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FT-NIR Monitoring of a Scattering Polyurethane Manufactured by Reaction Injection Molding (RIM): Univariate and Multivariate Analysis versus Kinetic Predictions

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Summary: Near InfraRed (NIR) spectroscopy was used to monitor *in situ* a polyurethane synthesis during a RIM process. Univariate and multivariate analysis of transmittance spectra were used to calculate the reaction extent. A very good agreement was observed between multivariate analysis (PCA), univariate (Beer-Lambert) analysis and kinetic predictions. It was demonstrated that, in this case, PCA methods can provide a good estimation of the reaction extent versus time, without time-consuming calibration. The spectral range of PCA has to be carefully chosen.

Introduction

Polyurethane represents the most important and one of the oldest families of block copolymers. Their development was enhanced by the invention, in the early eighties, of the Reaction Injection Moulding process, allowing the moulding of large parts in a couple of minutes. This process [1] is based on the high speed mixing of two or more reactive chemicals or prepolymers, just before they are injected into the mould at low temperature and pressure. While a variety of techniques have been used to study the final polymer [1],[2], very few are suitable for the study of the dynamics of the RIM process.

The quality of the moulded part is a function of the process conditions [3],[4], e.g.; mixing pressure, flow rates, mould temperature.

Pressure and flow rate are conventional process parameters that provide real-time information, but they do not supply the necessary chemical information essential for the process control. On the contrary, thermal methods – e.g. *in situ* temperature monitoring [5],[6] - or direct methods – e.g. *in situ* Infrared Spectroscopy [7] - can supply information on local cure extent or reaction rates. Vibrational spectroscopy was widely used for qualitative and

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quantitative analysis of chemical reactions. Mid Infrared Attenuated Total Reflectance (ATR) remote control sampling with chalcogenide fibres can be used for *in situ* analysis. Unfortunately, theses fibres are expensive, brittle and only available for short length (from 1 to 2 m). As a consequence, they are not convenient for industrial use. In addition, ATR only probes a very thin layer of the product, which may not be representative of the whole part (especially for thick parts).

On the contrary, the sensitivity and accuracy of rugged FT-NIR spectrometers provide versatile tools for polymer monitoring [7],[8],[9],[10] and the excellent NIR transmittance of low OH fused silica fibres allows remote measurements over long distances.

But one of the issues encountered with NIR Spectroscopy is the difficulty to make quantitative analysis [11]. In some case, techniques such as Partial Least Squares (PLS) [12],[13] must be used. In other cases Principal Component Analysis (PCA) [14] is sufficient enough to obtain quantitative results. Unfortunately, PLS need to be calibrated using samples of known concentrations or conversions: for a RIM formulation, it is impossible to stop the fast reaction at different extents, so that we are not able to prepare samples that can be used in a standardization procedure.

However, Dittmar and Siesler [15] studied the synthesis of diphenylurethane from phenol and phenylisocyanate in chloroform solution, by NIR and multivariate techniques: The PLS-models were calculated from HPLC data. Their comparison of the loading plot of the first factor with the original spectra representing the start and the end of the reaction reflects the similitary of their spectral features with respect to those components, which changes in concentration during the reaction. In our case, the final product is insoluble, so that HPLC calibration cannot be performed. On the other hand, Khettry et al. [16] studying EVA, or Aust et al.[17] studying epoxy resins, pointed out the advantage of PCA methods to monitor the extent of reaction.

In this paper, we present the use of FT-NIR spectroscopy in transmission mode to monitor *in situ* the curing of a polyurethane formulation. The conversion evolution versus time is obtained from Beer-Lambert analysis and using PCA. In parallel, a kinetic model is used to model this conversion as a function of time and temperature. The simulated conversions are compared with those obtained from PCA and Beer-Lambert analysis.

Experimental Part

Materials

The polyurethane is obtained from the reaction of two main components:

- an alcohol: polytetramethyleneetherglycol (PTMEG from DuPont), functionality 2 (measured according to NF T 52-112), containing 0.05 % of dibutyltin dilaurate catalyst (DBTDL from Fluka)
- an isocyanate prepolymer based on methylene diphenyl diisocyanate (MDI from Bayer), functionality 2.2 (measured according to NF T 52-132)

The RIM machine was specially manufactured by UREFLEX-Michel BAULE Mécanique, France. For all the experiments, both tanks of reactives are maintained at 45°C under stirring. In order to monitor the reaction using optical fibres, the mould has been fitted out with quartz windows and SMA connectors (see Figure 1).

NIR spectroscopy

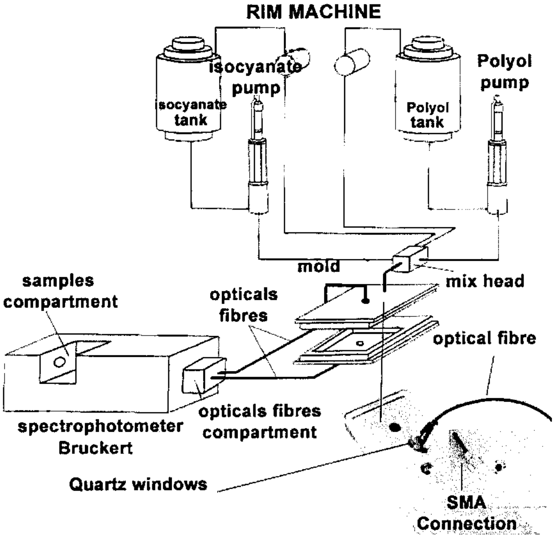

Figure 1. The RIM process and its instrumented mould.

The NIR spectra, in the range 4500-10000 cm^{-1}, are obtained with a FT-NIR spectrometer Brucker Equinox 55, equipped with a tungsten halogen source, a quartz beamsplitter and an InGaAs detector. All spectra are collected with a resolution of 8 or 12 cm^{-1}, 20 scans per spectrum, 4 spectra per minute.

Univariate analysis is performed using Grams32 software while PCA analysis is performed with a home-made software based on the Matlab programming language, allowing us to control rigorously the different steps of the calculus, which is not possible with a "black box" commercial software.

Two optical fibres (1 mm diameter, 4 metres long, equipped with SMA connectors) were supplied from Bruker. A thermo-regulated mould (250 × 150 × 3 mm) was manufactured with two quartz windows (15 mm diameter) equipped with SMA connectors to fix the optical fibres (see figure 1). The quartz windows allow collecting NIR spectra in transmission with a 3 mm pathlenght. The mould temperature is maintained at 45°C during all experiments.

Results and Discussion

The spectra collection starts just after the mould is filled and stops after 1 hour to ensure the reaction is finished. Good signal to noise ratio and reproducibility of NIR spectra were observed.

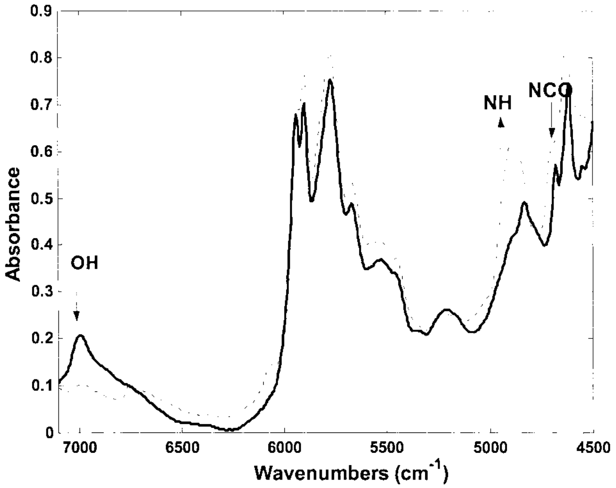

Figure 2. NIR spectra collected at the beginning (—) and the end (---) of the cure.

The absorption bands are assigned according to literature results [18],[19] and presented in Table 1.

Table 1. Main bands absorption and assignment.

Wave number (cm^{-1})	**Assignment**
4680	Isocyanate
4840	Polyol (-OH combination)
4900	Urethane (-NH combination)
6780	Urethane (-NH overtone)
7000	Polyol (-OH overtone)

For such a polyurethane formulation based on an isocyanate containing hard and soft segments, a phase separation takes place during the reaction [20], leading to an opaque product due to light scattering. This phenomenon can be a problem for the quantitative analysis of NIR spectra because spectra of diffusely transmitting samples are often characterised by poor signal to noise ratio and poor linearity due to deviations from Beer Lambert law [21]. Recently, factors affecting the diffuse transmittance have been discussed by Norris [22]. He observed that dividing absorbance spectra of diffusely transmitting samples by a selected second derivative allows correcting for scatter effects.

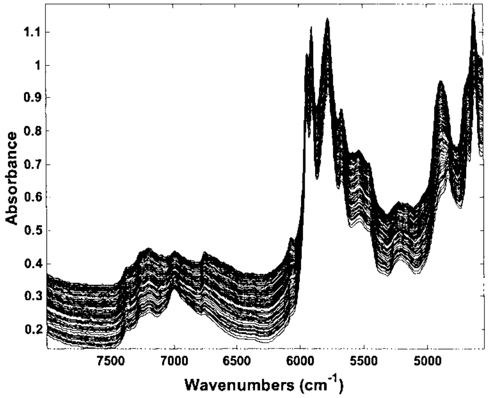

Figure 3. Effect of scattering on NIR data collection during cure.

A procedure to optimize the second derivative for the regression is also described. As can be seen in Figure 3, this light scattering induces a baseline shift during data collection.

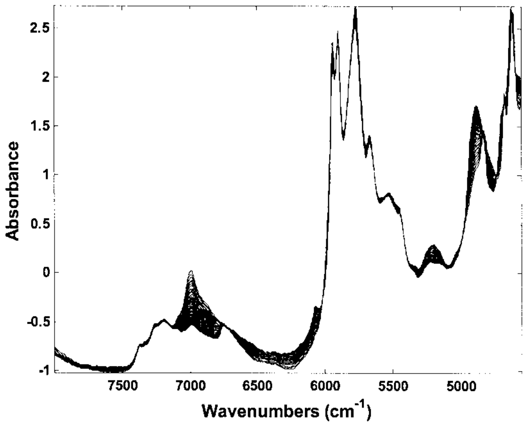

Figure 4. After SNV treatment on unsmoothed spectra.

To reduce this issue, a Standard Normal Variate (SNV) pre-treatment [23] is performed on the unsmoothed spectra: this SNV pre-treatment (see Figure 4) drastically reduces the baseline shift.

Quantitative analysis

One of the quantitative analysis that can be performed is based on the Beer-Lambert law. Figure 5 to 7 show a zoom of the NIR spectra on three wavelength region corresponding to functions appearing or disappearing during the cure.

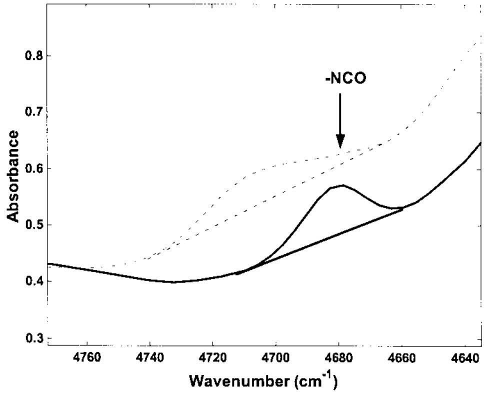

Figure 5. Absorption spectra between 4790-4650 cm^{-1} corresponding to NCO absorption peak at the beginning (—) and the end (---) of the cure.

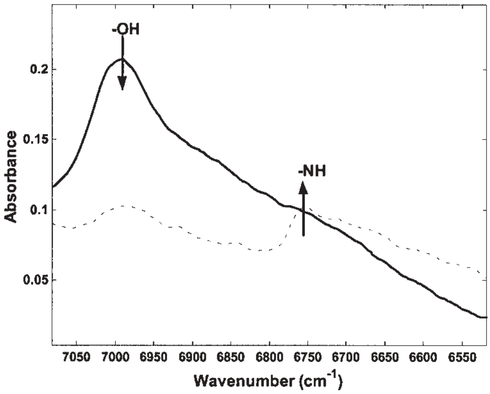

Figure 6. Absorption spectra between 7090 and 6620 cm^{-1} corresponding to OH and NH absorption peaks at the beginning (—) and the end (---) of the cure.

In Figures 6 and 7, the bands are overlapped so that simple peak area or height measurements are not possible.

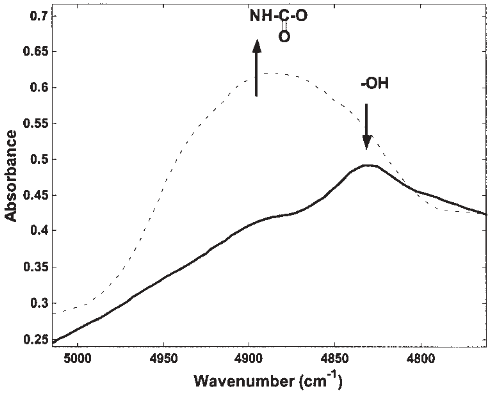

Figure 7. Absorption spectra between 5060 and 4740 cm^{-1} corresponding to NH and OH absorption peaks at the beginning (—) and the end (---) of the cure.

Although the isocyanate peak of Figure 5 is partially overlapped with an other band, the peak areas can be calculated using the baseline indicated on the figure. The choice of this band for quantitative univariate analysis has been discussed by Coleman [24].

For a disappearing function, the conversion x (at time t) can be correlated to the peak area A at time t and A_0 at time 0 (before reaction starts): $x = 1 - \frac{A}{A_0}$

But the choice of the baseline can affect the measured areas so that the errors on calculated conversions can be significant using this univariate analysis.

The result of this univariate analysis on the isocyanate band is presented on Figure 10. We must point out that this univariate analysis was performed with or without SNV pre-treatment with no noticeable change.

To compare the accuracy of the calculated conversions, another type of quantitative analysis can be performed: the Principal Component Analysis. This PCA is first performed on the 4500-7132 cm^{-1} spectral range (after a SNV pre-treatment of the data). Figure 8 shows a plot of the principal component 2 versus the principal component 1: the regular shape of the plot clearly shows that there is no outlier in the data collection. Furthermore, it should be noted that the first component explains about 98% of the spectral variations, so contains the quasi-totality of the available information.

As can be observed in figure 9, the first component is linearly correlated to the conversion (calculated at the same times using a kinetic model, see below).

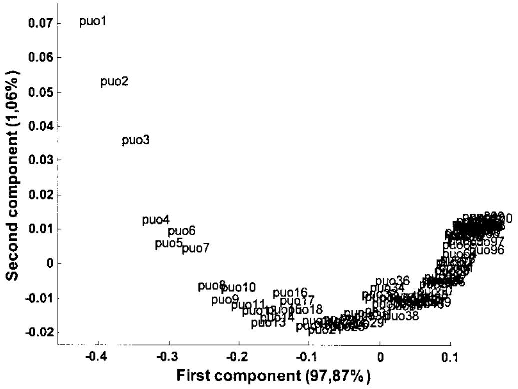

Figure 8. Score plot : principal component 2 as a function of principal component 1.

This first PCA approach on the 7132-4500 cm^{-1} spectral region can be performed on 2 reduced regions containing bands representative of the reaction (7132-6884 cm^{-1} for alcohol, 4751-4663 cm^{-1} for isocyanate). As with 7132-4500 cm^{-1} PCA, the first principal component represents, in both cases, more than 97% the spectral variations. Their plots (normalised between 0 and 100, see below) as a function of time can be representative of the conversion evolution (see Figure 10). We must point out that all these calculus where additionally performed using the second derivative of the spectra with no significant differences.

In order to compare the two quantitative approaches previously developed, a kinetic model can be applied to calculate the conversion as a function of time by using the real temperature profile measured in the centre of the mould with a thermocouple. The identification of the kinetic parameters using adiabatic reactions is described elsewhere [3,5].

This kinetic model is: $$\frac{dx}{dt} = 4.54\ 10^5\ \exp\left(\frac{-49000}{8.314\ T}\right)(1-x)\ s^{-1} \qquad (1)$$

Although the mould temperature is kept constant, the measured temperature inside the sample is not rigorously constant (a 4°C temperature increase can be observed) because of the very exothermic reaction combined with the low thermal conductivity of the sample. So that kinetic model is integrated with the measured time-temperature profile using a 4th order Runge-Kutta procedure. This kinetic model allows us to calculate the conversion for different experimental times, so that one can plot the 1st, 2nd and 3rd principal components of the PC as a function of the simulated conversion in spite of the measured times (see Figure 9).

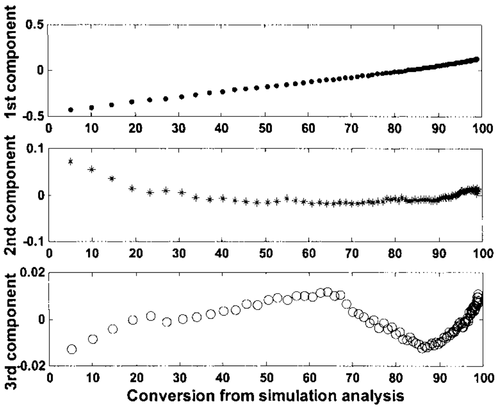

Figure 9: 1st, 2nd and 3rd principal component as a function of the simulated conversion.

We can observe that the first component is linearly correlated to the conversion, so that it can be used to calculate the conversion by normalising its values between 0 and 100. With s_{1x} being the first component score matrix of each spectra x, one can calculate:

$$x = 100\frac{s_{1x} - \min(s_{1x})}{\max(s_{1x}) - \min(s_{1x})} \qquad (2)$$

On the contrary, the second and third components do not seem linearly correlated to the conversion.

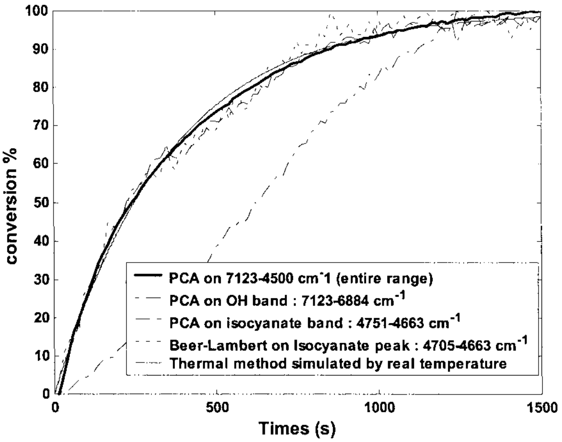

Figure 10. Conversion (obtained with different methods) as a function of time.

Figure 10 clearly shows that the simulated conversions (using the kinetic model), the conversions calculated with the Beer-Lambert law (isocyanate peak) and the conversions calculated with the PCA performed on the 7132-4500 cm^{-1} region or to the isocyanate region (4751-4663 cm^{-1}) are in very good agreement. The main difference is the high scatter on the curve representing the conversions calculated from Beer-Lambert law: this phenomenon is probably due to the choice of the baseline manually defined for each spectrum. On a lower extent, PCA applied to the isocyanate wave range gives rise to a curve with a much higher scatter than the one obtained with the whole region. This may be attributed to the fact that, when using the whole spectral region, the random defaults that can be observed on an NIR spectra are averaged on the whole spectrum, while they are only averaged on a shorter domain (so on much less points) when the user decides to make PCA on a restricted part of the spectra.

The only curve totally different from the others is the curve obtained after PCA on the hydroxyl domain: this clearly shows that quantitative analysis, performed on a function involved in hydrogen bonding, is not possible in this case. As it is well known, complex chain interactions (as hydrogen bonding [25],[26], phase separation [27]) lead to a complex nature of the absorbance bands explaining the observed difference in Figure 10. The information contained in the first principal component of the PCA in this OH range is strongly disturb by the hydrogen bonding and/or phase separation phenomen.

Conclusion

This paper demonstrates the potential of near infrared transmission spectroscopy for *in situ* cure monitoring of polyurethane in a RIM process. We noted that conversions calculated from PCA are in very good agreement with conversions calculated with univariate analysis based on Beer-Lambert law or with simulated conversions based on a kinetic model. In this case, the scores of first component can be used to calculate the reaction extent without time-consuming calibration. Nevertheless, the PCA spectral range has to be carefully chosen. However, a better understanding of the influence of scattering should be useful for diffuse transmittance quantitative analysis, and might be used, in the future, to monitor the phase separation phenomenon.

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