

Simultaneous near infrared spectroscopy and dynamic rheological analysis for process monitoring of reactive polymers

S. Benali,^a D. Bertrand,^b J. Dupuy^c and G. Lachenal^d

^aUniversité de Mons Hainaut, Matériaux Polymères et Composites, Place du Parc, 20, 7000 Mons, Belgium

^bENITIAA-INRA, Unité de Sensométrie et Chimiométrie, BP 82225, 44322 Nantes Cedex 03, France. E-mail: bertrand@enitiaa-nantes.fr

^cIngénierie des Matériaux Polymères / Laboratoire des Matériaux Macromoléculaires, INSA de Lyon (CNRS, UMR 5627), 20 Avenue Albert Einstein, F-69621 Villeurbanne Cedex, France. E-mail: Jerome.Dupuy@insa-lyon.fr

^dLaboratoire des Matériaux Polymères et des biomatériaux, UCBL, (UMR CNRS 5627), 43, bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France. E-mail: gilbert.lachenal@univ-lyon1.fr

Introduction

Knowledge of the reaction extent and rheological properties are critical for optimal control of polymer network structure during polymer processing. In this article we present a new coupling system that allows simultaneous Fourier transform near infrared (FT-NIR) transmission spectroscopy and rheological measurements. This system has been tested for monitoring the isothermal cure (polymerisation) of a polyurethane formulation.

Chemical processes depend on physical parameters, which play an important role in determining the characteristics of the final product. Temperature, pressure and flow rate are the most relevant process parameters, but they do not supply the necessary chemical information that is essential for process control. More sophisticated techniques must be used for collecting chemical information. In recent years considerable progress has been made with the development of dielectric measurements. Many studies dealing with the monitoring of reactive systems by *in situ* dielectric spectroscopy have been published. The overall extent of a given reaction may be calculated from impedance measurements. However, the nature of the observed correlations remains phenomenological. Direct and

theoretical correlations between dielectric values and gelation have not been proven, although very good agreement between dielectric results and rheological measurements have been observed.

Gelation and vitrification are the most important structural transitions for the processing of thermosets or composites because they govern both the injection time and the demoulding time. They can be monitored using rheological measurements, i.e. dynamical rheometers or Couette rheometers. However, neither dielectric spectroscopy nor rheological or dynamic mechanical analysis can provide the information necessary for understanding the chemical mechanisms during the cure cycle. Chemical sensors can provide additional real-time information about the chemistry that enables the process safety and efficiency, the quality of the final product and its consistency to be improved.

The large anharmonicity of C–H, N–H, O–H or S–H groups leads to absorption bands in the NIR region. NIR spectra are often used in conjunction with multivariate data analysis techniques (chemometrics). Multivariate analysis techniques enable the exploitation of complex and large sets of spectra that can lead to improvements in both the

analysis time and reliability. These techniques are now commonly accepted as routine data analysis methods in process analysis. As a rapid and non-destructive method, NIR spectroscopy has been successfully used in various fields for the characterisation of polymers. The coupling of a spectrometer with a fibre optic probe provides a means to a very easy spectroscopic measurement and allows for on-line control of a process.

The combination of a stress–strain test and various optical methods to give the so-called “rheo-optical methods” has been proposed as a way to characterise and to monitor the structural changes of polymers.¹ In the late 1970s, rheo-optical Fourier transform infrared (FT-IR) spectroscopy emerged for studying the deformation and the relaxation of solid polymers. Spectroscopic parameters related to the conformation, crystallisation or orientation of the polymer can be simultaneously monitored in both deformation and relaxation processes. In addition, 2D correlation spectroscopy may be applied for analysing data obtained in rheo-optical FT-IR experiments. Nevertheless, rheo-optical FT-IR experiments are restricted to thin films because of the large absorptivities in the mid-IR range. Rheo-optical FT-Raman

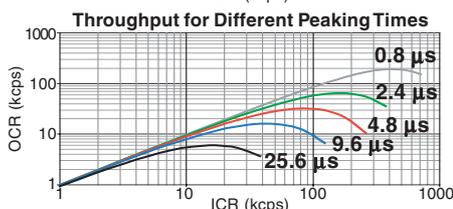
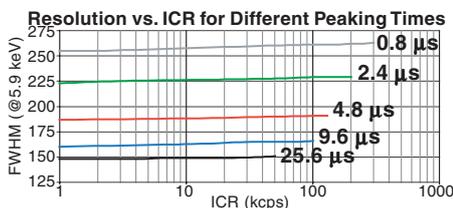
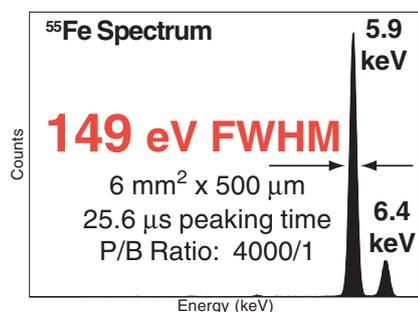
spectroscopy and FT-NIR instruments coupled to optical fibres have been successfully applied to measurements of thick polymeric solid materials. The use of dynamic temperature scanning FT-IR and dynamical rheometry provided new insights into the cure of blocked isocyanates. Although, in this case, the experiments were carried out separately.² The sample studied by FT-IR spectroscopy was a thin film cast from solution onto a NaCl window. The cure behaviour of a thin film can be different from a bulk polymer, surface interactions may catalyse or inhibit some chemical reactions and, in addition for thicker samples, it is often observed that there are significant chemical differences between the skin and the bulk of the PU sample. To our knowledge, no attempt has been made to carry out simultaneously the acqui-

sition of NIR spectra and the dynamic measurements of viscosity of liquid polymers during their polymerisation. This overcomes any problems of reproducibility related to using different sample geometries when comparing measurements from two distinct experiments.

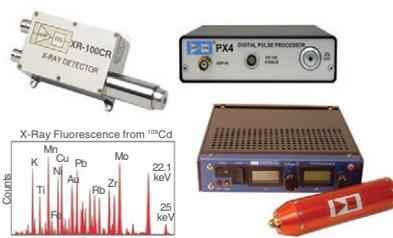
As mentioned above, during a thermoset cure, two main transitions take place. The first is gelation. Gelation occurs during a critical time interval in which the average molecular weight and the viscosity undergo a sudden increase: before gelation the system behaves like a liquid (low viscosity), after gelation it behaves like a rubbery solid (infinite viscosity). The viscosity η and the modulus G can be measured by dynamical rheology, for different frequencies of solicitation. For such viscoelastic systems, the modulus G is defined as a complex modulus (noted

G^*) by the relation $G^* = G' + iG''$, where G' is the elastic modulus (representative of the elastic behaviour of the polymer) and G'' is the loss modulus (representative of the viscous behaviour of the polymer). Before gelation, the polymer is a viscous liquid (i.e. $G' = 0$) while at the point of gelation viscoelastic behaviour occurs ($G' \neq 0$). This simple criteria developed for gelation can be considered to be the time where the elastic modulus is no longer zero, or the time where the elastic modulus becomes equal to the loss modulus ($G' = G''$). However, for viscoelastic polymers, G' and G'' are frequency dependent so that gelation times measured depend on the applied frequency. Therefore, more elaborate theories³ have been developed for correlating dynamical measurements and gelation. It is now accepted that, for

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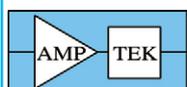


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simple systems, the ratio $G''/G' = \tan \delta$ (δ is called the loss angle) becomes independent of the frequency at the gel point. Unfortunately, for our formulation containing a prepolymer (already viscoelastic even before gelation) such a criterion cannot be applied. In our case, the gelation will be determined as the time where $\tan \delta = 1$, at a constant frequency.

The second important transition is vitrification. It appears when the glass transition, T_g , of the reactive system reaches the cure temperature. Before vitrification, the system is a rubber solid, while after vitrification, the polymer becomes a vitreous system where molecular motions are severely restricted, so that the chemical reaction tends to stop. Such a transition occurs with a characteristic mechanical relaxation (peak on the $\tan \delta$ curve), which depends on the frequency. After vitrification, the polymer modulus increases greatly (several decades) so that monitoring of the modulus can be used to measure the vitrification time (but this measurement is also frequency dependent). Vitrification does not take place, however, for all formulations: if the final glass transition of the thermoset is always lower than the cure temperature, the system will never vitrify. In this case, the chemical reaction can proceed until completion, because the mobility of the reactive species will never be decreased by vitrification. For our formulation, the final T_g is below room temperature (the polymer is a rubber) so that, for cure cycles at ambient temperature (or higher), no vitrification will occur.

Experimental NIR spectroscopy

The NIR spectra, in the range 4500–10,000 cm^{-1} were recorded with a NIR spectrophotometer, equipped with a tungsten halogen source, a quartz beam-splitter and an InGaAs detector. All spectra were collected with a spectral resolution of 8 cm^{-1} and four spectra were recorded per minute (15 scans per spectrum). Two low-OH optical fibres (1 mm diameter, 4 m long, equipped with SMA connectors) were used. Principal Component Analysis (PCA) was carried out using in-

house software in the MATLAB[®] environment.

Rheology

The rheological measurements were made using a Rheometrics RDA II. The measuring system consisted of two parallel 40 mm diameter quartz plates. A sinusoidal deformation (10 rads^{-1}) with a variable angular speed ω was applied to the upper plate and a transducer measured the resulting torque. The frequency covers the range from 0.01 to 200 Hz. It was also possible to carry out tests in a multifrequency mode. The thickness of the sample (which corresponds to the optical pathway of the NIR beam) can be varied by a vertical adjustment of the upper plate.

Reactants

The thermoset system studied is a blend of two main components, a polyol polytetramethylenetherglycol (PTMEG) and a prepolymer based on 4,4'-diphenylmethandiisocyanate (MDI). The functionality is 2 for the polyol (according to NFT 52-112) and 2.2 for the isocyanate (NFT 52-132). 0.05% of dibutyltin dilaurate (DBTDL, Fluka) was mixed with polyol in order to catalyse the reaction.

Simultaneous experiments

An experimental device coupling a NIR spectrometer and a dynamical rheometer was developed by the authors and is shown in Figure 1.

This system is based on the following special features:

- (i) In order to allow spectroscopic measurements in transmission, the light

aluminium parallel plates of the rheometer were replaced by heavier quartz plates manufactured by Hellma (France).

- (ii) The NIR beam from the spectrometer passes through an optical fibre towards a collimator lens. The beam is reflected by a parabolic mirror onto the sample. After transmission through the sample, the beam is reflected by another parabolic mirror and focused by a lens, and then returned to the spectrometer.
- (iii) The position of the mirrors and lenses are adjustable in order to minimise energy loss.

Results and discussion

We first checked that the increased weight of the plates (quartz plates were heavier than aluminium plates) did not modify the rheological measurements. It was observed that the measurements for the formulation studied were not significantly disturbed up to a 100 Hz solicitation. New calibrations of the rheometer would need to be performed if the heavier plates modified the rheological results.

Figure 2 shows the NIR spectra obtained before and after SNV (standard normal variate) pretreatment. The quality of the NIR spectra was slightly lower than those obtained in a static mould. These spectra were first analysed using the Lambert–Beer law on the band assigned to the isocyanate function (4677cm^{-1}). The determined reaction extent is presented in Figure 3. Then quantitative analysis was performed using multivariate analysis.

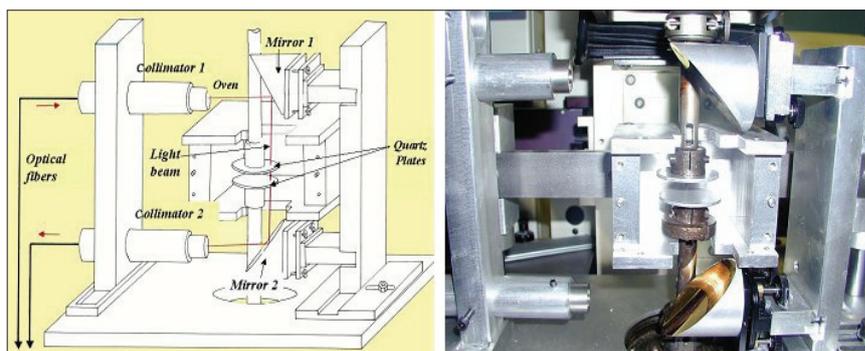


Figure 1. Experimental design for the simultaneous NIR spectroscopic and rheological measurements.

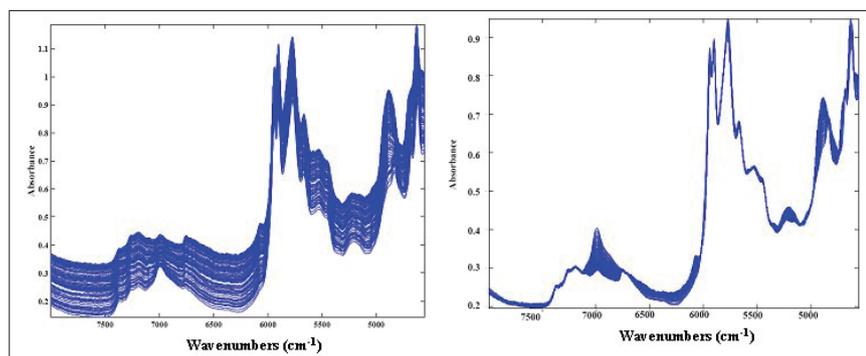


Figure 2. Overlays of (left) raw NIR spectra during the PU reaction and (right) spectra after SNV pre-treatment.

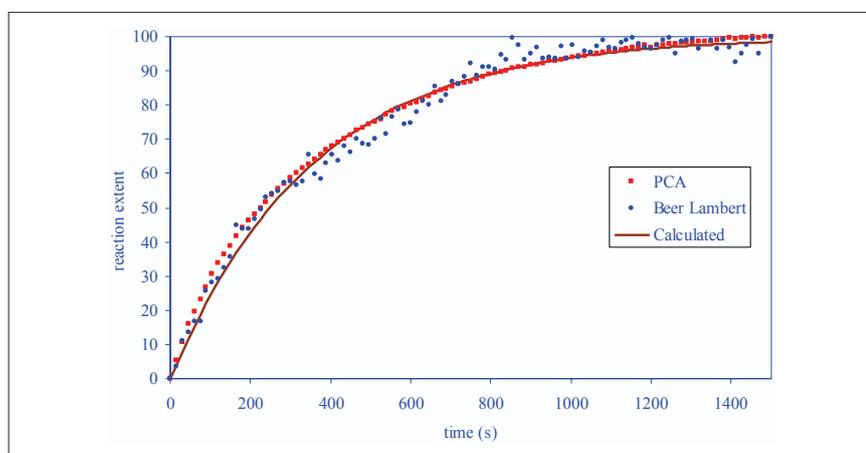


Figure 3. Calculated and measured (Beer–Lambert and PCA) reaction extents as a function of time.

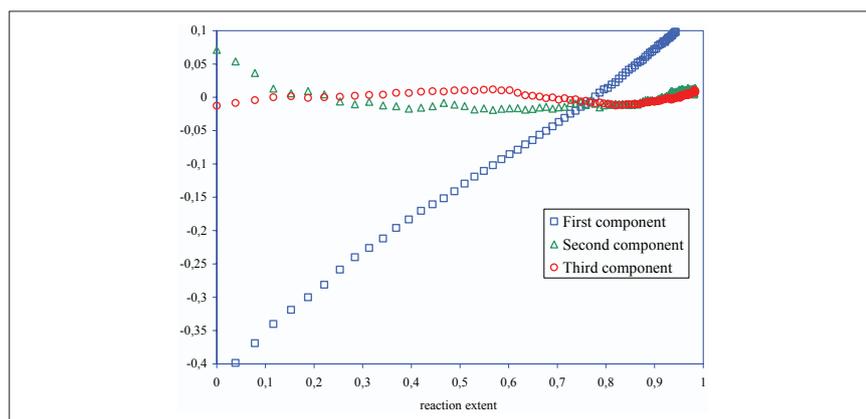


Figure 4. Principal components PC1, PC2 and PC3 as a function of reaction extent.

Principal component analysis (PCA) was first performed using all spectra over the $4000\text{--}7000\text{ cm}^{-1}$ spectral range. After removing any outliers, PCA was undertaken again. The first component contained about 98% of the spectral variance. It can be used to calculate

the conversion by normalising its values between 0 and 1.⁴ The reaction extent calculated using the Beer–Lambert law and the one determined using the first component of the PCA performed on the $7000\text{--}4000\text{ cm}^{-1}$ region are in very good agreement (Figure 3). The main

difference is the high scatter on the curve calculated using the Beer–Lambert law.

In order to validate our quantitative approach based on the spectroscopic data, a kinetic model was developed as described in a previous paper.⁴ This kinetic model makes it possible to compute the reaction extent as a function of time (even if the temperature varies), as shown in Figure 3. It is then possible to plot, for a given experiment, the calculated data using the kinetic model versus spectroscopic or PCA data. So that one can plot the 1st, 2nd and 3rd principal components of the PCA as a function of the calculated reaction extent. It can be observed in Figure 4 that the first principal component is merely linearly correlated with the reaction extent, which is not the case for the second and third components. As already observed in Figure 3, the very good agreement between the three curves validates the use of the PCA without any calibration. This kind of result had been already discussed by Maeda *et al.*⁵ They observed that if the spectral variations are very regular, the signal-to-noise ratio is high and the changes in baseline are small, the loading plot of factor 1 should become very similar to the difference spectrum. This suggests that the plot of this first component as a function of time may be representative of the evolution of the conversion. PC2 and PC3 may be representative of the change of hydrogen bonding and slight change of temperature during the cure.

Figure 5 illustrates the viscosity measurements during the same experiment. In this case, the gel time (corresponding to the crossover between G' and G'' curves) is about 1050s, which corresponds to 94% reaction extent (close to the theoretical value of 92% obtained with the Macosko–Miller law taking into account the functionality of the two reactants). For this formulation, no vitrification occurred because the polymer is a rubber at ambient temperature.

But the real advantage of this device is to be able to plot the rheological measurement (for instance the elastic modulus G') as a function of the conversion (see Figure 6). It should then be possible to use such experimental data (that should be obtained at various

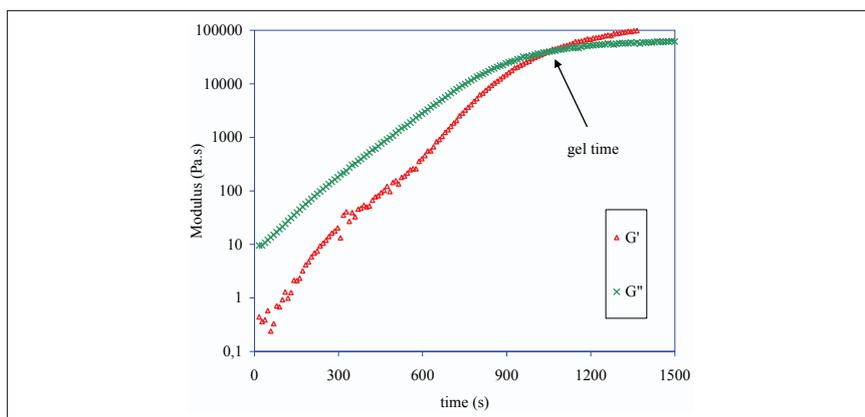


Figure 5. Elastic and loss modulus as a function of time.

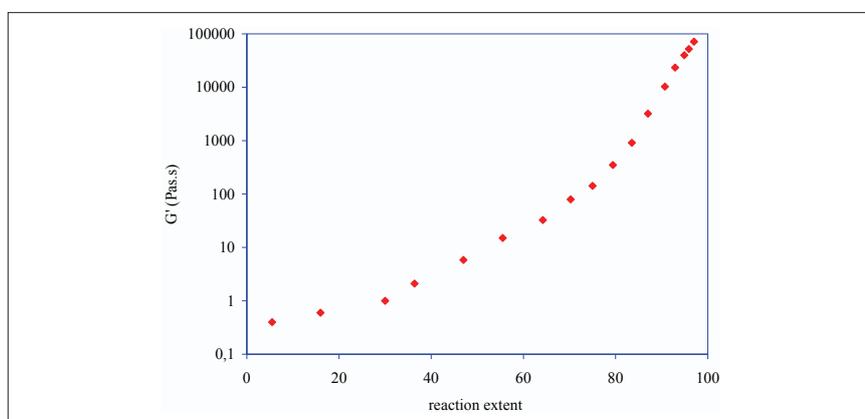


Figure 6. Elastic modulus as a function of reaction extent obtained in a single experiment.

experimental temperatures) to make a rheokinetic model in order to model the evolution of the viscosity during the filling of a mould.

Conclusion

This article demonstrates the feasibility of monitoring, in a single experiment, the

cure of a polymer by NIR transmission spectroscopy during rheological measurements in order to plot the rheological measurement as a function of the conversion. More experiments need to be performed at different temperatures in order to identify a rheokinetic model

for the polymer and to get a better understanding of the reaction.

The proposed multi-detection approach might be a valuable tool for the process engineer who needs to evaluate on-line the quality and the durability of moulded objects. These techniques make it possible to control *in situ* the viscosity changes during polycondensation and leads to a better monitoring of the polymer transformation. A better understanding and control of the process would eventually result in a reduction of the production costs and the energy consumption.

Acknowledgement

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