Infrared Spectroscopic Monitoring of Urea Addition to Oriented Strandboard Resins

Chi-Leung So,[1,2] Thomas L. Eberhardt,[2] Ernest Hsu,[3] Brian K. Via,[3] Chung Y. Hse[2]

[1]*School of Renewable Natural Resources, LSU Agricultural Center, Baton Rouge, Louisiana 70803*
[2]*USDA-Forest Service, Southern Research Station, 2500 Shreveport Highway, Pineville, Louisiana 71360*
[3]*Louisiana Pacific Corporation, 308 Mallory Station Road, Franklin, Tennessee 37067*

Received 27 March 2006; accepted 27 December 2006
DOI 10.1002/app.26094
Published online 2 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: One of the variables in phenol formaldehyde adhesive resin formulation is the addition of urea, which allows the resin manufacturer to manipulate both product functionality and cost. Nitrogen content can be used as a measure of the level of urea addition because most of the nitrogen present is derived from urea added at the end of the preparation process. Nitrogen analyses of a set of commercial oriented strandboard resins were first determined by combustion analysis. IR spectroscopic data were then collected and used along with the values for nitrogen content to generate predictive models. First, principal component analysis demonstrated the ability to separate resin mixtures from low to high nitrogen content. Partial least squares regression was then performed and gave excellent correlations between the measured and predicted nitrogen contents for a set of unrelated (test) resins and a set of mixtures prepared through combinations of resins with known nitrogen contents. Similar results were obtained on both a wet and dry mass basis. Given the flexibility of this instrumentation, such analyses could be placed in-line for real time monitoring of resin applied during panel manufacturing. © 2007 Wiley Periodicals, Inc. JAppl Polym Sci 105: 733–738, 2007

Key words: infrared spectroscopy; adhesives; oriented strandboard; phenol formaldehyde; resins; urea

INTRODUCTION

Phenol-formaldehyde (PF) adhesive resins are widely used for the manufacture of wood composites, especially those for exterior applications. Specifically, more than 80% of the resin solids used for oriented strandboard (OSB) are based on PF resole (base-catalyzed) resins; diphenyl methane diisocyanate (MDI) resins are also used, but are generally restricted to panel core layers due to adhesion to the press surfaces.[1] The proprietary nature of OSB manufacture affords products that may have attributes beyond their compliance with performance-based standards (e.g., U.S. Department of Commerce Voluntary Product Standard PS 2-92). Likewise, adhesive resin formulations are proprietary and subject to change to accommodate the resin producer's product strategy and the requirements of the OSB manufacturer as they relate to functionality and cost.

One variable in PF adhesive resin formulation is the level of urea addition. Different resin formulations, with varying urea contents, are often employed for the face and core layers. When added after resin synthesis, urea reacts with the residual free formaldehyde to form hydroxymethylureas.[2] The benefit of this reaction is the reduction in the levels of formaldehyde odor at the adhesive blending and matting stations within the manufacturing plant. It has been reported that hydroxymethylureas may react with PF resins,[3] however, the extent to which this reaction occurs during the short press cycles used for OSB manufacture is questionable. Since the price of urea is much lower than the cost of the resin, the same final solids content can be achieved with significantly different costs depending upon the level of urea addition. While lower urea additions may have negligible effects on resin performance, high urea additions can decrease the rate of resin cure and negatively impact panel performance with decreased internal bond and increased water absorption.[2]

Efforts to maximize operational efficiency and product performance may be facilitated by the ability to monitor adjustments to the level of urea in the resins prior to use. One obvious means to measure urea levels is the measurement of nitrogen content by combustion. However, in an industrial environment, it would be essential to have a robust and rapid method that would allow for timely adjustments to the operations. Near infrared (NIR) spectra, collected with a transmission probe, have been successfully used to develop multivariate models for measuring the urea content of solutions as well as the on-line monitoring of reaction progress during urea–formaldehyde resin synthesis.[4] Alternatively, a

Correspondence to: C.-L. So (cso@fs.fed.us).

Journal of Applied Polymer Science, Vol. 105, 733–738 (2007)
©2007 Wiley Periodicals, Inc.
WILEY InterScience DISCOVER SOMETHING GREAT

greater level of information on resin chemistry may be obtained using the mid-IR spectroscopic range, in which the sample under investigation provides a definitive mid-IR spectral fingerprint. In a study on the effects of pH and hardener levels, chemical differences in urea–formaldehyde resins were detected by IR spectroscopy.[5] Although informative, analyses were cumbersome since they were carried out in transmission after the preparation of KBr pellets from freeze-dried and powdered samples. Holopainen et al.[6] combined IR spectroscopy with statistical techniques for the quantitative analysis of PF resole resins, in which the amount of free phenol and the formaldehyde-to-phenol (F/P) ratio were predicted and compared with values determined using ^{13}C NMR spectroscopy. They concluded that the results using the two methods matched fairly well. The IR spectra of the resins used in the study were collected as surface films on the top of KBr pellets.

We were particularly interested in assessing the utility of a more facile sampling method; the application of liquid samples directly on a diamond attenuated total reflectance (ATR) accessory. This method was used by Holopainen et al.[7] in another study of PF resole resins, in which a comprehensive statistical analysis was applied to the IR spectra to determine the F/P ratios. The best model was successful in predicting the F/P ratios even when the values were beyond the narrow range of the calibration samples. Here, we report our success in developing a multivariate model based on IR spectroscopic analyses to predict with great accuracy the nitrogen content; this can then be extended to estimate the urea content of commercial PF adhesive resins used for OSB manufacture.

EXPERIMENTAL

Resin source

Fifteen commercial PF adhesive resins, used in the production of OSB, were selected as a calibration set for this study. Each resin had a different (unknown) composition and was labeled A–P. Another set of resins (labeled AA–AT) was used to test the calibration. Table I lists the two sets of resins used for calibration and testing. A further series of ten resin mixtures (KF1–10) were produced by mixing together different ratios of resins K and F. These formulations are listed in Table II.

Nitrogen analysis

Nitrogen levels were determined for the resins using a carbon–nitrogen–sulfur analyzer (CNS-2000, Leco, St. Joseph, MI). The liquid resin sample was transferred to a foil-lined, ceramic sample boat that was then inserted into the combustion furnace. The samples were tested using the standard operating conditions recommended in the operating manual. The nitrogen levels were determined on an "as received" (wet mass) basis. Two samples for each resin were analyzed and an averaged nitrogen value determined. Values for solids were determined by drying liquid resin samples in an oven [(103 ± 2)°C]; these were then used to calculate the nitrogen levels on a dry mass basis. Nitrogen levels for the resin mixtures (KF1–10) were not determined experimentally but instead calculated on the basis of the ratios of K and F.

TABLE I
Nitrogen, Carbon, and Solids Contents Determined for Calibration (A–P) and Test (AA–AT) Resins

	Resin (wet mass basis)			Resin (dry mass basis)	
Resin	C (%)	N (%)	Solids (%)	C (%)	N (%)
A	30.11	7.36	59.68	50.44	13.11
B	28.35	5.37	56.74	49.96	9.46
C	23.74	7.89	49.13	48.31	16.07
D	25.90	6.08	58.44	44.30	10.40
E	26.80	8.13	63.41	42.26	12.82
F	27.17	9.43	57.39	47.33	16.43
G	32.92	7.84	62.50	52.66	12.54
I	31.27	6.85	63.52	49.22	10.79
J	27.94	6.25	56.26	49.66	11.10
K	32.03	3.24	58.60	54.66	5.53
L	32.84	3.46	61.10	53.75	5.66
M	22.81	5.12	51.81	44.03	9.89
N	25.13	7.20	55.44	45.33	12.98
O	29.41	8.19	59.87	49.12	13.69
P	29.41	6.67	58.89	49.93	11.32
AA	30.98	7.36	59.32	52.23	12.41
AC	24.36	7.70	50.08	48.64	15.38
AE	31.57	7.50	60.24	52.41	12.44
AH	29.39	8.85	58.10	50.59	15.23
AI	33.26	7.24	64.59	51.49	11.21
AJ	29.29	6.30	55.06	53.20	11.45
AL	35.00	3.63	58.10	60.24	6.24
AM	25.14	5.42	51.45	48.86	10.53
AO	31.06	8.31	58.82	52.81	14.12
AQ	28.39	9.20	56.43	50.31	16.30
AR	31.88	6.70	59.52	53.56	11.25
AS	37.16	6.60	62.83	59.14	10.50
AT	30.99	6.65	56.73	54.63	11.72

Infrared spectroscopy and multivariate analysis

IR spectra of the resins were collected in the mid-IR region (4000–650 cm^{-1}) using a Nexus model 670 FTIR spectrometer (Thermo Nicolet Instruments, Madison, WI), equipped with a Golden Gate MKII Single Reflection ATR accessory. Resin samples were applied directly to the diamond window. Three spectra were collected for each sample.

Multivariate analysis of the data was performed using the Unscrambler (version 8.0) software (CAMO, Corvallis, OR). The IR data were first aver-

TABLE II
Nitrogen, Carbon, and Solids Contents Calculated for Resin Mixtures (KF1–10)

Resin mixture	Components		Resin (wet mass basis)		Solids	Resin (dry mass basis)	
	%K	%F	C (%)	N (%)	(%)	C (%)	N (%)
KF1	0	100	27.17	9.43	57.39	47.35	16.43
KF2	27	73	28.46	7.78	57.71	49.32	13.49
KF3	49	51	29.53	6.42	57.98	50.94	11.07
KF4	73	27	30.73	4.90	58.28	52.73	8.41
KF5	100	0	32.03	3.24	58.60	54.66	5.53
KF6	100	0	32.03	3.24	58.60	54.66	5.53
KF7	78	22	31.01	4.55	58.34	53.14	7.79
KF8	59	41	30.05	5.76	58.11	51.71	9.92
KF9	25	75	28.39	7.88	57.69	49.21	13.65
KF10	0	100	27.17	9.43	57.39	47.34	16.43

aged to one spectrum per sample. Principal component analysis (PCA) was used to observe any clustering and separation in each of the sample sets, while partial least squares (PLS) regression was used to predict the amount of nitrogen in the samples. Models were generated using full cross validation[8] and were assessed using several common measures of calibration performance. The correlation coefficient, 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, and is often expressed as a percentage of the mean value of interest (%RMSEC or %RMSEP of mean).

RESULTS AND DISCUSSION

The primary goal of this study was to develop a facile means to measure the amount of nitrogen, and thus urea, in commercial PF adhesive resins received by an OSB plant. It should be noted at this juncture that the intent was not to attribute operational problems to resin urea content, but to develop a means to better understand the effect, if any, of different resin formulations on plant operations. The urea content can be estimated from the nitrogen content by using the molecular weight of urea relative to the atomic weight of nitrogen. This is based on the assumption that the contribution of any other nitrogen-containing components in the resin is negligible. However, it is possible that some of the nitrogen may be due to the very small quantities of ammonia or hexamethylenetetramine that are sometimes added to the resin.

Nitrogen analysis

The average nitrogen and carbon contents for the resins (on an "as received"/wet mass basis) were determined with the carbon–nitrogen–sulfur analyzer, and are shown in Table I. Values on a dry mass basis were calculated using the solids contents determined by oven drying sample aliquots. It can be seen that resins K and F have the lowest and highest nitrogen contents, respectively. To generate additional samples with known nitrogen contents, resin mixtures (KF1–10) were prepared by mixing predetermined amounts of resins K and F. Table II shows the values for nitrogen content for these mixtures as calculated by the relative weight of each resin added to the mixture. Two samples of each of the pure resins, K (KF5 and KF6) and F (KF1 and KF10), were included, and in each case, the samples had identical nitrogen, carbon, and solids contents due to calculation rather than experimental determination. This further enhanced the controlled nature of this resin mixture sample set.

Infrared spectroscopy

IR spectra of the resins were collected between 4000 and 650 cm^{-1} and these are shown in Figure 1 for the resins K (lowest nitrogen) and F (highest nitro-

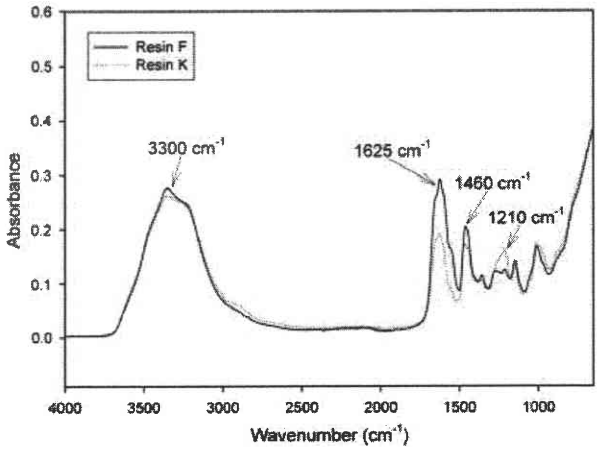

Figure 1 IR spectra of resins F (solid line) and K (dotted line) between 4000 and 650 cm^{-1}.

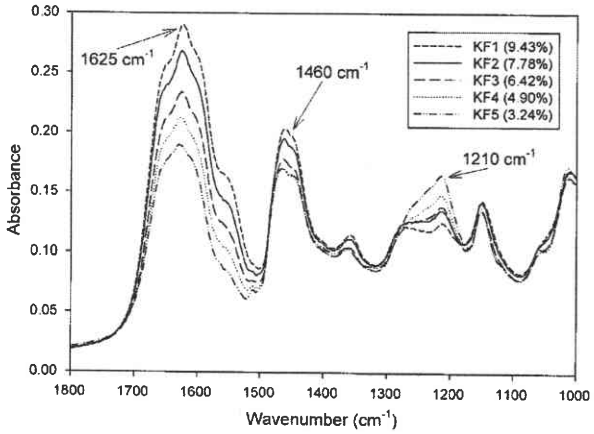

Figure 2 IR spectra of mixtures KF1–5 between 1800 and 1000 cm^{-1}. Values for nitrogen content (% w/w, liquid resins) are given in parentheses.

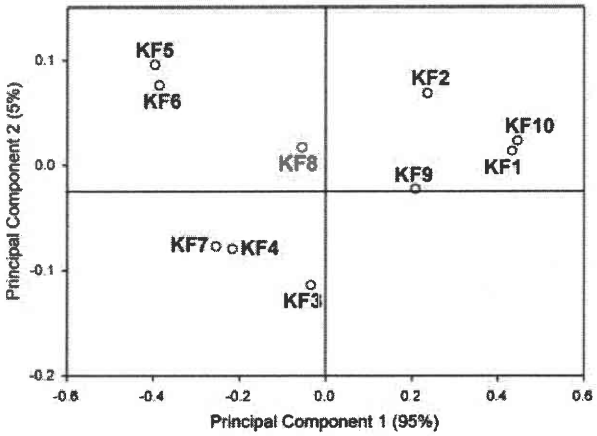

Figure 4 Principal component analysis (PCA) scores plot for mixtures KF1–10.

gen). As would be expected for phenolic adhesive resins, the spectra show a large broad peak at 3300 cm^{-1} attributed to water and the hydroxyl functionality inherent to the resin. Peaks at the 1625 cm^{-1} (amide C=O stretch) and 1460 cm^{-1} (amide C—N stretch) are attributed to the amide functionality of urea. Thus, the magnitude of these IR bands would be expected to be significantly greater for a resin with higher nitrogen (i.e., urea) content (Fig. 1). This was particularly true for the controlled set of resin mixtures (with different ratios of resins K and F), in which the relationship between the magnitude of 1625 cm^{-1} peak and nitrogen content appeared very strong. Figure 2 shows the amide region (1800–1000 cm^{-1}) of the spectra for several of the resin mixtures (KF1–5) together with their corresponding calculated nitrogen levels (on a wet mass basis). This clearly shows the relative increase in the absorbance of the 1625 cm^{-1} peak with nitrogen content. The same is observed with the 1460 cm^{-1} peak to a lesser extent, whereas the 1210 cm^{-1} peak appears to decrease with increasing nitrogen content. Standard linear regression was therefore used to investigate the relationship between nitrogen content and the absorbance values at these individual wavenumbers. Excellent correlations were obtained from the resin mixtures (KF1–10) with R^2 values of 0.99 (1625 cm^{-1}), 0.93 (1460 cm^{-1}), and 0.96 (1210 cm^{-1}). The only variable in this controlled set was the nitrogen content. The relationship with the resins (A–P) were, however, much poorer with R^2 values of 0.82 (1625 cm^{-1}), 0.41 (1460 cm^{-1}), and 0.11 (1210 cm^{-1}). These formulations for the resins were proprietary, and the nitrogen content was unlikely to be the only variable in this case. The same results on a dry mass basis provided little or no improvement.

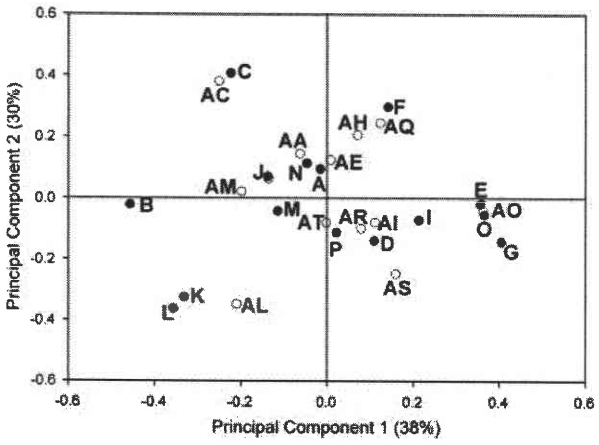

Figure 3 Principal component analysis (PCA) scores plot for resins A–P (filled circles) and AA–AT (open circles).

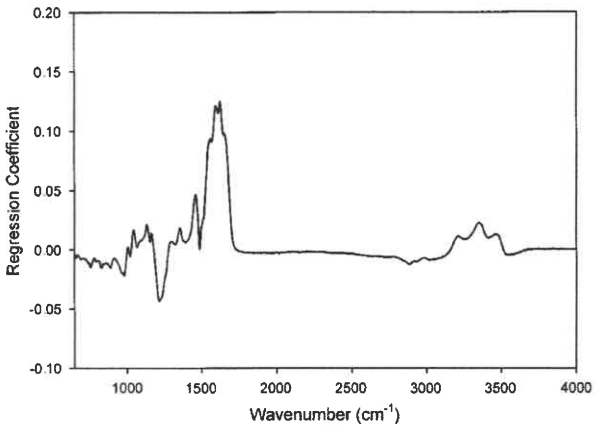

Figure 5 PCA loadings plot for mixtures between 4000 and 650 cm^{-1}.

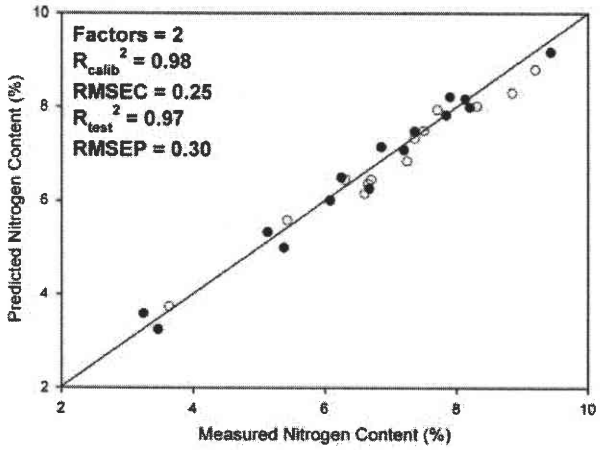

Figure 6 IR predicted versus measured nitrogen content (wet mass basis) for calibration set A–P (filled circles) and test set AA–AT (open circles).

Multivariate analysis

A PCA was carried out on the IR spectra obtained from the resins. The resultant scores plot is shown in Figure 3, in which there are regions of low and high nitrogen content but no clear trends are observable, especially with principal components 1 and 2 accounting for only 38 and 30% of the variation, respectively. This result demonstrated that the resins could not be readily separated by their nitrogen or carbon levels. A more definitive result was obtained when the same analysis was performed for the resin mixtures. The scores plot in Figure 4 clearly indicates that the separation of the mixtures was influenced by nitrogen content. It can be seen that the mixtures vary from low to high nitrogen content, along principal component 1, with principal components 1 and 2 accounting for 95 and 5% of the variation, respectively. The corresponding loadings plot (Fig. 5) shows that the bands at 3300, 1625, and 1210 cm^{-1} have the largest influence on the formation of the PCA scores plot in Figure 4. The use of a reduced wavenumber range (1800–1000 cm^{-1}), avoiding the peak at 3300 cm^{-1} (attributed to water and the hydroxyl functionality), did not have any significant effect on the PCAs in Figures 3 and 4.

The main focus of this study was to predict the nitrogen contents of the resins and mixtures using IR spectroscopy. Thus, a partial least squares (PLS) regression was performed on the calibration data (filled circles) using the full wavenumber range (4000–650 cm^{-1}); the results are shown in Figure 6. An excellent correlation was achieved with nitrogen content (wet mass basis) giving a R^2_{calib} of 0.98 with a RMSEC of 0.25 (Table III) using only two factors. The validity of this calibration was tested by predicting nitrogen values from the set of thirteen unrelated (test) samples (resins AA–AT) with the results also plotted in Figure 6. The resultant R^2_{test} of 0.97 with a RMSEP approaching that for the calibration indicates the validity of the calibration. Furthermore, when the test samples and calibration samples were combined, the calibration improved slightly with a R_{all}^2 of 0.98 and a RMSEP of 0.24 (Table III). A plot of the regression coefficients appeared almost identical to the loadings plot in Figure 5, thus verifying the bands at 1625, 1460, and 1210 cm^{-1} (and also the 3300 cm^{-1} band) have the largest influence on the nitrogen correlation. The same analysis using nitrogen content on a dry mass basis gave slightly poorer results (Table III). Further analyses of the data using

TABLE III
Regression Statistics for Calibration Resins (A–P), Test Resins (AA–AT), and Resin Mixtures (KF1–10)

Sample set	Parameter	Wavelength range	Samples	PCs	R^2	RMSEC/P	%RMSEC/P of mean
Resins (calibration)	N (wet)	4000–650	15	2	0.98	0.25	3.7
		1800–1000	15	2	0.97	0.30	4.5
	N (dry)	4000–650	15	2	0.97	0.53	4.6
		1800–1000	15	2	0.97	0.55	4.8
Resins (test)	N (wet)	4000–650	13	2	0.97	0.30	4.3
		1800–1000	13	2	0.96	0.30	4.3
	N (dry)	4000–650	13	2	0.94	0.65	5.4
		1800–1000	13	2	0.94	0.69	5.6
Resins (all)[a]	N (wet)	4000–650	28	2	0.98	0.24	3.5
		1800–1000	28	2	0.95	0.36	5.3
	N (dry)	4000–650	28	2	0.96	0.55	4.6
		1800–1000	28	2	0.97	0.51	4.3
Mixtures	N (wet)	4000–650	10	1	0.99	0.18	2.9
		1800–1000	10	1	0.99	0.18	2.9
	N (dry)	4000–650	10	1	0.99	0.30	2.8
		1800–1000	10	1	0.99	0.31	2.9

[a] Combination of resins (calibration) and resins (test).

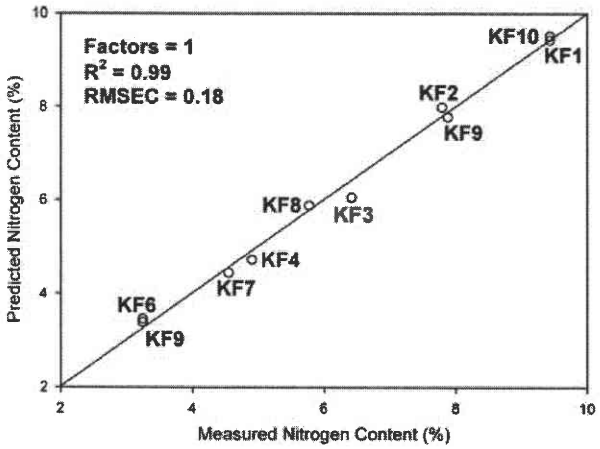

Figure 7 IR predicted versus measured nitrogen content (wet mass basis) for mixtures (KF1–10).

the reduced wavenumber range of 1800–1000 cm^{-1} similarly resulted in slightly poorer correlations. Holopainen et al.[7] found omitting the 4000–2900 cm^{-1} region resulted in lower values of standard error of estimate and standard error of prediction; the best results were obtained in the 1800–700 cm^{-1} range. They also noted that the first derivative preprocessing appeared to have a negative influence on the results but improved when the number of smoothing points was increased. However, this could lead to the loss of some data relevant to the modeling and predicting.[9] Spectral preprocessing techniques, such as first and second derivatives, did not appear to have any significant effect on the calibrations. The application of PLS regression to the resin mixtures, as expected, provided even further improvement in the correlations with nitrogen content (Fig. 7) achieving correlations of R^2 of 0.99 on both a wet and dry mass basis (Table III) requiring only one factor. The controlled nature of this sample set is closer to the variation encountered in a manufacturing environment, where smaller variations of the same resin type are likely to be employed, and thus, such correlations may be attained.

CONCLUSIONS

IR spectroscopy, coupled with multivariate analysis, can be used to predict the nitrogen contents of PF adhesive resins; nitrogen contents can be extended to estimate values for urea content. Compared to elemental analyses, the technique outlined here is simple to perform and can provide more information than nitrogen values alone. Although the best results are obtained with a controlled set of resins, the technique is sufficiently robust as to allow model development even when specific information about the formulations is not available. Given the availability of probes for continuous monitoring, this technique can be implemented in a manufacturing environment as a valuable tool for monitoring variables contributing to panel performance.

The authors are grateful to Karen Reed for the sample preparation and spectra collection, and Michael Elliot-Smith for the nitrogen analyses.

References

1. Sellers, T., Jr. Forest Prod J 2001, 51, 12.
2. Kim, M. G.; Watt, C.; Davis, C. R. J Wood Chem Technol 1996, 16, 21.
3. Scopelitis, D.; Pizzi, A. J Appl Polym Sci 1993, 47, 351.
4. Dessipri, E.; Minopoulou, E.; Chryssikos, G. D.; Gionis, V.; Paipetis, A.; Panayiotou, C. Eur Polym J 2003, 39, 1533.
5. Park, B.-D.; Kim, Y. S.; Singh, A. P.; Lim, K. P. J Appl Polym Sci 2003, 88, 2677.
6. Holopainen, T.; Alvila, L.; Rainio, J.; Pakkanen, T. T. J Appl Polym Sci 1998, 69, 2175.
7. Holopainen, H.; Alvila, L.; Pakkanen, T. T.; Rainio, J. J Appl Polym Sci 2003, 89, 3582.
8. Martens, H.; Naes, T. Multivariate Calibration; Wiley: Chichester, UK, 1989; p 419.
9. Wold, S.; Sjostrom, M. Chemom Intell Lab Syst 1998, 44, 3.