

VISCOSITY DETERMINATION OF AMINO RESINS DURING SYNTHESIS USING NEAR-INFRARED SPECTROSCOPY

Ana Henriques*¹, João Ferra², Paulo Cruz³, Jorge Martins⁴, Fernão Magalhães⁵,
Luísa Carvalho⁶

¹Research Fellow, LEPAE, Dept. of Chemical Engineering, University of Porto- Faculty of Engineering, Rua Drº Roberto Frias, 4200-465, Porto, Portugal

²Research & Development, EuroResinas – Industrias Químicas, 7520-195 Sines, Portugal

³Product & Business Development, EuroResinas – Industrias Químicas, 7520-195 Sines, Portugal

⁴Coordinator Professor, DEMad-Dept of Wood Engineering, Polytechnic Institute of Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, Portugal; Researcher, LEPAE-FEUP

⁵Assistant Professor, LEPAE, Dept. of Chemical Engineering, University of Porto- Faculty of Engineering, Rua Drº Roberto Frias, 4200-465, Porto, Portugal

⁶Coordinator Professor, DEMad-Dept of Wood Engineering, Polytechnic Institute of Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, Portugal; Researcher, LEPAE-FEUP

*EMAIL: EQ05006@FE.UP.PT

ABSTRACT

FT-NIR spectroscopy was been describe with a powerful technique to on-line monitoring and control of polymerizations. . In this work this technique was used to monitoring the viscosity of urea-formaldehyde resins during the condensation reaction. The main objective of this study was to develop a chemometric technique that can be used on-line or off-line for determining the resins' viscosity in the condensation stage. The best model uses the spectral region between 4400-4800 cm⁻¹ and the first derivative with vector normalization for preprocessing.

INTRODUCTION

The conventional synthesis process of a urea-formaldehyde (UF) resin is composed of two steps: basic methylation and acidic condensation. Formation of methylolureas, namely mono, di, tri and tetra-methylolureas, occurs in the first stage (Dunky,1998). In the condensation stage, linear and branched polymer with varied molecular masses is formed due to reactions involving methylol end groups, urea and formaldehyde still present in the reaction mixture (Mehdiabadi, Nehzat et al.,1998)

In the industrial process, in order to monitor reaction progress samples are taken sequentially from the reactor during the condensation stage and viscosity is measured after cooling. When the desired viscosity is attained, the reaction is stopped by increasing pH and cooling. However, the method for off-line viscosity determination is labour intensive and introduces a significant delay in the measurement. The objective of our work is to develop a calibration method for viscosity estimation, based on measurement of FT-NIR spectra acquired by optical fibre.

NIR analysis usually involves the rapid acquisition of a large number of absorbance values. The spectral information is then used to predict the composition of the samples by extracting the

variables of interest. Generally, NIR spectroscopy is used in combination with multivariate techniques, like partial least squares (PLS), target transformation factor analysis (TTFA) and curve resolution (MCR) for qualitative or quantitative analysis (Xiaobo, Jiewen et al.,2010)

To improve the capabilities of PLS modeling, a technique called iPLS (interval partial least squares regression) has been used, in which data are subdivided into nonoverlapping sections that each undergo a separate PLS processing to determinate the most useful variable range (Xiaobo, Jiewen et al.,2010)

Interval PLS models are developed on spectral subintervals of equal width. The purpose is to find intervals, which gives better predictions. The comparison is mainly based on the validation parameter root mean squared error of cross-validation (RMSECV), but other parameters such as correlation between measured and predicted values, number of components are also evaluated (Andersen and Bro,2010)

To optimize the PLS models, both cross-validation or external validation can be used. Spectrum quality can be affected by several factors, so it is necessary to select the preprocessing method judiciously, in order to minimize the influence of adverse effects (Büning-Pfaue,2003; Pizarro, Esteban-Díez et al.,2004).

The aim of this work is therefore to: (i) use iPLS to ascertain the spectra wavenumber range(s) that provide better predictions and (ii) determine the feasibility of FT-NIR spectroscopy for estimating the viscosity of amino resins during condensation step.

MATERIALS AND METHODS

Laboratorial resin synthesis

Samples of two UF resins were produced in a 7 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.

UF resins were produced using the so-called conventional process (Ferra, Mena et al.,2010). Solid urea was added at constant flow rate to a basic formaldehyde solution. Then pH was adjusted to a slightly acid value by adding acetic acid and the polymer was condensed until the desired viscosity (~500 cP). After this step, the pH was adjusted to 7.5-8.5, and the solution cooled down and a second amount of urea added at constant rate and temperature. Finally, a third amount of urea was added to achieve the desired F/U molar ratio.

FT-NIR analysis

NIR spectra were acquired as described in Henriques et al (2012). The transmission probe had an optical sapphire window, 1 mm path length and 600 μm diameter. The probe was connected, via optical fiber, 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 was previously collected in air, to account for possible impurities present in the probe surface. The probe was carefully washed prior to switching to a different resin. The resins were stored at 25 °C before spectra collection.

Chemometrics

To develop the statistical model, the influence of various regions of the UF 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 Regression (PLS-R) method was used to establish a quantitative relation with UF resins viscosity

RESULTS AND DISCUSSION

Kasprzyk and co-workers (Kasprzyk H.,2001) identified the regions between 7502-6098 cm^{-1} and 5000-4246 cm^{-1} as being the most important for UF resins, and assigned them to the most significant vibration from important groups, namely amide, amine and hydroxyl.

Figure 1 shows an iPLS model with 20 intervals and the predictions obtained for each interval. As expected, the RMSECVs values are higher in the range closer to the visible spectrum (Andersen and Bro,2010). Figure 1 indicates that the lowest RMSECV values are obtained for wavenumbers between 4400 and 4800 cm^{-1} (darker grey bar in the Figure 1).

This region as described by Kasprzyk et al. (Kasprzyk H.,2001) is associated the vibrations of the CH bands and NH (4800 - 4400 cm^{-1}). This is in agreement with the known formation of methylene ether (-CH₂-O-CH₂-) and methylene (-CH₂-) linkages during the condensation (Dunky,1998)

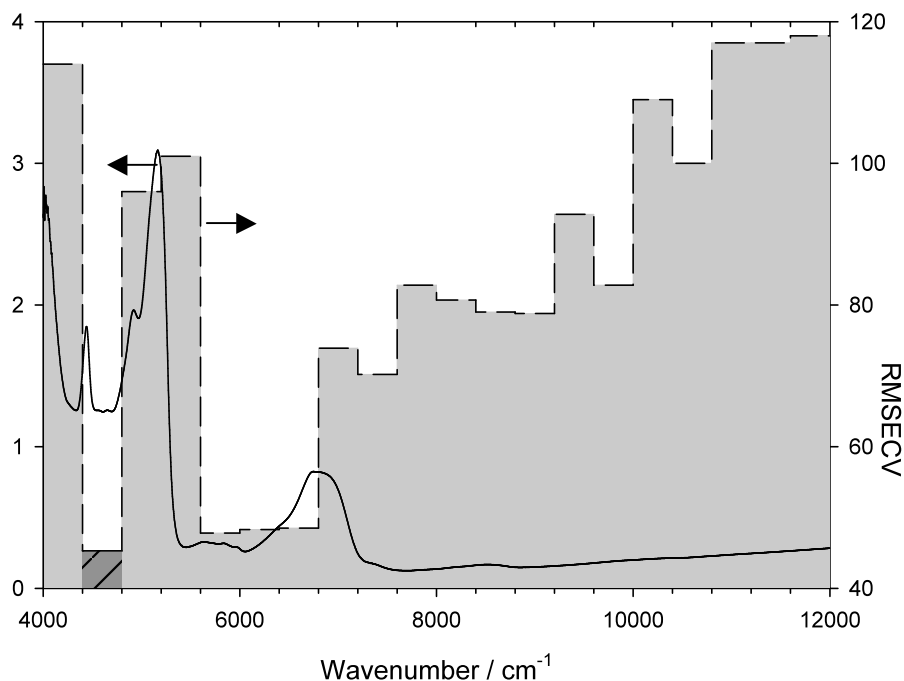


Figure 1 - Average NIR spectrum of UF resin during condensation stage (line) and RMSECV values for iPLS model on 20 wavenumber intervals (bars)

Calibration models for viscosity were developed taking into account these spectral regions, and different preprocessing methods: first derivative, multiplicative scatter correction (MSC) and standard normal variate transformation (SNV).

Error! Reference source not found. shows the statistical parameters of all preprocessings for this region. The R^2_{cal} correlation values were used to quantify the predictability of each method (Büning-Pfaue, 2003). The general goal was to obtain low values of RMSECV (standard error of calibration) and high values of R^2_{cal} (Conzen, 2006). The results indicate that the model developed using first derivative with vector normalization (SNV) as preprocessing yields the lowest values of RMSECV and the highest values of R^2_{cal} .

Table 1 – PLS-R model using the wave number 4800-4400 cm^{-1}

Preprocessing method	Calibration model	
	R^2	RMSECV
First derivative	87.13	42.9
MSC	83.43	45.7
SNV	83.96	47.9
First derivative with MSC	82.86	49.6
First derivative with SNV	88.44	40.7

CONCLUSIONS

A calibration method for the viscosity estimation of UF resins synthesized by the conventional process, based on measurement of FT-NIR spectra acquired by optical fibre was developed. Spectral region 4400-4800 cm^{-1} was identified by iPLS as providing the best results.

Calibration models are developed taking into account this region, different preprocessing methods were tested, resulting in different calibration models. Some methods gave high correlation values, validating their applicability. First derivative with vector normalization was identified as the best preprocessing.

This method allows the prevision of the reaction mixture viscosity during the condensation step for UF resin using FT-NIR analysis. This simplifies the measurement procedure, avoiding the need to remove samples from the reactor, and reducing operator intervention. Future work will

involve the application of this approach to on-line control of a pilot reactor during the synthesis of a UF resin.

ACKNOWLEDGEMENT

This work is co-funded by FEDER (Fundo Europeu de Desenvolvimento Regional) / QREN FCOMP-01-0124-FEDER-015239 and national funds through FCT (project PTDC/EQU-EQU/111571/2009) under the framework of COMPETE-Programa Operacional Factor de Competitividade (POFC)

REFERENCES

- Andersen, C. M. and R. Bro (2010). "Variable selection in regression—a tutorial." Journal of Chemometrics **24**(11-12): 728-737.
- Büning-Pfaue, H. (2003). "Analysis of water in food by near infrared spectroscopy." Food Chemistry **82**(1): 107-115.
- Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive resins for wood." International Journal of Adhesion and Adhesives **18**(2): 95-107.
- Ferra, J. M., P. C. Mena, et al. (2010). "Optimization of the Synthesis of Urea-Formaldehyde Resins using Response Surface Methodology." Journal of Adhesion Science and Technology **24**(8-10): 1454-1471.
- Kasprzyk H., J. M., Proszkyk S. (2001). "Application of NIR spectroscopy for analysis of amino adhesive resins applied on wood based materials." Folia Forestalia Polonica.
- Mehdiabadi, S., M. S. Nehzat, et al. (1998). "Correlating viscosity in urea-formaldehyde polymerization." Journal of Applied Polymer Science **69**(4): 631-636.
- Pizarro, C., I. Esteban-Díez, et al. (2004). "Influence of data pre-processing on the quantitative determination of the ash content and lipids in roasted coffee by near infrared spectroscopy." Analytica Chimica Acta **509**(2): 217-227.
- Xiaobo, Z., Z. Jiewen, et al. (2010). "Variables selection methods in near-infrared spectroscopy." Analytica Chimica Acta **667**(1-2): 14-32.