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Chemical composition of melamine-urea-formaldehyde (MUF) resins assessed by near-infrared (NIR) spectroscopy

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ABSTRACT

Melamine-urea-formaldehyde (MUF) resins are commonly used in the production of wood-based panels. The composition of the resin influences many properties of the final product. In industrial production, some properties, such as viscosity, pH, solid content, or molar ratio, are assessed after resin production in order to evaluate if they are within the desired parameters. These properties are useful for quality control of amino resins. However, almost no information is obtained if a certain type of reagent or filler is wrongly added to the formulation, even though the resin's final adhesive performance will be affected. Evaluation of the molar ratio of the reagents might be the only of the few industrially used tests capable of making this assessment. Near-infrared spectroscopy (NIR) is a fast and reliable technique for quality control of amino resins and can give a wide range of information regarding chemical composition of these products. This work intends to test the capability of NIR to assess several properties related to MUF resins' chemical composition. The approach considered two types of problems: 1) whether there was a flaw on resin manufacture process and 2) which raw-material (amount or kind) was incorrectly added to the reactor. Using NIR spectra of a wide range of MUF resins, several models were established to predict the molar ratio of formaldehyde and urea (F/U), molar ratio of formaldehyde and melamine (F/M), molar ratio of formaldehyde and amino groups ($F/(NH_2)_2$), total urea (% U) and total melamine (% M). These models were constructed using the multivariate technique of Partial Least Squares (PLS) and could successfully determine the properties of a set of industrial resins. The coefficients of variation (CV) obtained were equal or lower than 5%, except for the property of F/M, which was 17%. A more thorough analysis of the established models reveals that spectral components of melamine are harder to extract by PLS than components of formaldehyde or urea.

1. Introduction

Amino resins are a type of synthetic adhesives used extensively in the wood-based panels industry. The three main types are urea-formaldehyde (UF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde resins (MUF) [1]. UF are the cheapest of these resins and MF are the most expensive resins but provide certain increased advantages over UF resins such as higher resistance to heat and moisture and colorlessness [2]. MUF resins are an intermediate polymer between UF and MF resins that possess a mix of advantages of the two resins. Up to 25% melamine by weight can be substituted from urea in UF resins [2,3]. Some researchers have presented compounds that enhance the characteristics of MUF resins that can be used industrially [4,5], other additives commercially available are added to the formulation depending on the manufacturer process. Generally, the process of MUF production is done in successive steps of addition of reagents [1,6]. The reaction, in simple terms, is divided in two phases: the methylolation and condensation. The mehylolation stage is characterized by producing methylolurea and methylolmelamine groups. During the condensation phase these methylated monomers react and produce bigger polymer chains like the one presented in Fig. 1.

After resin production, common industrial methods for quality control of amino resins are the pH, viscosity, density, and solid content. These are related to the performance of the resin but fail to provide the cause of errors that may occur during manufacture. One example is the addition of a reagent, either by operator error or a malfunctioning flow meter. Not only that, but sometimes fresh resins are mixed with previously produced resins in the storage tank, and the general composition of the mix might change significantly [7].

Several methods have been developed to determine different

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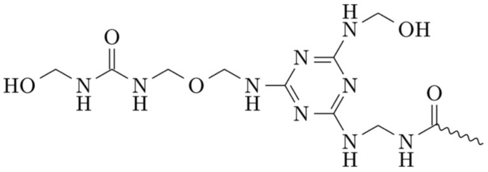

Fig. 1. Example of MUF polymer.

constituent species in amino resins. Gel Permeation Chromatography has been used to determine polymer size and High-Pressure Liquid Chromatography (HPLC) methods have been developed for determining free urea, monomethylolurea and dimethylolurea of amino resins [8]. The European standard EN 1243 [9] describes a method for the determination of free formaldehyde of amino resins. These measurements also help to determine if something out of the ordinary happened during the production process but fail to give a broader chemical composition of the resin. Other methods provide a more meaningful chemical analysis. Nuclear magnetic resonance spectroscopy is a technique capable of quantitatively determining different groups, bonds, and chemical composition of amino resins [10–12]. Infrared spectroscopy is also capable of not only to distinguish different chemical groups of amino resins [6] but also capable of distinguishing bonds of other added compounds to amino resin formulations such as lignin [13], oil palm starch [14], or isocyanates [15]. Hirt et al. have presented a technique for the quantification of melamine based in ultraviolet spectroscopy [16]. These and other techniques are capable of either quantitatively or qualitatively determining chemical composition of amino resins but imply expensive equipment or long sample preparation or analysis times.

Near-infrared (NIR) spectroscopy is a technique also capable of assessing many components (such as N-H, and O-H bonds, among others [17]) of a sample without problems associated with other enumerated techniques. This technique has been successfully applied to evaluate many properties of amino resins, either quantitatively or qualitatively. Melamine content of amino resins of MUF resins has been determined by NIR infrared spectroscopy by Kasprzyk et al. [18] and later by Henriques et al. [19], the results showed that the methodology allows the determination of this property either for calibration, either for validation (coefficient of determination (R^2) ≥ 0.98). The molar ratio of formaldehyde/urea (F/U), or formaldehyde/melamine (F/M) or formaldehyde/amino groups ($F/(NH_2)_2$) are properties that have great impact in resin performance [20–22], so a tight control of the process must be performed. The molar ratio of F/U has previously been determined for a UF resin by NIR using an interval Partial Least Squares (interval PLS) methodology with R^2 above 0.999 [23]. Meder et al. [7] have proven that NIR spectroscopy can be used at-line of a process for quality control of MUF resins. Several properties were studied in Meder's et al. work, which include: free formaldehyde, F/U, specific gravity, and solids content, among other properties. The current paper tries to assess some properties of MUF resins giving an in-depth approach of the models generated by PLS. This is a multivariate technique often used in NIR spectroscopy for quantitative model developments [24].

This work aimed to achieve two goals: 1) study the capability of NIR spectroscopy to determine some parameters related to MUF resin chemical composition (F/U, $F/(NH_2)_2$, F/M, % U, and % M), and 2) apply the NIR method to an industrial set of resins to evaluate the model capacity for quality control of MUF resins.

2. Materials and methods

2.1. Resin synthesis

For the set of calibration spectra, 4 different types of MUF resins were synthesized in duplicate. Each type of resin had a final ratio $F/(NH_2)_2$ of 1.15. The difference between resins consisted in the amount of melamine substituted in the process which varied from around 8% m/m to around 20% m/m. For each of the 8 resins, different quantities of urea and melamine were added to decrease the ratio $F/(NH_2)_2$ to around 1.05. Note that the process of adding urea decreases the value of F/U and the value of $F/(NH_2)_2$ and increases the value of % U (m/m). The process of adding melamine decreases the ratios $F/(NH_2)_2$ and F/M but increases the values of % M (m/m). The reference values were obtained by weighing the reagents before adding to the reaction medium.

2.2. Spectral acquisition

Spectra of each sample were acquired in the day of production and a day later, in order to account for spectral changes in the NIR model during storage. 3 measurement replicates were performed for each sample between wavenumbers 4000 cm^{-1} and 12000 cm^{-1}. However, the spectra treatment with PLS methodology was performed only from 4100 cm^{-1} to 8000 cm^{-1}. This narrower range was chosen based on the spectral zones with more peaks visible to the naked eye and discarding noise present in the removed regions. Each spectrum acquisition was performed in intervals of 8 cm^{-1} (totaling 2074 data points) and the reference spectrum was an air background spectrum. Each spectrum consisted in an average of 32 scans and the spectrophotometer used was a Fourier Transform-NIR instrument Matrix-F from Bruker. In total, 327 spectra (from 109 resin solutions) were used for calibration. The validation of each model was done using 87 industrial MUF resins of three types which differed in % M and $F/(NH_2)_2$, provided by EuroResinas- Indústrias Químicas S.A. The software used for measuring each sample was OPUS from Bruker but the spectra were treated using Matlab 2018 and the freely available code of *i*Toolbox which is based on the Nonlinear Iterative Partial Least Squares (NIPALS) [25].

2.3. Data evaluation

The calibration set was evaluated using: 1) the coefficient of determination (R^2_{cal}) and 2) the root mean square error of cross-validation (RMSECV). The coefficient of determination is a commonly employed statistical measure, and cross-validation is a commonly used technique to evaluate model quality [26]. For the model calibration, the leave-one-out cross validation was used, the procedure took the following steps:

1) Remove spectrum number 1 from calibration;
2) Create a calibration model using the rest of the spectra;
3) Determine the predicted value ($\hat{y}_i$) of spectrum number 1 using the calibrated model;
4) Place spectrum 1 in calibration and remove spectrum 2 from calibration;
5) Repeat every step until every spectrum is removed from calibration and the rest of the spectra have been used for prediction of each individual spectrum.

The expression to calculate the RMSECV is presented in Eq. (1).

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

N_c- number of calibration spectra; i- sample number; $\hat{y}_i$ predicted value of the model for sample i; y_i- reference value for sample i.

To validate the model three parameters were chosen: the coefficient of determination (R^2_{val}), the root mean square error of prediction (RMSEP), and the coefficient of variation (CV). The RMSEP was calculated using Eq. (2).

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{N_v} (\bar{y}_{vali} - y_i)^2}{N_v}} \tag{2}$$

where N_v- number of validation samples; i- sample number; $\bar{y}_{vali}$- mean of the predicted value using three spectra measurements for each resin sample i; y_i in this equation represents the reference value from resin's manufacturer. CV is calculated by dividing RMSEP by the mean of the reference values of the samples ($\bar{y}_i$) so that the value is dimensionless, as shown in Eq. (3). CV was calculated for the calibration set (CV_{cal}) and validation set (CV_{val}).

$$CV = \frac{RMSEP}{\bar{y}_i} \tag{3}$$

Another important aspect in PLS methodology is the number of latent variables (LV) used in the model. When a PLS analysis is performed, the huge number of data is reduced to a smaller set of variables, the LV. These new variables are calculated in a procedure that each variable represents directions of most variance in the data set. This means that if we truncate our data to just a few LV that represent a big explained variance of our data, we can discard the remaining variables and variance. This enables the possibility of using just a few variables to analyze an NIR spectra. The number of LV in this work was chosen based on the package Quant for software OPUS from Bruker, given a maximum of 10 LV calculated. The NIPALS algorithm also involves the concept of Loadings. This algorithm is based in inflating or deflating the data matrix (adding or removing components from the analysis). The plot of these variables helps in visualizing spectral zones contributing to the model. The reference models were normalized by auto scaling the values: subtracting the mean from each value and then dividing each subtraction by the standard deviation.

3. Results and discussion

The spectra used for the calibration of the models are presented in Fig. 2. The picture shows NIR spectra of MUF resins with different $F/(NH_2)_2$ ratios. The spectra are similar to those found in the literature for the same type of resin [7,27–29]. The large and small peaks are numbered from 1 to 11 and each peak is associated with a bond shown in Table 1. The calibration spectra are colored according to $F/(NH_2)_2$ ratio. The baseline of the spectra is unaffected by this parameter, however a visual inspection tells that peaks 1, 2, 3 and 4 increase in absorbance with the decrease of $F/(NH_2)_2$, and peak 6 has the opposite behavior. For the rest of the peaks, such behavior is not as easily observed.

The results obtained for each NIR model are presented in Table 2. The models attained a good calibration performance: high R^2 (≥ 99%) and low CV (below 1% for all properties except for the property of F/M which had a CV of 3.1%). After calibration, the models were applied to a set of industrial spectra that presented a lower R^2 than the R^2 of calibration. At first, low R^2 might seem that the model is unsuitable for any prediction, but in this case the validation set had a narrow range of reference values that consequentially lowered the R^2 (the variances in reference values are low when compared to the variance of the predicted spectra). Thus, the R^2 of validation is inappropriate to measure the model quality. The RMSEP and CV are a much better analysis parameter because there is no dependence of the low variation of the reference values.

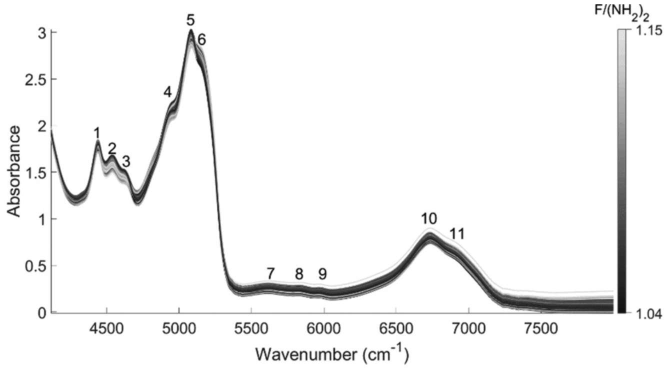

Fig. 2. Spectra of MUF resins used for calibration of the models.

The RMSEP for every model was bigger than the RMSECV of the respective model, which might indicate an overfitting of the values. Still, the values of CV for validation were kept equal or less than 5%, except for the F/M property, which was 17%. This property also had the highest CV for calibration, therefore a high CV for validation was also expected. This proves that the methodology used is adequate to determine the properties of F/U, $F/(NH_2)_2$, % U, and % M but inadequate to determine F/M. However, F/M relates to other properties such as F/U, % U, and % M. For example, F/M can be calculated by expression 4.

$$F/M = \frac{F/U \frac{\% U}{MM_U}}{\frac{\% M}{MM_M}} \tag{4}$$

In which, MM_i represents the molar mass of component i that can be U (urea) or M (melamine). Using this equation, the CV_{val} obtained is 6.4%, which is close to the 7.8% estimation of the errors using the error propagation theory (see Eq. (5)). These errors are lower than the 17% obtained for CV_{val} for model 3 (see Table 2), therefore, the application of the PLS methodology shows some difficulties in establishing a model to predict F/M.

$$CV(F/M) = \sqrt{CV(F/U)^2 + CV(\% U)^2 + CV(\% M)^2} \tag{5}$$

The algorithm used for the calculation of the number of LV determined that the optimum number for every model was 10, the maximum number of LV considered. Probably, if a higher number of LV was used for the calculation of the models, the number of LV calculated by the model would not correspond to the maximum defined of 10 LV for this experiment. The results obtained have errors close or below 5% for CV_{val}, (except for model 3) indicating that the models are not overfitting the calibration set and removing determination capacity of the models to validation set of resins. This also shows that the maximum number of LV can be used for prediction of these properties.

The first three LV for each model account for more than 90% of the explained variance in the spectra matrix. The first three loadings corresponding to those LV's are presented in Fig. 3. Looking carefully at the loadings of model 1 (F/U) and 4 (% U), the two are almost symmetrical to each other in the vertical axis, although with small differences. The reason for this is that in model 1 the % U is present in denominator, in model 4 the % U is present in numerator, so the loadings appear vertically inverted. This symmetry means that these two models are looking at similar spectral features, which are related to urea. The magnitude of the loadings is similar between models, because the reference values were auto scaled prior to the model calculation, otherwise the magnitude would also change. The same behavior happens for model 3 (F/M) and model 5 (% M) for the same reasons, but instead of urea, the chemical specie is melamine. The loadings of model 3 and model 5 are very similar (but not equal in value) to models 1 and 4, with peaks present in the same bands. Table 2 shows that the errors (CV_{val}) for the models with melamine (model 3 and 5) are superior in magnitude than those of the models that have urea (models 1 and 4). Since the first three loadings of models with melamine are similar to the loadings of models with urea and the models with urea have smaller errors (CV_{val}) than the models with melamine, an obvious conclusion is that the methodology used presents more difficulties in distinguishing melamine components in the spectra than urea components.

The CV_{val} for model 3 is greater than for the rest of the models. This model needs to distinguish two components in the NIR spectra: F and M. As mentioned above, NIR presents more difficulties in distinguishing

Table 1
Peaks in NIR region of MUF resins.

Peak number	Peak wavenumber (cm^{-1})	Assignment
1	4439	CH stretching and CH bending combination band [27]
2	4550	NH symmetrical stretching and NH bending combination band [27]
3	4617	Associated with NH_2 species from urea [30]
4	4960	Associated with $C{=}ONH_2$ groups [31]
5	5084	NH stretching and bending of OH combination band [31]
6	5149	Stretching of OH [31]
7	5624	Second overtone of CH methylene [31]
8	5847	CH from methyl [31]
9	5975	CH from methyl [31]
10	6736	Second overtone of NH stretching from urea, amine, or amide [31]
11	6897	Forth overtone of C=O carbonyl and OH polymeric stretching, also OH stretch from the broad band of water between around 7 100 cm^{-1} and 6 250 cm^{-1} [31]

M components in spectra than U components. Model 3 not only needs to overcome this adversity, but also needs to withdraw F components. This in turn gives a higher error than the rest of the models. Possibly, using another methodology would give different results for this model. However, as demonstrated before, using information from other models, an estimation of the F/U ratio can be calculated with fewer errors than just PLS alone.

Model 2 gave the best results for calibration and validation in terms of CV, which further proves that NIR has some trouble in separating M bands from U bands, because when no separation of the components U and M is needed the errors are the lowest. In other words, models that look at the ratio $F/(NH_2)_2$ present better prediction capacity than models that separate U from M. Although melamine features are more masked in the NIR spectra than F or U, a determination capability was found for the % M m/m. The capacity of this model has been demonstrated before by Kasprzyk et al. [18] and Henriques et al. [28], but the increased difficulty of the model in distinguishing melamine when compared to other components has not yet been reported, to the best of our knowledge.

The loadings for all models also show features on bands identified in Fig. 2. Two band regions with prominent peaks are identifiable:

1) The region between around 4400 cm^{-1} and 5400 cm^{-1} which corresponds to a large region with many combination bands from NH and CH. Closer to the 5400 cm^{-1} region sharp peaks appear due to combination bands of NH and OH. These peaks are correspondent to peaks number 1 to 6 presented at Fig. 2;
2) The region between around 6400 cm^{-1} and 7250 cm^{-1}. These bands correspond to peak 10 and 11 in Fig. 2, which represent NH stretching and C=O vibration and OH stretch.

The low CV_{val} for models 1, 2, 4, and 5 proves that the models created can be used to evaluate industrial resins with a quick NIR spectra evaluation. However, the process of producing these resins might differ among producers, and although some resins might have the same amount of reagents, the process of production may vary and different calibration results could be obtained. Another important fact to be noticed is that the established models seem to be valid throughout all the variations studied and throughout the range of analysis (see Table 2 for the range of analysis of each model), extrapolation of these models outside those ranges might not provide good results. Use of NIR and PLS methodology alone to determine F/M ratio was not found to be applicable for quality control of industrial resins.

Comparatively to other systems of analysis, such as 13C NMR [10–12], FTIR [6] or even UV spectroscopy [16], NIR spectroscopy coupled with a PLS methodology provides fast, reliable and quantitative results without the need for sample preparation, and can be easily implemented in industrial sites. Most importantly for the scope of this work, NIR can be used for quality control of industrial amino resins.

4. Conclusions

Among the techniques capable of detecting formaldehyde, urea, and melamine chemical species of amino resins such as UV spectroscopy and/or NMR, NIR spectroscopy is the fastest and implies little sample manipulation. The current work studied the ability of NIR spectroscopy to determine 5 different properties of MUF resins: F/U, $F/(NH_2)_2$, F/M, % U, and % M. The results show that 4 models had coefficients of variation for validation using industrial resins around 5% or lower (2.7% for F/U model, 1.5% for $F/(NH_2)_2$ model, 2.6% for % U m/m model, and 5.2% for % M m/m model). These results show that these models can assess industrial resins formulations. The model for the determination of F/M was found unsuitable for prediction because of the high CV_{val} (17%). Using information from the other models and analytically calculating the F/M ratio provided better results than an NIR model based in PLS methodology focused only on this property. A loadings analysis shows that the PLS methodology gives worse results when trying to generate models with urea and melamine separated, a reason for this is the increased difficulty in separating melamine contribution to the NIR spectra of MUF resins. This work further proves the capacity of NIR spectroscopy for providing quality control data in MUF resins: not only alerts to possible deviations in the formulations, but also provides the magnitude of the deviations occurred during manufacture, derived from incorrect reagents addition.

Table 2
Results for calibration and validation of the models.

Model	Property	LV	R^2_{cal} (%)	RMSECV	CV_{cal} (%)	Range of analysis (calibration)	RMSEP	R^2_{val}	CV_{val} (%)
1	F/U	10	99.1	0.012	0.9	1.17 to 1.64	0.040	0.8	2.7
2	$F/(NH_2)_2$	10	98.6	0.004	0.4	1.04 to 1.15	0.017	0.3	1.5
3	F/M	10	99.2	0.3	3.1	5.6 to 13.8	1.1	0.8	17
4	% U (m/m)	10	99.8	0.2	0.5	30 to 43	0.9	0.91	2.6
5	% M (m/m)	10	99.9	0.1	0.8	8 to 19	0.9	0.93	5.2

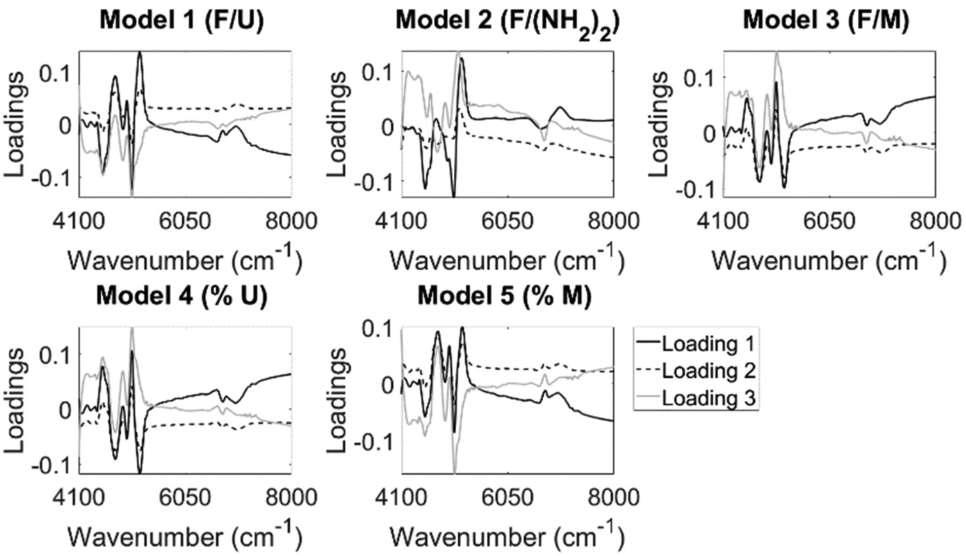

Fig. 3. Loadings 1, 2, and 3 of each NIR model.

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