both the X- and Y-matrices and the regression of the Y-matrix onto the X-matrix, e.g., the mechanical properties onto the spectra.

There are two common ways to construct PLS models. A PLS-I analysis allows for predicting one Y-variable at a time, while PLS-2 analysis allows for simultaneous prediction of several Y-variables. The PLS models were constructed with all 2,150 wavelengths (350–2500 nm) as the X-matrix, and the MOE, MOR, IB, and panel formulation variables were used to generate the Y-matrix. Both the X- and Y-matrices were mean centered variance normalized prior to performing the PLS analysis. To compensate for the large difference in the magnitude of the MOE and MOR values, the inverse of their standard deviations was used for PLS-2 models. The number of principal components (factors) used for a model was selected by observing the response of the residual Y-variance to added factors. The model was completed when additional factors did not substantially decrease the residual Y-variance. Most of the models contained between 20 and 40 individual samples and required between 2 and 4 factors.

Models were constructed using full cross-

validation with all of the samples. Cross-validation systematically removes a single sample from the data set, constructs a model with the remaining samples, and uses that model to predict the value(s) of the Y-variable(s) for the extracted sample. This process continues until each individual sample has been removed from the data set and a fully cross-validated model is constructed (Martens and Naes 1991).

#### EXPERIMENTAL RESULTS

The MDF panels were prepared using a variety of formulations to produce panels with a wide range of characteristics and properties. The NIR spectra gathered from the exterior surface and the failed interior surface of two MDF panels representing formulation extremes (number 1 and 5, Table 1) are shown

in Fig. 1. The spectra exemplify several features common to the NIR spectra of wood-based materials. The MDF samples are dark brown as indicated by the strong absorbance in the 500–800-nm range. However, given the significant differences in the formulation of the two panels, the longer wavelength region of the NIR spectra is remarkably similar. This is because the underlying chemical composition (e.g., cellulose, hemicellulose, lignin, and resin) of the two sets of samples is very similar. This figure also indicates that there are greater differences between the NIR spectra of the two panels than between the locations (interior versus exterior) of spectral data collection.

A detailed assignment of the different vibrations can be found elsewhere (Martens and Naes 1991; Fourty *et al.* 1996; Curran *et al.*

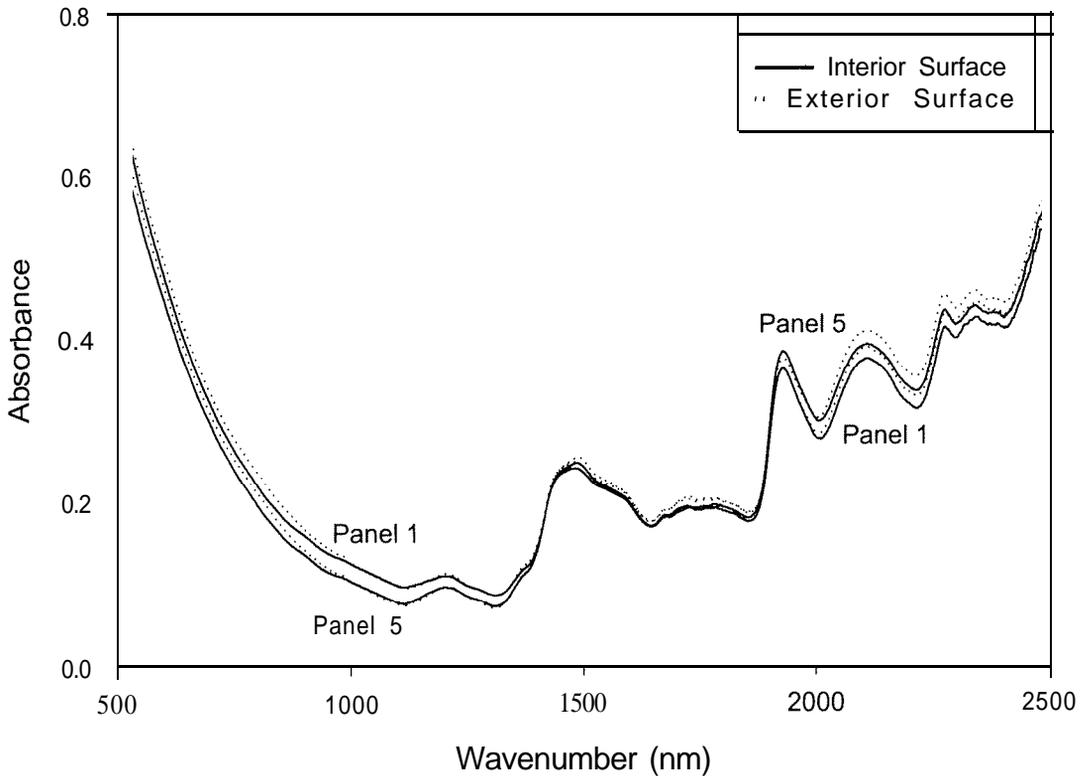


FIG. 1. Comparison of near infrared spectra collected from the interior and exterior surface of medium density fiberboard panels.

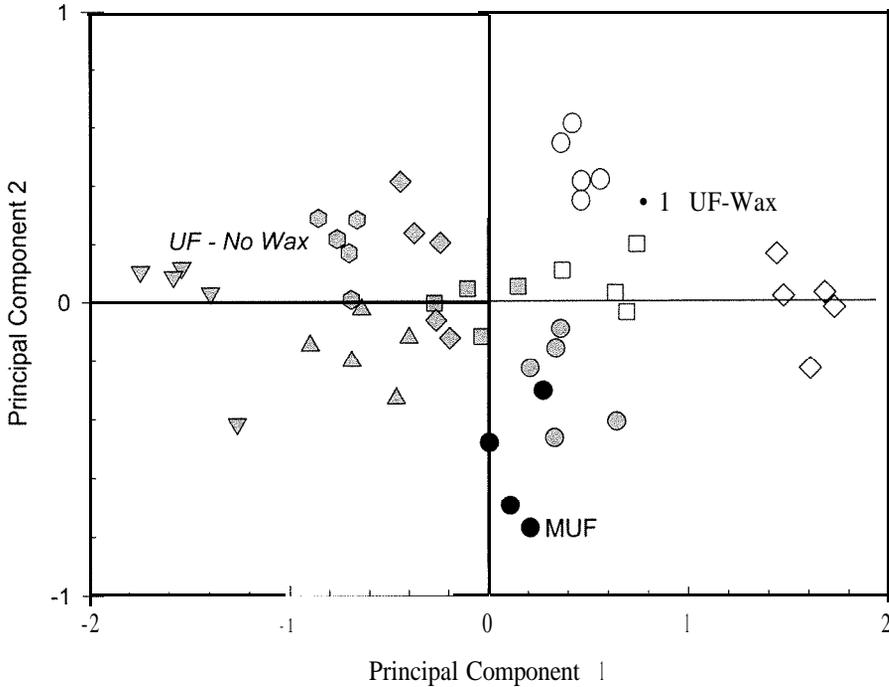


FIG. 2. Principal component results from NIR spectra collected from the interior (failure surface) of the individual IB sample blocks. The symbols correspond to the panels in Table 1: Number 1 (○), 2 (□), 3 (▽), 4 (◇), 5 (●), 7 (▽), 8 (●), 9 (A), 10 (■), 12 (●).

1992), but some important NIR spectral features include: the first overtone of cellulose hydroxyls (1400-1660 nm), the interactions between cellulose hydroxyls and water (1890-2020 nm), and the first overtone of lignin carbon/hydrogen vibrations (1635-1825 nm). There is some overlap of the cellulose and lignin hydroxyl vibrations—for example, the first overtones of the cellulose and lignin hydroxyl vibrations occur between 1400-1520 nm. The urea-based adhesive component also exhibits strong peaks at 900-1000 nm and 1500-1600 nm.

Although it is not immediately apparent through visual inspection of the spectra, differences between the samples are readily recognized by the application of MVA to the NIR spectra. Figure 2 shows the results of PCA of the NIR spectra obtained from the internal surface of the failed MDF IB samples. Relatively tight clusters of samples taken from individual panels can be identified, and these groupings

show that the variations within the MDF panels are generally small compared to difference between the panels. Panels 3 (*inverted triangles*) and 7 (*unfilled diamonds*) are isolated along the horizontal axis (principal component 1) and represent the formulation extremes (Table 1) of high resin content/high wax and low resin content/low temperature, respectively. This axis also separates the samples containing wax (Panels 1-3, *unfilled symbols*) from those that do not contain wax (Panels 4-12, *filled symbols*). While some overlap exists, the single melamine-urea-formaldehyde bonded panel (Panel 5, *solid circles*) is separated from all the urea-formaldehyde bonded panels along principal component 2. The ability to resolve the different composite panels shows that the NIR spectra contain chemical information related to the panel manufacturing process. To further demonstrate relationships between NIR spectra and panel properties, PLS-I models were developed for density, resin

TABLE 3. Summary of PLS-1 prediction of panel manufacturing variables by NIR sampled from the panel interior.

	Resin Cont. (Wt. %)	Panel Temp. (°C)	Density (g/cm <sup>3</sup> )
Correlation (R <sup>2</sup> )	0.80	0.56	0.73
RMSEP <sup>a</sup>	1.36	8.7	0.03
% RMSEP of mean)	12	8	4

<sup>a</sup> Root mean square error of prediction

content, and press temperature. As seen in Table 3, reasonable correlations were obtained with R<sup>2</sup> values ranging from 0.56 for temperature to 0.80 for resin content. It should be noted that because of the limited size of the data set, only two principal components were used in the models. These results indicate that manufacturing differences are clearly reflected in the chemical and physical characteristics of the panels, and that NIR spectroscopy is sensitive to these pertinent panel properties.

The same NIR spectra were used to construct PLS models for MOE, MOR, and IB. The models were constructed using spectra collected directly from the sample surface used for the property measurement (e.g., the internal, failure surface of IB blocks or the exterior surface of bending samples). Figure 3 presents the results of these models: the actual measured value of the property against the value predicted from the NIR spectra. The models give very good estimates of MOE and MOR over the entire range of samples. Reasonably good agreement between the predicted and measured IB is also found; however, slightly more uncertainty is apparent from the increased scatter. The model appears to overestimate very low internal bond strength, which may indicate sensitivity limits at lower adhesive additions or the contribution of additional factors to IB development that are not detectable by NIR. Recognizing the complexity of this multi-component system, the strong correlations (Table 4) obtained from this limited dataset are very encouraging.

TABLE 4. Summary predictions of modulus of elasticity (MOE), modulus of rupture (MOR), and internal bond (IB) for medium-density fiberboard by NIR sampled from the panel surface.

	MOE <sup>a</sup> (MPa)	MOR <sup>a</sup> (MPa)	IB <sup>b</sup> (MPa)
Correlation (R <sup>2</sup> )	0.80	0.82	0.76
RMSEP <sup>c</sup>	341	3.55	0.07
% RMSEP (of mean)	11	12	18

<sup>a</sup> PLS-2 algorithm.

<sup>b</sup> PLS-1 algorithm.

<sup>c</sup> Root mean square error of prediction.

## DISCUSSION

The ability to predict important performance properties of MDF composite through multivariate analysis of NIR spectra is of considerable value. The PLS models also generate regression coefficients, or information on the chemical features that drive the calibrations. The regression coefficients can be used to relate chemical features in the NIR spectra to the physical properties of interest, e.g., MOE, density, or resin content. Figure 4 shows the regression coefficients of the PLS models (normalized for comparison and expressed as relative intensity) for IB (A) and MOE (B). Figure 4 also shows the PLS regression coefficients for resin content (A) and density (B). The regression coefficients for IB and resin chemistry (Fig. 4-A) are very similar, suggesting that the chemical features that drive these two correlations are very similar. The regression coefficients indicate that the chemical features characterized by absorbance at 1500 nm, 2050 nm, and 2250 nm impact both the IB and resin content. The absorbances at these wavelengths are related to carbohydrates (1500 nm) in the MDF and the N-H (2050 and 2250 nm) overtones arising from the adhesive. Clearly, changes in specific chemical features are important in the development of internal bond properties. Prior work has also shown a relationship between IB and resin content (Hague et al. 1999; Scott 2001).

Figure 4-B shows the regression coefficients for MOE and density. The spectra used for these correlations were taken from the surface

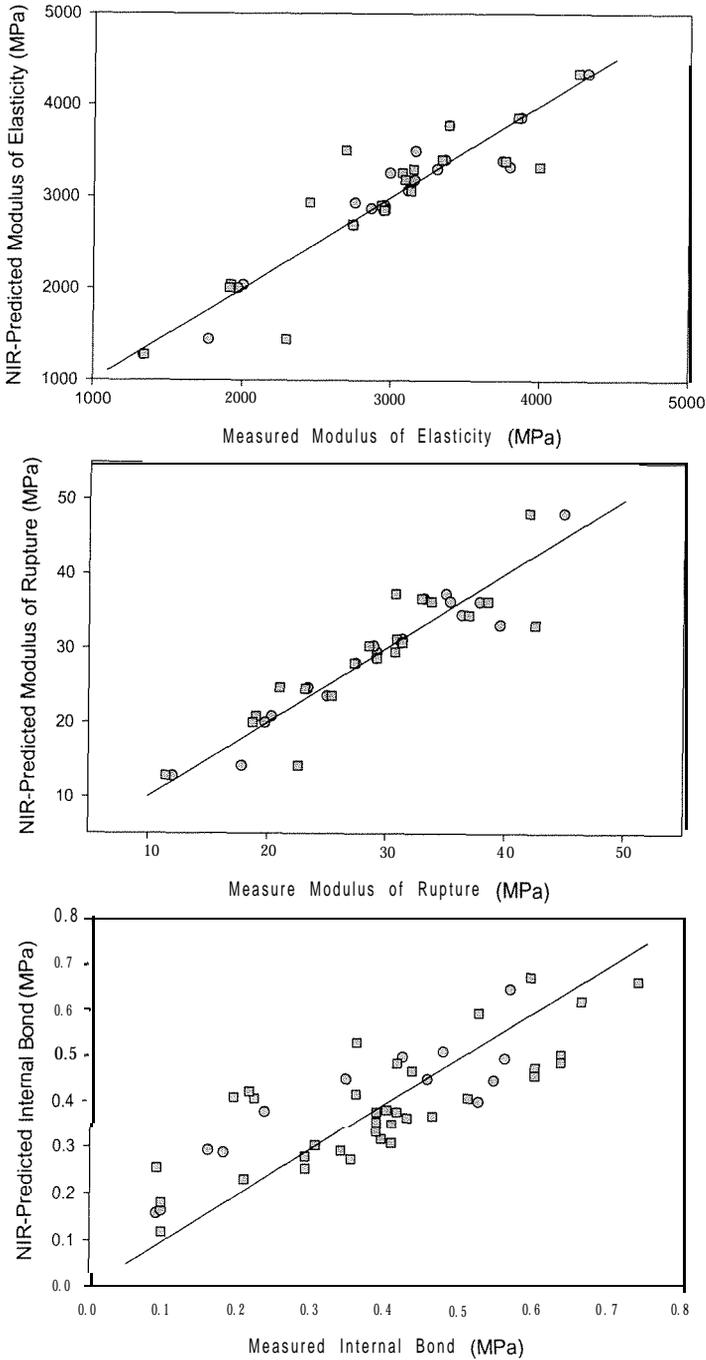


FIG. 3. Relationship between the measured values for MOE (top), MOR (middle), and IB (bottom), and the values predicted by PLS models constructed from the NIR spectra: calibration (○), validation (□).



FIG. 4. Comparison of regression coefficients from PLS models for: A) internal bond (—) and resin content (---), and B) MOE (—) and density (---) of MDF panels.

of the MDF panels. In this case, there is a great deal of similarity between the regression coefficients for MOE and density. Again, this indicates that the same chemical features are

driving the PLS correlations seen for both of these MDF panel properties. The absorbance profiles arise from the O-H stretching vibrations in carbohydrates and lignin at 1500 nm,

the first overtone of C-H stretching vibrations of lignin at 1725 nm and 1754 nm, and aliphatic C-H stretching vibrations at 2310 nm. Unlike the IB PLS models, there was no similarity between the regression coefficients for resin content and MOE (not shown). These results support the widely accepted relationship between the surface density of MDF panels and their MOE (Suchsland and Woodson 1987; Bucur et al. 1998), but little relationship between resin content and MOE (Scott 2001).

The material properties of wood composites are fundamentally determined by the properties of the individual components, which in this case include the wood fiber and the adhesive resin. However, it is important to recognize that the properties of interest extend beyond direct consideration of strength properties of the fiber or strength of the cured resin. Chemical structure also determines rheological behavior, wetting properties, and compatibility, as well as a litany of other important characteristics. These parameters are further influenced by the local environment that is created during mat consolidation to drive structure development of the material at the macroscopic and microscopic levels, as well as the molecular level. The results reported here show that NIR spectroscopic methods open new avenues to study the chemistry of these complex material systems by allowing important information to be extracted from extensive volumes of spectral data.

#### CONCLUSIONS

NIR spectroscopy, in combination with MVA techniques, is a promising new technology for the characterization of wood-based composites. Using a relatively small dataset, good predictive models were generated for MOE, MOR, and IB of MDF panels. Also, reasonable estimates of pertinent formulation and manufacturing variables could be made from the data. These results reveal the potential for using NIR technology as process monitoring sensors. The analysis also suggests that this approach may provide important new in-

sights into the chemical processes responsible for strength development in MDF. Additional work will consider the significance of sampling methods and the potential value of multiple sample locations for investigating the complex behaviors that drive performance properties

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