

Determination of Formaldehyde/Urea Molar Ratio in Amino Resins by Near-Infrared Spectroscopy

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ABSTRACT: New processes for synthesis of urea-formaldehyde (UF) and melamine-fortified urea-formaldehyde (mUF) resins have been developed in the last years, motivated by the current concerns about the effects of formaldehyde on human health. All these formulations are quite susceptible to possible operation error, which can significantly influence the characteristics of the final product. The main objective of this work was to implement chemometric techniques for off-line monitoring of the product's formaldehyde/urea (F/U) molar ratio using near infrared (NIR) spectroscopy. This allows the timely implementation of the necessary corrections in case the product is off-specification. Calibration models for F/U molar ratio were developed taking into account the most relevant spectral regions for these resins, individually or

in combination (7502–6098 cm^{-1} and 5000–4246 cm^{-1}) and using different preprocessing methods. When the appropriate spectral range and preprocessing methods are selected, it is possible to obtain calibration models with high correlation values for these resins. The best preprocessing methods were identified for three cases: UF resin (produced by strongly-acid process), mUF resin (alkaline-acid process), and a combined model that involves both UF and mUF resins. It was concluded that significantly better accuracy is obtained when a new model is developed for each particular resin system. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2441–2448, 2012

Key words: urea-formaldehyde resins; spectroscopy; partial least-squares regression; chemometrics

INTRODUCTION

Amino resins, the most employed binders in wood-based panels industry, are formed by the reaction between amine or amide groups with an aldehyde, usually formaldehyde. In this family one can consider urea-formaldehyde (UF), melamine-formaldehyde (MF), and melamine-urea-formaldehyde resins (MUF).¹ UF resins represent 80 % of the amino resins produced worldwide² and the remainder resins are mostly MUF.¹

The widespread use of UF resins in the wood industry is due to their excellent thermal properties, low curing temperatures, lack of color after cure, low cost, and ease of use under a wide variety of conditions.² The major disadvantages are the low

resistance against hydrolysis caused by moisture and water and the need to control formaldehyde emissions. Melamine-fortified urea-formaldehyde resins (mUF), with 3 % melamine, have been introduced since the more stable chemical bonds result in lower formaldehyde emissions. A wide range of formulations for synthesis of these resins originates different properties, performance and durability.^{3,4}

Over the past 20 years measures have been taken to reduce the emission of formaldehyde from UF-bonded wood-based panels (WBP), taking into account the numerous studies that reported its harmful effects on human health. This has led to significant changes in the formulation of UF resins.⁵

The goal of these new formulations has been the decrease of the F/U molar ratio in the synthesis process, which leads to lower reactivity and degree of curing, with negative consequences on the mechanical properties. On the other hand, the process becomes more sensitive to perturbations in the operating conditions. The addition of small amounts of melamine to the UF resins is another possible strategy,² as mentioned above.

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In industry, generally, the reaction control is based on indirect and inaccurate measurements of the synthesis progress, such as viscosity, water tolerance, and cloudiness index. Moreover, there is also the possibility of measurement errors in the dosage of raw materials. It is therefore important to implement more accurate and expedite methods for determining the F/U molar ratio of the synthesized product. This way, the occurrence of higher ratios than specified (which would penalize formaldehyde emissions) can be corrected by adding urea while the resin is still in the reactor.

To characterize a liquid UF resin, several analytical tools have been used, namely ^{13}C -NMR, FTIR, and GPC/SEC,⁶ but these are not suitable for on-line monitoring. The monitoring of the reaction progress is a very difficult task due to the large variety of chemical structures present, like methylene bridges, ether bridges, methylols, amide groups, or even cyclic derivatives like uron rings, and the variety of possible reactions occurring during synthesis.⁷

Recently, the capabilities of FT-NIR spectroscopy have been exploited in several industries, like pharmaceutical,⁸ biomedical,⁹ petrochemical,¹⁰ food,¹¹ and polymers,¹² among others. Regarding polymerization reactions, published works focus mainly on the characterization of the final product and not on the control and monitoring of the reaction stages.¹³

In the particular case of UF resin synthesis, NIR spectroscopy has been used for the analysis of intermediates and to check the conformity of raw materials.¹⁴ Moreover, NIR has been used on-line for continuously evaluating the urea and formaldehyde content during synthesis, to provide a methodology for monitoring the resin production and to ensure the reproducibility of the final product.¹⁴ NIR was also used to provide a method for assessing the influence of pH and temperature on the structure of the final product.¹²

These works demonstrated that FT-NIR spectroscopy can be used for on-line monitoring of the consumption of $-\text{NH}_2$ groups during the early stages of the synthesis and the decrease of both primary and secondary amides during polycondensation.¹⁴

Kasprzyk et al.¹⁵ used NIR spectroscopy for qualitative and quantitative analysis of liquid MUF resins, particularly for the determination of melamine content. This study also described a number of relevant spectrum bands in UF resins.

To implement this technique it is necessary to appeal to chemometrics (e.g., data-based modeling techniques), permitting to establish relations between several measurements and the characteristics of the analyzed product. However, being an indirect method, NIR needs calibration, to allow determining a set of parameters that minimizes the prediction errors of the model. The next step is the model validation, which evaluates the accuracy and robustness of the calibration equations, also using real data.

The models are constructed applying multivariate calibration techniques to the NIR spectra, partial least squares (PLS), target transformation factor analysis (TTFA), and curve resolution (MCR).¹⁶

To optimize the PLS models, a type of validation that can be used is crossvalidation. This is based on calibration data, and used to evaluate the predictive ability of PLS models for all samples. The advantage of cross validation is the smaller number of samples required, especially when the number of samples available is limited.

In NIR, the relevant information is contained in a small spectral range. The quality of the spectra in the selected frequency window is usually influenced by several factors like background noise, baseline drift, and light-scattering. These may cause unwanted effects in the development of a calibration model and consequently produce biased results.¹⁷ It is therefore important to take into account not only the selection of the frequency window, but also of the preprocessing method, since they can minimize the influence of those adverse effects and enhance the models prediction ability.¹⁷ To eliminate baseline shift and improve resolution of overlapping peaks, first and second derivatives are the most commonly used approaches.¹⁸ Other preprocessing methods that may be used in conjunction with the former are multiplicative scatter correction (MSC) and standard normal variate transformation (SNV). These consist on applying an additive or a multiplicative correction to each sample.^{17,18} In addition to these common methods, others can be applied, such as subtraction of a straight line, min-max normalization, and subtraction of a constant offset.¹⁹

A common problem in NIR analysis is related the large absorbance of water. This is relevant in UF resins, since they are aqueous solutions.¹⁸ The calibration model development must take this into account.

During the calibration process, as only a few wavelengths are used, some important information may be lost. This problem may be minimized by implementing a Principal Component Analysis (PCA) to rearrange the data information of the sampling.²⁰

The objectives of this study were: (i) to determine for both UF and mUF systems the feasibility of FT-NIR spectroscopy for estimating F/U molar ratio, (ii) to compare the use of different preprocessing methods and identify the best wavenumber range of interest, and (iii) use PCA to identify how differences in resin composition mainly influence the spectral responses.

MATERIALS AND METHODS

Laboratory resin synthesis

Samples of UF and mUF resins were produced in a 2.5 L round bottom flask, equipped with thermometer,

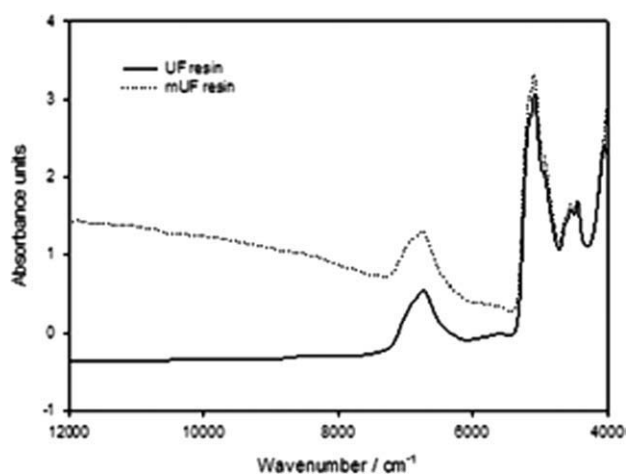


Figure 1 Representation of UF and mUF resins spectra without preprocessing.

mechanical stirrer, and condenser. The temperature is controlled manually using a heating mantle. The pH is measured off-line using a pH meter.

Two UF resins were produced using the strongly acid process.²¹ Solid urea is added at constant flow rate to a strongly acidic formaldehyde solution, with pH between 1.5 and 2.5 due to the addition of sulfuric acid. Because reaction between formaldehyde and urea at such low pH is very exothermic, the urea feed rate is adjusted to obtain a controlled temperature increase rate. A second amount of urea is added at a constant feed rate and constant temperature, promoting a controlled methylation. Then the pH is adjusted to a slightly alkaline value by adding sodium hydroxide and the polymer was condensed until the desired viscosity (~ 500 cP). After this step, the pH was adjusted to 7.5–8.5, the solution is

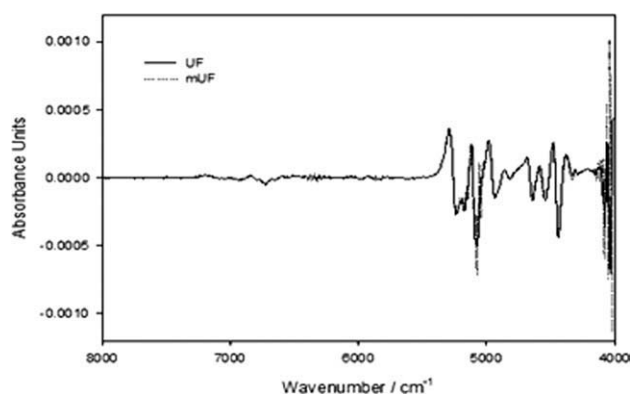


Figure 2 Representation of UF and mUF resins spectra with second derivative.

cooled down, and a final amount of urea is added to achieve the desired F/U molar ratio.

Five mUF resins were produced through an alkaline-acid process.^{5,21} The reaction between formaldehyde and urea occurs basically in two steps: basic methylation and slightly acid condensation. Methylation refers to the first addition of urea and melamine to formaldehyde; this usually occurs at 60 °C and a pH about 8. The polymer growth occurs mainly in the stage of condensation, this step occurs at a pH between 5 and 6 and a temperature varying between 90 and 100 °C. The reaction proceeds until it reaches the desired viscosity, and is terminated by neutralization at a slightly basic pH. In a third step a final amount of urea is added, to reduce the molar ratio.

To obtain samples with different F/U molar ratios, the resins were divided in several portions, to which urea was added to achieve F/U molar ratios between 0.95 and 1.15 for UF resins, and 0.84–1.15 for mUF.

TABLE I
Band Assignments for the Major UF and mUF Resins Bands (adapted from (15))

Wavenumber in FT-NIR spectra (cm^{-1})	Bands	Observation
7042	1^{st} overtone $2\nu\text{NH}_{\text{asymmetrical}}$	Triplet of overtones of basic vibrations NH and their complex vibrations
6920	Combination $\nu\text{NH}_{\text{asymmetrical}} + 2\nu\text{NH}_{\text{asymmetrical}}$	
6720	1^{st} overtone $2\nu\text{NH}_{\text{symmetrical}}$	Bands of composite vibrations occur derived from amino and amide groups; Vibration of methylene groups
5973	1^{st} overtone $2\nu\text{CH}_2_{\text{asymmetrical}}$	
5834	1^{st} overtone $2\nu\text{CH}_2_{\text{asymmetrical}}$	
5055	$\nu\text{NH}_{\text{asymmetrical}} + \delta\text{NH}$ amide II	
5050	$\nu\text{NH}_{\text{symmetrical}} + \nu\text{CO}$ amide I	Bands of composite vibrations occur derived from amino and amide groups
4916	$\nu\text{NH}_{\text{asymmetrical}} + \nu\text{CN}$ amide III	Bands of composite vibrations occur derived from amino and amide groups; The range is overlapped of vibrations of OH hydroxyl groups methylol
4878	$\nu\text{NH}_{\text{symmetrical}} + \nu\text{CN}$ amide III	
4642	$\nu\text{NH}_{\text{asymmetrical}} + \nu\delta\text{NH}_{\text{rocking}}$	Bands composed of NH
4549	$\nu\text{NH}_{\text{symmetrical}} + \nu\delta\text{NH}_{\text{rocking}}$	
4436	$\nu\text{CH}_2_{\text{asymmetrical}} + \delta\text{CH}$ and $\nu\text{CH}_2_{\text{symmetrical}} + \delta\text{CH}$	Bands composed of CH

From a total of 29-UF resin samples with different F/U molar ratios, 22 were used for crossvalidation set and 7 for test set. From a total of 65 mUF resin samples with different F/U molar ratios, 55 were used for crossvalidation set and 10 for test set.

Calibration models were developed for mUF and UF resins separately. A third model, the combined model was developed, combining spectra of 22 samples of different UF and mUF resins with final F/U molar ratio between 0.84 and 1.15.

FT-NIR analysis

The FT-NIR spectra were acquired using a transmission probe 2 m long, with 1-mm path length, 600- μm diameter, and with an optical sapphire window. The probe was connected to a Bruker (www.bruker.de) Zaffiro FT-NIR process-spectrometer with a TE-InGaAs detector and spectral range between 12000 and 4000 cm^{-1} . Spectra for each resin were collected with a spectral resolution of 8 cm^{-1} in triplicate at a zero-filling factor of 2 each representing an average of 32 scans. A reference spectrum is previously collected in air, to account for possible impurities present in the probe surface. The probe was washed carefully when switching to a different resin.

Chemometrics

To develop the statistical model, the influence of various regions of the UF and mUF polymer spectrum was analyzed, both in combination and individually. The influence of several preprocessing techniques was also studied.

The spectral manipulations were performed using OPUS Quant 2 software, by Bruker. Partial Least Squares (PLS) method was used for perform quantitative analysis.

The standard error of prediction (RMSEP) and the standard error of calibration (RMSEE) were adopted as error estimation parameters for both calibration and validation procedures²²

$$\text{RMSEE} = \left\{ \sum_{i=1}^{n_r} (t_i - \hat{t}_i)^2 / (n_r - h - 1) \right\}^{1/2} \quad (1)$$

$$\text{RMSEP} = \left\{ \sum_{i=1}^{n_m} (m_i - \hat{m}_i)^2 / n_m \right\}^{1/2} \quad (2)$$

In RMSEP, m_i is the reference value of molar ratio F/U, \hat{m}_i is the PLS predicted value, and n_m is the total number of test samples. In RMSEE, t_i is the reference molar ratio F/U, \hat{t}_i is the predicted PLS value, n_r is the total number of validation samples, and h the number of PLS factors (ranging from 1 to 10).

The best number of factors is found when the lowest value of mean square error of cross validation is obtained.¹⁹

The R_{cal}^2 and R_{val}^2 correlation values were used to quantify the predictability of each method.¹⁸ The general goal was to obtain low values of RMSEE and RMSEP and high values of R_{cal}^2 and R_{val}^2 .¹⁹

RESULTS AND DISCUSSION

Characterization of FT-NIR spectrum

Figure 1 shows FT-NIR spectra of UF and mUF resins without any preprocessing and Figure 2 shows the second derivatives of those spectra. The different

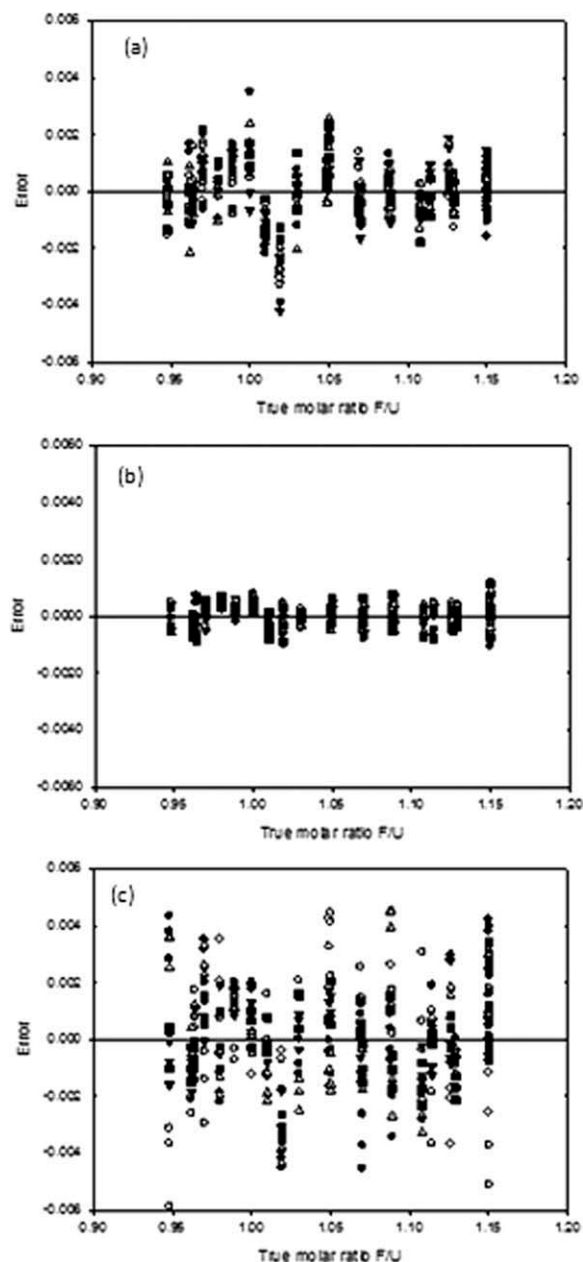


Figure 3 Relationship between the error, and the true (experimental) value of the F/U molar ratio obtained from the PLS-R models using UF resins: (a) 7502–6098 cm^{-1} ; (b) 7502–6098 cm^{-1} ; (c) 5000–4246 cm^{-1} .

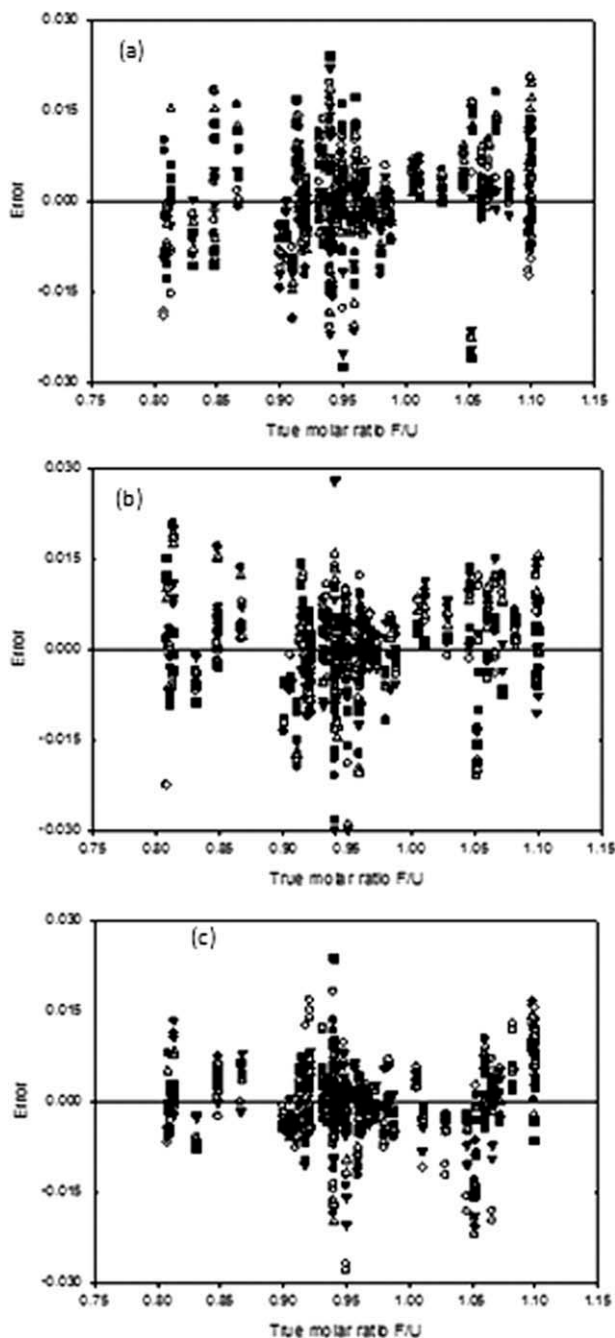


Figure 4 Relationship between the error, and the true (experimental) value of the F/U molar ratio obtained from the PLS-R models using mUF resins: (a) 7502–6098 cm^{-1} and 5000–4246 cm^{-1} ; (b) 7502–6098 cm^{-1} ; (c) 5000–4246 cm^{-1} .

wavenumber absorption values can be justified by different particle sizes distribution which causes light scattering in the ranges of the corresponding wavenumber (range between 12000 and 4000 cm^{-1}). Figures 1 and 2 show that the most evident peaks are at $\sim 6900, 5100, 4900, 4600,$ and 4500 cm^{-1} in both resins. Kasprzyk et al.¹⁵ identified the regions between 7502 and 6098 cm^{-1} and 5000–4246 cm^{-1} as being the most important for UF and mUF resins, and assigned them to the most significant vibrations

(see Table I). On the other hand, these regions exclude the peaks associated to the presence of water, which absorbs at 8600, 5200, 11,800, 5620, 5150, 6900, and 4115 cm^{-1} .^{23,24}

Influence of preprocessing method and spectral range on the calibration model

Calibration models for F/U molar ratio were developed taking into account the most important spectral

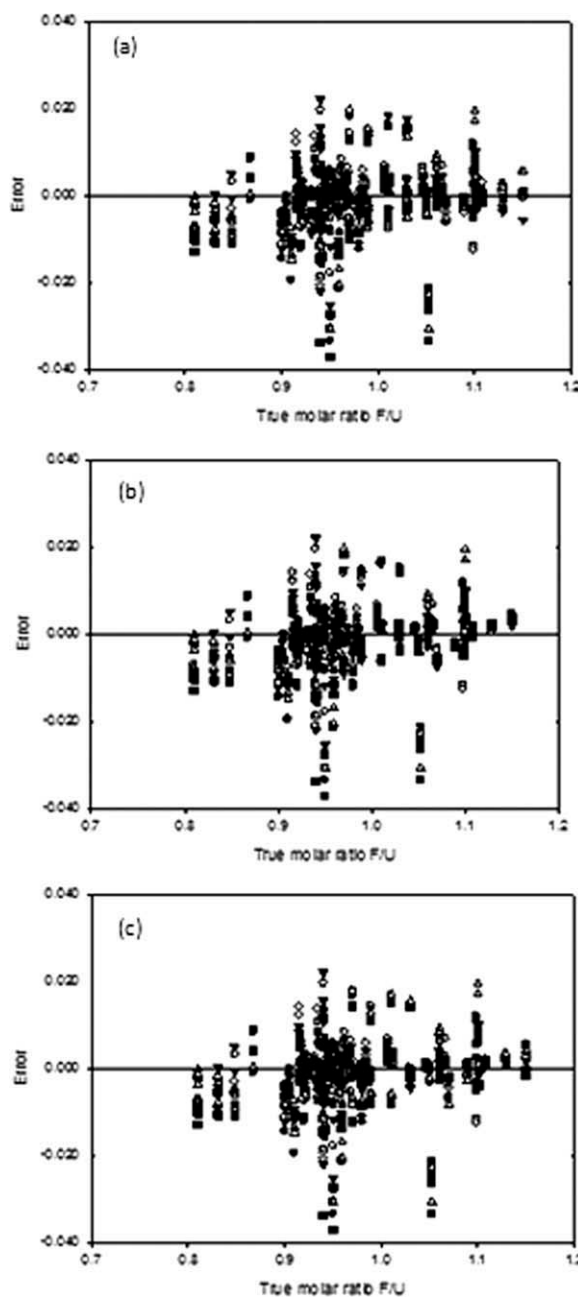


Figure 5 Relationship between the error, and the true (experimental) value of the F/U molar ratio obtained from the PLS-R models using mUF and UF resins: (a) 7502–6098 cm^{-1} and 5000–4246 cm^{-1} ; (b) 7502–6098 cm^{-1} ; (c) 5000–4246 cm^{-1} .

TABLE II
Summary of the PLS-R Models with UF Resins Using the Wavenumber Ranges 7502-6098 and 5000-4246 cm⁻¹

Preprocessing method	Cross validation set					Test set				
	R ²	RMSECV	RPD	Bias	PLS	R ²	RMSEP	RPD	Bias	PLS
First derivative	96.54	0.00133	50.9	1.34×10 ⁻⁶	5	99.96	0.00102	99.5	-2.81×10 ⁻⁵	5
MSC	92.23	0.00184	37	-2.81×10 ⁻⁵	5	99.98	0.00219	37.7	-0.00117	5
VN	95.65	0.0017	39.9	-2.98×10 ⁻⁵	5	99.99	0.00232	39.9	-0.000133	4
First derivative with MSC	97.97	0.00102	66.5	-6.82×10 ⁻⁶	5	99.94	0.000761	66.5	-0.000369	5
First derivative with VN	99.88	0.00202	33.6	-1.22×10 ⁻⁵	4	99.98	0.00246	33.6	-0.0015	4
Preprocessing method	Calibration model					Validation model				
				RMSEE					RMSEP	
First derivative				0.0119					0.00126	
MSC				0.0183					0.00082	
VN				0.0137					0.00074	
First derivative with MSC				0.0094					0.00062	
First derivative with VN				0.0023					0.00232	

regions, individually or in combination (7502–6098 and 5000–4246 cm⁻¹) and using the different preprocessing methods. The results are summarized in Figure 3 for UF resins, in Figure 4 for mUF resins and in Figure 5 for the combined method.

These figures show the relationship between the errors obtained with the calibration method and the true, i.e., the experimental, value of the F/U molar ratios, for different preprocessing methods. The calibration error was defined as the difference between the “true” value and the value predicted by the method.

From the graphical analysis of Figure 3, for UF resins, it appears that the methods that use a combination of the two spectral regions [Fig. 3(a)] yield the lower errors. This was therefore the adopted strategy. Table II shows the statistical parameters of the different models, when the two spectral regions are used simultaneously. The preprocessing method that yields the lower values of SEP and SEC and high values of R_{cal}^2 and R_{val}^2 is the first derivative with VN.

The same type of conclusions can be taken for the mUF and combined models by the analysis of Figures 4 and 5, and Tables III and IV. Note that for mUF resins the best model uses a combination of the two spectral regions and uses MSC for preprocessing and the same happens for the combined model by the analysis of Tables III and IV.

Figure 6 shows the score plot for the two principal components (PCs). From its analysis it seems that PC1 is related to the difference between the mUF and UF resins, possibly associated to the presence of melamine, while PC2 is related to the urea/formaldehyde molar ratio. Figure 7 shows the two loadings of combined model obtained from PCA for the spectral regions 7502–6098 and 5000–4246 cm⁻¹. PC1 presents peaks near 4563 and 6710 cm⁻¹, these peaks are related to the vibrations of NH groups from melamine and urea, respectively. Figure 8 shows a linear relationship between formaldehyde/urea molar ratio (RM) and PC2. Therefore, peaks 4534, 4400, and 6656 cm⁻¹, corresponding to NH and CH

TABLE III
Summary of the PLS-R Models with mUF Resins Using the Wavenumber Ranges 7502-6098 and 5000-4246 cm⁻¹

Preprocessing method	Cross validation set					Test set				
	R ²	RMSECV	RPD	Bias	PLS	R ²	RMSEP	RPD	Bias	PLS
First derivative	98.17	0.00359	24.3	-2.05×10 ⁻⁵	7	98.59	0.00354	23.5	7.86×10 ⁻⁶	9
MSC	98.94	0.00296	29.4	-2.87×10 ⁻⁴	9	99.39	0.00379	22.1	-2.87×10 ⁻⁵	6
VN	96.91	0.00402	21.7	6.45×10 ⁻⁵	8	98.44	0.000532	15.9	-0.00102	7
First derivative with MSC	98.28	0.00346	25.1	-6.06×10 ⁻⁵	9	99.23	0.00422	20.2	-0.000903	7
First derivative with VN	98.20	0.00384	22.7	1.7×10 ⁻⁵	9	98.65	0.00365	22.8	0.000222	9
Preprocessing method	Calibration model					Validation model				
				RMSEE					RMSEP	
First derivative				0.00862					0.00966	
MSC				0.00862					0.00634	
VN				0.01470					0.01020	
First derivative with MSC				0.00917					0.00714	
First derivative with VN				0.01120					0.00947	

TABLE IV
Summary of the PLS-R Models for the Combined Models Using the Wavenumber Ranges 7502-6098 and 5000-4246 cm^{-1}

Preprocessing method	Cross validation set					Test set				
	R ²	RMSECV	RPD	Bias	PLS	R ²	RMSEP	RPD	Bias	PLS
First derivative	99.22	0.00531	11.3	4.66×10^{-5}	2	99.96	0.00158	58.8	-0.000885	4
MSC	99.35	0.00486	12.4	-6.57×10^{-5}	3	99.97	0.00123	71.4	-0.000593	5
VN	99.29	0.00509	11.8	-1.73×10^{-5}	2	99.92	0.00212	39.7	-0.000861	2
First derivative with MSC	99.20	0.00541	11.1	5.13×10^{-5}	2	99.92	0.00215	58.3	-0.000771	4
First derivative with VN	99.29	0.00524	11.5	4.39×10^{-5}	2	99.92	0.00211	38.7	-0.000725	4
Preprocessing method	Calibration model					Validation model				
				RMSEE					RMSEP	
First derivative				0.00531					0.00157	
MSC				0.00486					0.00123	
VN				0.00509					0.00211	
First derivative with MSC				0.00540					0.00214	
First derivative with VN				0.00624					0.00212	

vibrations, in Figure 7 can be associated to the different formaldehyde/urea molar ratios.

CONCLUSIONS

For selected synthesis processes (strongly-acid for UF resins and alkaline-acid for mUF resins), spectral regions 7502–6098 and 5000–4246 cm^{-1} were identified as being the most relevant for implementation of calibration methods. This is in agreement with the known molecular vibration peaks present in these polymeric structures. The models developed took into account each of these regions individually or in combination. It was found that a combined approach yields the lowest errors.

For each spectral region, different preprocessing methods were tested, resulting in different calibration models. Some methods gave high correlation values, validating their applicability.

When a specific calibration model was developed for each resin type, accurate results were obtained. However, good models can be obtained when using a combined method that incorporates information from both resins, as long as the relevant bands are taken into account. The PCA analysis indicated that the main spectral differences between the mUF and UF resins are associated to bands near 4500 and 6700 cm^{-1} , whereas different molar ratios affect bands near 4530, 4440 and 6650 cm^{-1} .

The results obtained indicated that for each type of resin, once an appropriate model is developed and validated, the NIR technique may lead to a fast and accurate tool for F/U molar ratio process control in industrially synthesized UF and mUF resins.

This work showed that it is possible to extend the approach previously developed by Kasprzyk et al.,¹⁵ to determine the final F/U molar ratio in UF and mUF resins.

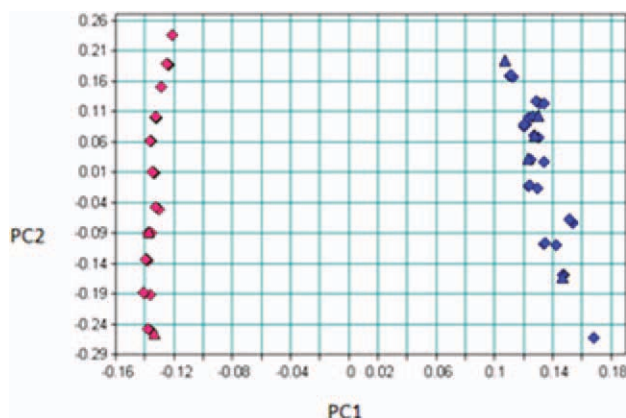


Figure 6 Score plot for the two principal components. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

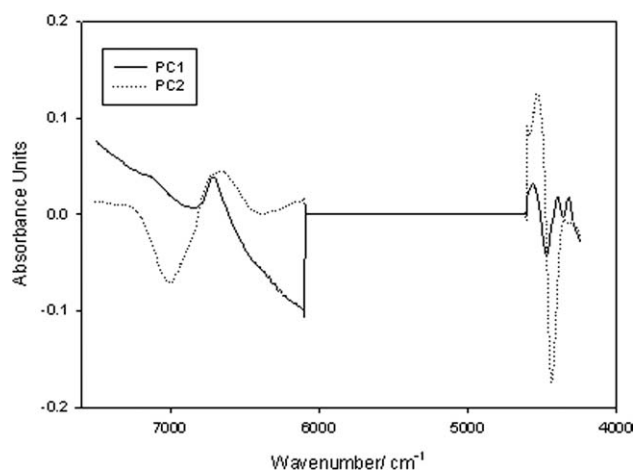


Figure 7 Loadings of the first two principal components.

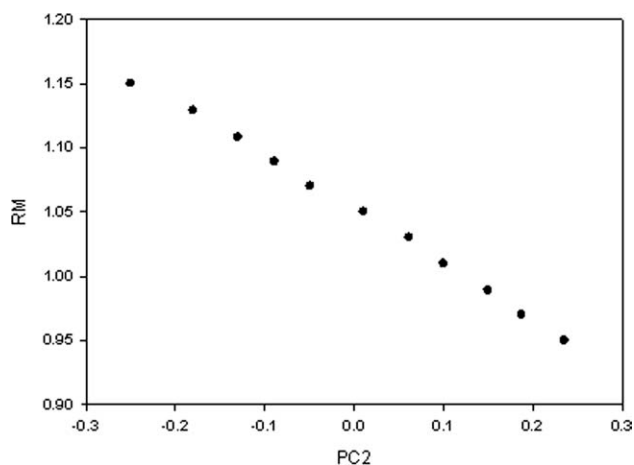


Figure 8 Relationship between formaldehyde/urea molar ratio and PC2.

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References

- Pizzi, A.; Mittal, K. L. *Handbook of Adhesive Technology*; New York: M. Dekker; 2003.
- Conner, A. In *Concise Polymeric Materials Encyclopedia*; Joseph C. Salamone, Ed.; New York: CRC Press; 1999, 1760.
- No, B. Y.; Kim, M. G. *J Appl Polym Sci* 2004, 93, 2559.
- No, B. Y.; Kim, M. G. *J Appl Polym Sci* 2007, 106, 4148.
- Dunky, M. *Int J Adhes Adhes* 1998, 18, 95.
- Ferra, J. M.; Mendes, A. M.; Costa, M. R. N.; Magalhães, F. D.; Carvalho, L. H. *J Adhes Sci Technol* 2010, 24, 1535.
- Carvalho, L. M. H.; Costa, M. R. P. F. N.; Costa, C. A. V. *J Appl Polym Sci* 2006, 102, 5977.
- Ciurczak, E. *Appl Spectrosc Rev* 1987, 23, 147.
- Ellis, D. I.; Goodacre, R. *Analyst* 2006, 131, 875.
- Macho, S.; Larrechi, M. S. *TrAC Trends Anal Chem* 2002, 21, 799.
- Paradkar, M. M.; Irudayaraj, J. *Int J Dairy Technol* 2002, 55, 127.
- Minopoulou, E.; Dessipri, E.; Chryssikos, G. D.; Gionis, V.; Paipetis, A.; Panayiotou, C. *Int J Adhes Adhes* 2003, 23, 473.
- Santos, A. F.; Silva, F. M.; Lenzi, M. K.; Pinto, J. C. *Polym Plast Technol Eng* 2005, 44, 1.
- Dessipri, E.; Minopoulou, E.; Chryssikos, G. D.; Gionis, V.; Paipetis, A.; Panayiotou, C. *Eur Polym J* 2003, 39, 1533.
- Kasprzyk, J. M. H.; Proszkyk, S. *Folia Forestalia Polonica* 2001, 32, 67–74.
- Thennadil, S. N.; Martin, E. B. *J Chemometrics* 2005, 19, 77.
- Pizarro, C.; Esteban-Díez, I.; Nistal, A.-J.; González-Sáiz, J.-M. *Anal Chim Acta* 2004, 509, 217.
- Büning-Pfaue, H. *Food Chem* 2003, 82, 107.
- Conzen, J. P. *Multivariate Calibration—A Practical Guide for Developing Methods in the Quantitative Analytical Chemistry*; Ettlingen, Germany: Burker Optik GmbH; 2006.
- Czarnik-Matusewicz, B.; Pilorz, S. *Vibrat Spectrosc* 2006, 40, 235.
- Ferra, J.; Henriques, A.; Mendes, A.; Costa, M.; Carvalho, L.; Magalhães, F. D. *J Appl Polym Sci* 2011. In press.
- Ham, F. M.; Kostanic, I. N.; Cohen, G. M. Determination of glucose concentrations in an aqueous matrix from NIR spectra using optimical time-domain filtering and partial least-squares regression. G. B. R. *IEEE Trans Biomed Eng* 1997, 44, 475–485.
- Eddy, C. V.; Arnold, M. A. *Clin Chem* 2001, 47, 1279.
- Workman, J. W. L. *Practical Guide to Interpretive Near-Infrared Spectroscopy*; CRC Press: Boca Raton; 2007.