DETERMINATION OF FORMALDEHYDE/ MELAMINE MOLAR RATIO IN AMINO RESINS BY NEAR-INFRARED SPECTROSCOPY

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ABSTRACT

Melamine-urea-formaldehyde (MUF) resin production has increased in the last years motivated by the current concerns about the effects of formaldehyde on human health and to improve the physical properties of wood panels. Thereby, new processes for MUF synthesis have been developed. All such formulations are susceptible to possible operation error, which can significantly influence the characteristics of the final product. It is therefore crucial for industry to determine the formaldehyde/melamine (F/M) molar ratio of the product using near infrared (NIR) spectroscopy.The use of iPLS (interval Partial Least Squares) enabled to recognize the most interesting spectral ranges for analysis (4400-4800 cm^{-1}). Applying this method, it is possible to measure the error in the dosage of raw materials, determining in a more accurate and expedite method the F/M molar ratio in resins.

1. INTRODUCTION

Melamine-urea-formaldehyde (MUF) resin production has increased in the last years motivated by the current concerns about the effects of formaldehyde on human health since MUF resins are characterized by a low rate of formaldehyde emission (Tohmura et al., 2001) and to improve the physical properties of wood panels. (Pizzi et al., 2003)

In industry, generally, the reaction control is based on indirect and inaccurate measurements of the synthesis progress, such as viscosity, pH, and water tolerance. 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 formaldehyde/melamine (F/M) molar ratio of the synthesized product. In this way, the occurrences of higher rations than specified (which would penalize formaldehyde emissions) can be corrected.

The objective of our work was to develop a calibration method for determine the F/M molar ratio, based on measurement of FT-NIR spectra acquired by an optical fibre. Recently, the capabilities of FT-NIR spectroscopy have been exploited in several industries including: pharmaceutical (Ciurczak, 1987), biomedical (Ellis et al., 2006), petrochemical (Macho et al., 2002), (Paradkar et al., 2002) and polymer synthesis (Minopoulou et al., 2003).

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 (Dessipri et al., 2003). Kasprzyk and co-workers (Kasprzyk et al., 2001) used the technique for qualitative and quantitative analysis of liquid MUF resins, particularly for the determination of melamine content.

Generally, NIR spectroscopy is used in combination with multivariate techniques, such as principal components analysis (PCA) and principal least-squares regression (PLSR) methods. (Rodriguez-Saona et al., 2001)

To improve the capabilities of PLS modeling, a technique called iPLS (interval least squares regression), in which data are subdivided into nonoverlapping sections. Cross-validation is performed for each of these models and the interval which provides the lowest model root-mean-square error of cross-validation (RMSECV) is selected (Xiaobo et al., 2010).

In NIR, it is 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 several factors such as background noise, baseline drift and light-scattering (Pizarro et al., 2004).

The main objective of this study was to develop a method to determine formaldehyde/melamine molar ratios in MUF resins.

2. MATERIALS AND METHODS

2.1. LABORATORY RESIN SYNTHESIS

All resins were produced in a 2.5 L round bottom flask, equipped with thermometer, mechanical stirrer and condenser. The temperature was controlled manually using a heating mantle. The pH was measured off-line using a pH meter. MUF resins were produced using the so-called single-stage process described in literature (Kamoun et al., 2000, Hse et al., 2008, Tohmura et al., 2001).

Solid urea is added manually at constant flow rate to an alkaline environment formaldehyde solution, promoting a methylolation reaction.

To initiate the reaction, the mixture was heated and maintained at 80 - 90 °C. At 30 minutes reaction time, melamine was added (16, 14 and 10 %) and the polymer was condensed until the desired viscosity (~500 cP)

In the third stage the pH was adjusted to a slightly basic value. The final amount of urea added should be sufficient for the formaldehyde/urea molar ratio to reach values of 2.0 to 1.5 at the end of this step.

A total of 216 lab-synthesized resin samples were used for calibration. 162 lab-synthesized resins were used for test validation.

2.2. FT-NIR ANALYSIS

NIR transmission spectra were collected on a Bruker (www.bruker.de) Zaffiro FT-NIR process-spectrometer with a TE-InGaAs detector and spectral range between 12,000 and 4,000 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.

The reference spectrum was acquired in air, to prevent any impurities on the surface of the probe.

2.3. CHEMOMETRICS

The spectral manipulations were performed using OPUS quant 2 software package by Bruker.

To develop the statistical model, the influence of various regions was analyzed using iPLS with 20 intervals, where the error estimation parameter adopted was the root mean square error of cross validation (RMSECV):

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n}} \qquad (1)$$

In RMSECV, y_i is the actual value of F/M, is the PLS predicted value, and n is the total number of test samples (Li et al., 2006)

The standard error of prediction (SEP) and the standard error of calibration (SEC) were adopted as error estimation parameters for both calibration and validation procedures (Czarnik-Matusewicz et al., 2006):

$$\mathbf{SEP} = \left\{ \sum_{i=1}^{n_m} (m_i - \hat{m}_i)^2 / n_m \right\}^{1/2} \qquad (2)$$

$$\mathbf{SEC} = \left\{ \sum_{i=1}^{n_t} (t_i - \hat{t}_i)^2 / (n_t - h - 1) \right\}^{1/2} \qquad (3)$$

In SEP, is the reference value of molar ratio F/U, is the PLS predicted value, and is the total number of test samples. In SEC, is the reference molar ratio F/U, is the predicted PLS value, is the total number of training samples, and h is the number of PLS factors (ranging from 1 to 10).

The quality of calibration is usually determined by the accuracy in the prediition of new unknown samples (Czarnik-Matusewicz and Pilorz, 2006).

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF FT-NIR SPECTRA

Figure 1 represents the iPLS model using the calibration samples. The interval with the lowest RMSECV is obtained for wavenumbers between 4400 and 4800 cm^{-1} (darker grey bar in the Figure 1).

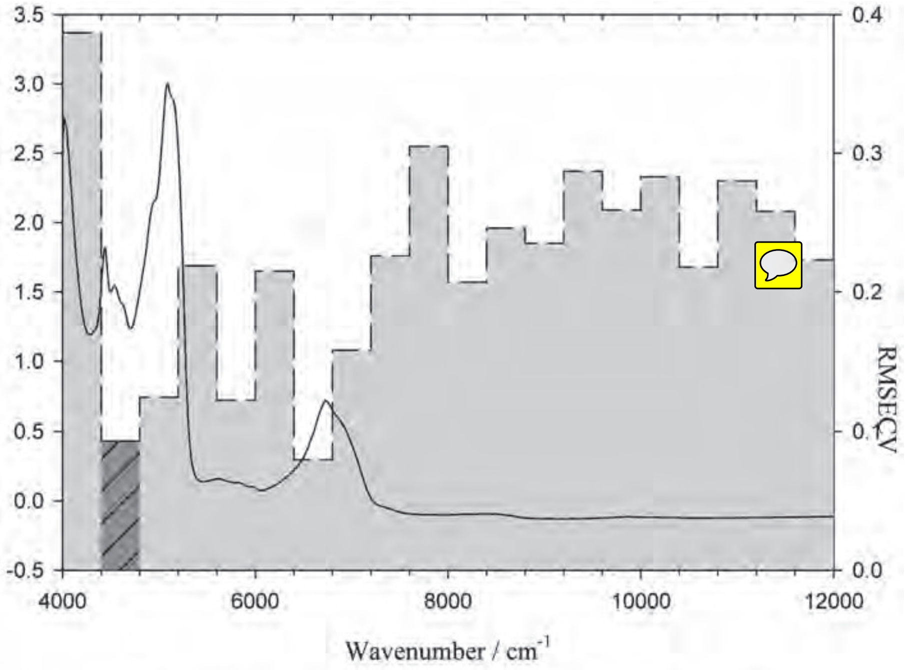


Figure 1: Average NIR spectrum of MUF resin (line) and RMSECV values for iPLS model on 20 wavenumber intervals (bars).

To increase the amount of information available to the model, an additional test was done. This test consists in combining the range of 4,400-4,800 cm^{-1} with other ranges available. The results are shown in Figure 2. The model that combines the intervals 4,400-4,800 and 6,800-7,200 cm^{-1} (darker grey bar in Figure 2) gave a RMSECV value slightly lower than the one obtained before considering only the 4,400-4,800 cm^{-1} interval.

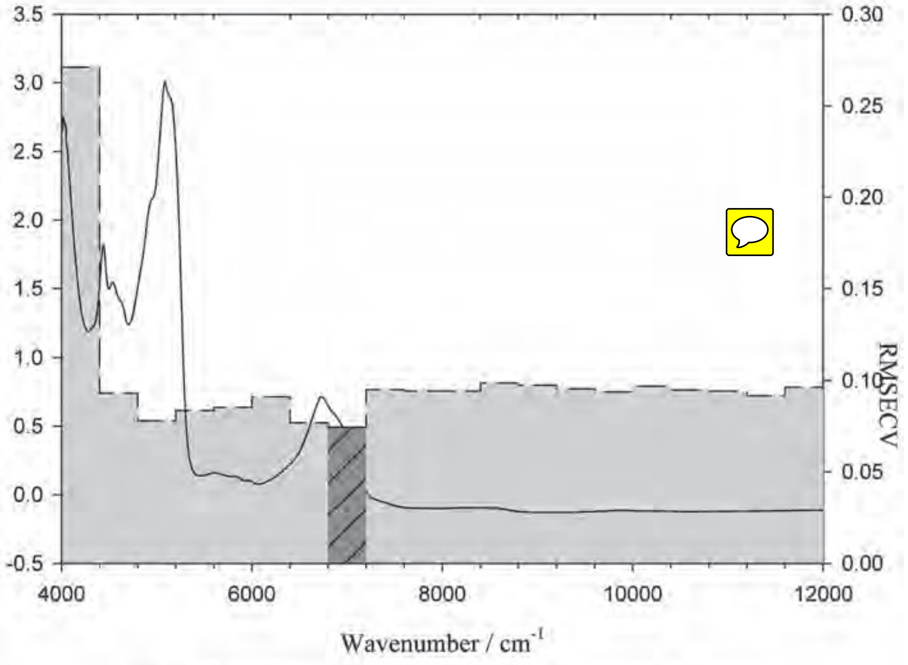
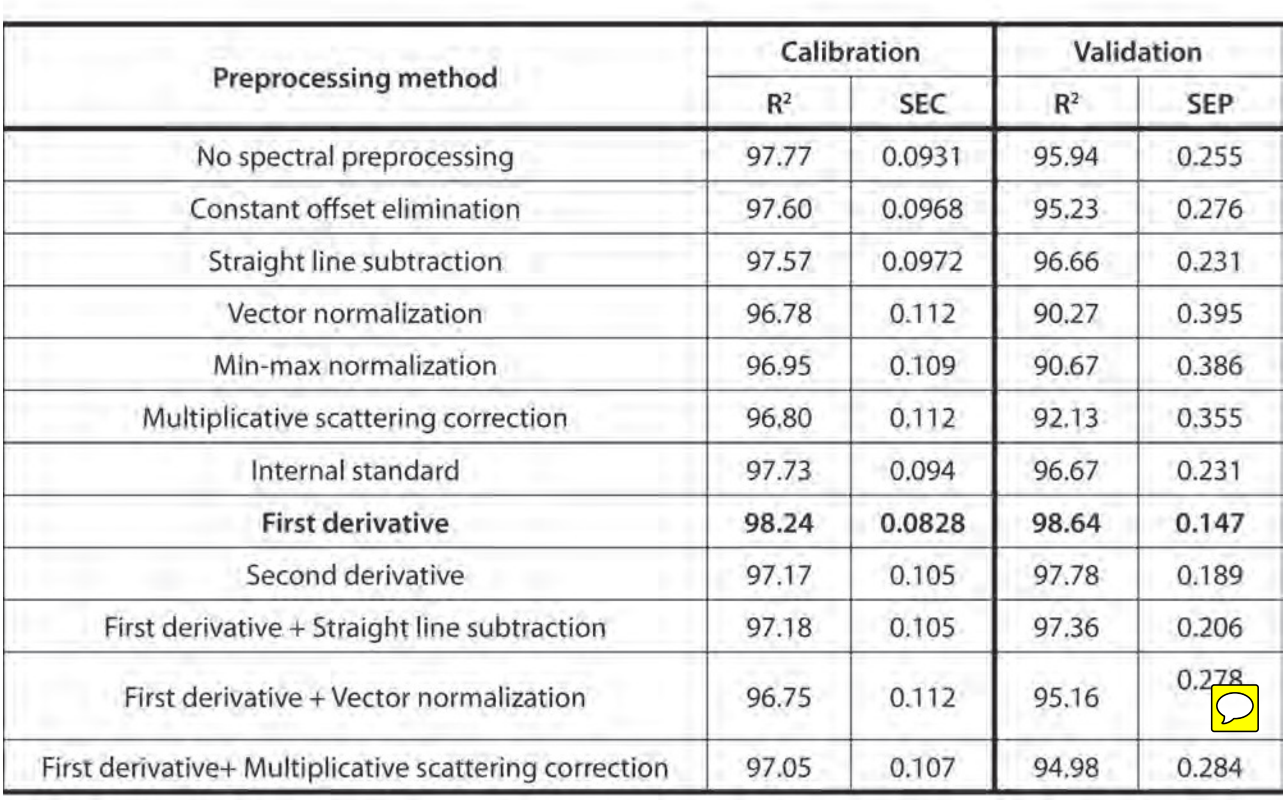


Figure 2: Average NIR spectrum of MUF resin (line) and RMSECV values for iPLS model on 20 wavenumber intervals (bars).

However, these regions include the peaks associated to the presence of water (Eddy et al., 2001), so only the wavenumbers between 4,400 and 4,800 cm^{-1} will be used. This region, as described by Kasprzy et al. (2001), is associated with vibration bands from starch and amino groups, vibrations from methylol hydroxyl groups and CH vibration bands.

The possibility of using different preprocessing's was also studied. Table 1 shows the statistical parameters of all preprocessing methods for the wavenumbers between 4,400 and 4,800 cm^{-1}. The R^2_{cal} and R^2_{val} correlation values were used to quantify the predictability of each method (Büning-Pfaue, 2003). The general goal was to obtain low values of standard error of calibration (SEC) and standard error of prediction (SEP) and high values of R^2_{cal} and R^2_{val} (Conzen, 2006). The results indicate that the model developed using the first derivative as preprocessing yields the lowest values of SEP and SEC and the highest values of R^2_{cal} and R^2_{val}.



Preprocessing method	Calibration		Validation	
	R^2	SEC	R^2	SEP
No spectral preprocessing	97.77	0.0931	95.94	0.255
Constant offset elimination	97.60	0.0968	95.23	0.276
Straight line subtraction	97.57	0.0972	96.66	0.231
Vector normalization	96.78	0.112	90.27	0.395
Min-max normalization	96.95	0.109	90.67	0.386
Multiplicative scattering correction	96.80	0.112	92.13	0.355
Internal standard	97.73	0.094	96.67	0.231
First derivative	**98.24**	**0.0828**	**98.64**	**0.147**
Second derivative	97.17	0.105	97.78	0.189
First derivative + Straight line subtraction	97.18	0.105	97.36	0.206
First derivative + Vector normalization	96.75	0.112	95.16	0.278
First derivative+ Multiplicative scattering correction	97.05	0.107	94.98	0.284

Table 1: Summary of PLS –R model results.

4. CONCLUSION

For the selected property (F/M molar ratio), spectral region 4,400-4,800 cm^{-1} was identified by iPLS as providing the best results for implementation of calibration methods.

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

Once an appropriate model is developed and validated, the NIR technique may lead to a fast and accurate tool for F/M molar ratio process control in industrially synthesized MUF resins.

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