Film Formation of 2K Waterborne Polyurethane Systems

By **Philippe Olier**
Perstorp

Imke Ludwig, **Mathias Kind**, **Wilhelm Schabel**, and **Joachim Krenn**,
Institut für Thermische Verfahrenstechnik

Steve Meeker
Rhodia

INTRODUCTION

Two-pack (2K) waterborne polyurethanes are increasingly used in coatings technologies. Examples of such coatings can be encountered in many different fields including metal coatings (for railway carriage, car refinish...), wood coatings (e.g., parquet flooring, furniture) or soft-feel coatings for plastic in the automotive industry. The benefits brought by waterborne technology can explain this growth. It is fully compliant with the new volatile organic compounds (VOC) regulations and contributes to better health and safety conditions for both workers and end users. Of course, switching from solvent-based to waterborne technology implies technical challenges. Many improvements have been achieved during the past years to develop waterborne systems that can compete with solvent-based coatings. In the case of polyisocyanates, for instance, the ease of mixing in the formulation and the control of side reactions with water have been greatly improved by using hydrophilically modified polyisocyanates.

However, a deeper understanding of the film formation mechanisms and the impact of different key parameters is still essential in order to finetune the formulation and achieve optimal results. Many techniques have been used to investigate these aspects such as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), or even mechanical measurements.[1-3] Confocal Raman spectroscopy has also been widely used but only a few reports mention its use for the investigation of aqueous systems.[4]

Here we present the use of Inverse Micro Raman spectroscopy (IMRS) in order to investigate the drying behavior and film composition of 2K waterborne polyurethanes.

INVESTIGATION OF 2K WATERBORNE POLYURETHANE SYSTEMS USING IMRS: PRINCIPLES

The bands of a Raman spectrum represent the frequency shift due to the interaction of a laser beam with the chemical bonds of a molecule. Therefore, Raman spectra are characteristic for the chemical species. IMRS is a non-invasive technique that allows investigation of dynamic processes like drying or chemical crosslinking.

Two-pack waterborne polyurethane coatings are chemically crosslinked systems; their Raman spectrum will change not only as a result of water evaporation during drying, but also due to the formation of new chemical bonds, as shown in *Figure* 1.

The reaction between a polyol and polyisocyanate leads to the disappearance of N=C double-bonds and

This paper was published in the European Coatings Journal, *March 2008, and is reprinted courtesy of Vincentz Network.*

the formation of N–H groups. Unfortunately, both bonds display only weak Raman vibrational bands and, as long as water is present, the N–H band is hidden by the broad band from O–H bonding. Fortunately, crosslinking takes a much longer time than the drying of the film, which makes it possible to study crosslinking after the water has evaporated.

QUANTITATIVE EVALUATION

Composition and chemical crosslinking can be followed by the changes in the respective peak height between 2500 cm^{-1} and 3800 cm^{-1}. The Raman intensity can be expressed by equation (1), which shows a linear dependence of the Raman intensity with the concentration of the chemical species under investigation.[5]

$$I_i = c_i \, (\partial\sigma_i / \partial\Omega) \, \tilde{M}_i^{-1} \, I_0 \, N_A \, V \, C \, F^{-1} \Omega_{obs} \quad (1)$$

where:

$\partial\sigma/\partial\Omega$	=	differential scattering cross-section
c_i	=	concentration of component i
	=	molar mass of component i
$\tilde{M}_i$	=	Avogadro constant
V	=	sample volume
Ω_{obs}	=	observation angle of objective
F	=	projection screen of the detector aperture onto the sample volume
C	=	constant, considers the detector efficiency
I_0	=	intensity of incident laser light

All experimental factors can be neglected if we do consider the relative concentration of a compound to a fixed (non-volatile) reference compound. In our case, the polyol is the reference and the relative Raman intensity can be expressed as follows:

$$I_i = c_i \underbrace{(\partial\sigma_i / \partial\Omega) \, \tilde{M}_i^{-1}}_{\text{specific}} \underbrace{I_0 \, N_A \, VCF^{-1}\Omega_{obs}}_{\text{experimental}}$$

$$\frac{I_i}{I_P} = \underbrace{\left(\frac{c_i}{c_P}\right)}_{X_i} \underbrace{\left(\frac{\partial\sigma_i / \partial\Omega}{\partial\sigma_P / \partial\Omega} \, \frac{\tilde{M}_i^{-1}}{\tilde{M}_P^{-1}}\right)}_{K_{i,p}} \left(\frac{I_0 \, N_A \, VCF^{-1}\Omega_{obs}}{I_0 \, N_A \, VCF^{-1}\Omega_{obs}}\right)$$

Or $$\frac{I_i}{I_p} = X_i \, K_{i,p}$$

X_i is the concentration ratio of component i to the polyol and $K_{i,p}$ is a proportionality factor that can be obtained from the Raman spectrum of one single calibration sample of known concentration. K is specific for the system under investigation.

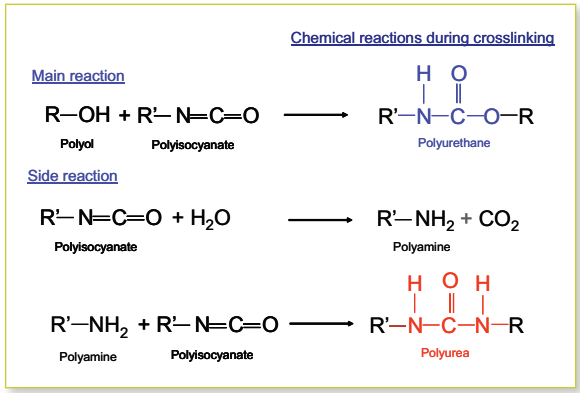

Figure 1—Main chemical reactions in 2K waterborne polyurethane systems.

EXPERIMENTAL

Inverse Micro Raman Spectroscopy (IMRS) Experimental Setup

The IMRS device is schematically represented in *Figure* 2. With IMRS, the local concentration of different species can be determined in thin polymer films (up to 60–80 µm) online during drying with a high space and time resolution of 2-3 µm and 1–2 sec.

Due to the inverse setup, the drying conditions, i.e., air humidity, drying temperature, and air velocity above the sample film can be adjusted. During a film drying experiment, a monochromatic, parallel laser beam is focused into the sample film by a system of mirrors and optical lenses. Within the polymer film, the laser light is scattered—elastically (Raleigh) and inelastically (Raman)—due to the interaction of the laser beam with the molecules of the sample. Returning by the same path, only the inelastically scattered light, which is the Raman light, can pass the interference pattern of the notch filter. The high spatial resolution is the result of a confocal pinhole which is optically coupled with the objective's focus.

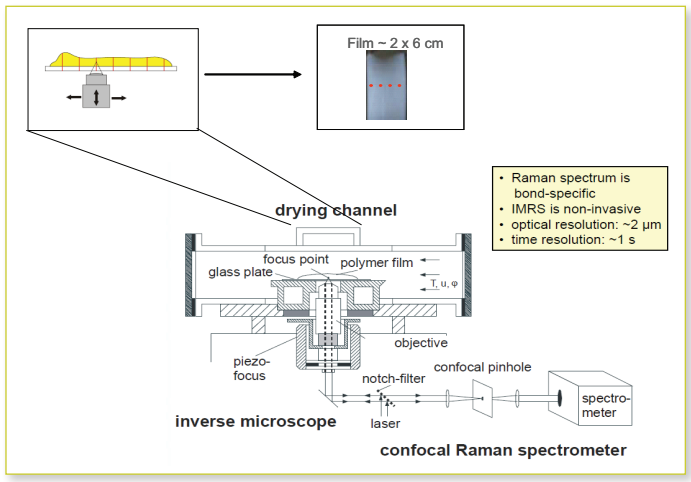

Figure 2—Experimental setup of IMRS.

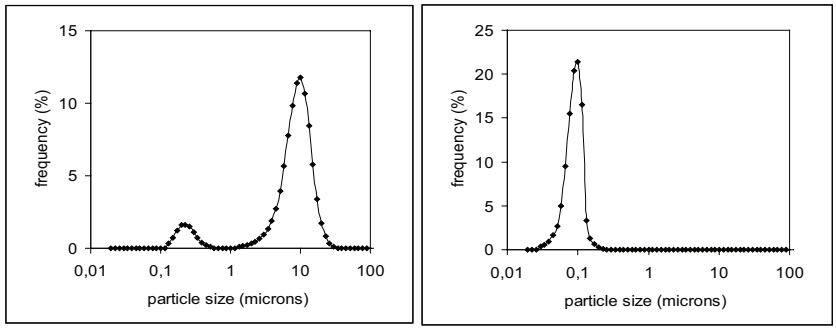

Figure 3—Distribution of the particles size of a 2K waterborne polyurethane composition regarding the initial dry content of the polyol. Left: case A: ~42% dry content = poor emulsification; Right: case B ~36% = good emulsification.

Table 1—Characteristics of the Polyol

Dry Content (%)	Particle Size (D 90- µm)	OH value (mg KOH/g)
42	0.105	130

Table 2—Characteristics of the Hydrophilic Polyisocyanate

Dry Content (%)	Viscosity (mPa.s)	NCO Content (%)
100	~ 3000	18.7

Table 3—Relative Weight Composition of the Formulators Studied

Water[a]	Polyol	Hydrophilic Polyisocyanate
1.8	1.0	0.7

(a) *The amount of water includes both dilution water and water coming from the polyol.*

Materials

The system which was studied is based on the reaction of an acrylic polyol and a hydrophilic polyisocyanate. Characteristics of the products are given in *Tables* 1 and 2.

The NCO/OH ratio used for the study is 1.4 in order to take into account the side reactions with water. Weight ratios shown in *Table* 3 were used for all experiments.

RESULTS

Influence of the Dry Content of the Polyol

In the conventional way of formulating a 2K waterborne polyurethane coating, part A is prepared first. It contains polyol, additives, pigments, and additional water. Then, part B consisting of the hydrophilic polyisocyanate [as such or further diluted with organic solvent(s)] is added and mixed

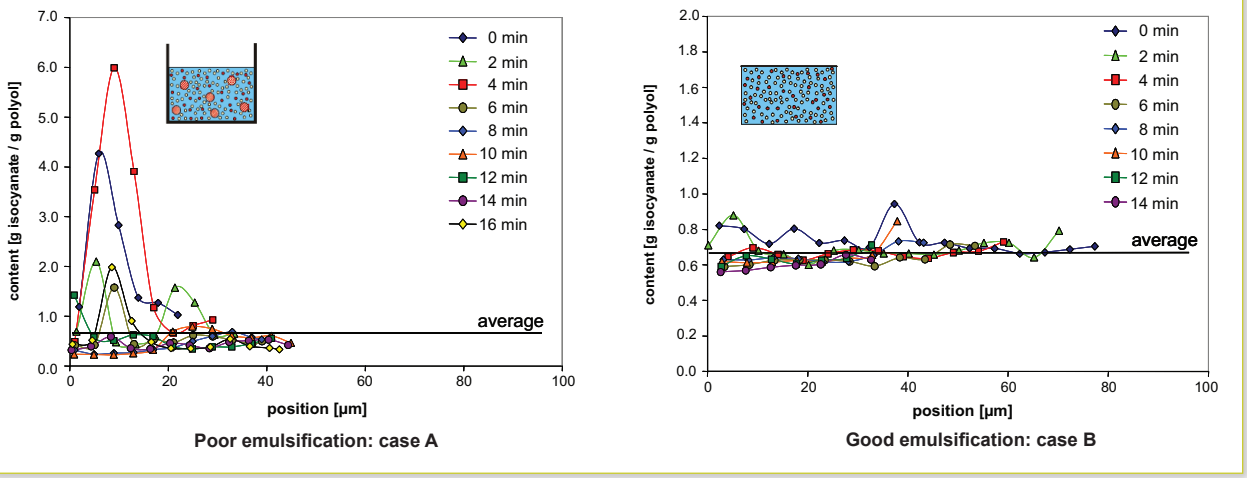

Figure 4—Evolution of the ratio isocyanate/polyol regarding the preparation. Case A = poor emulsification; Case B = good emulsification.

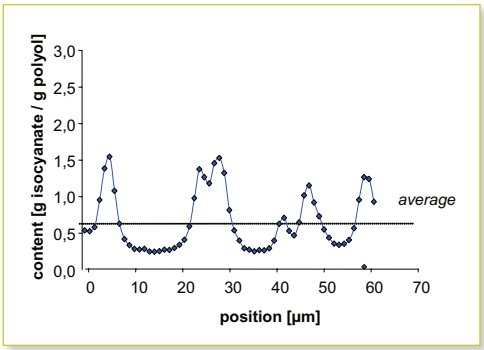

Figure 5—Evolution of the ratio isocyanate/polyol in a polyurethane film (case A – poor emulsification after phase inversion).

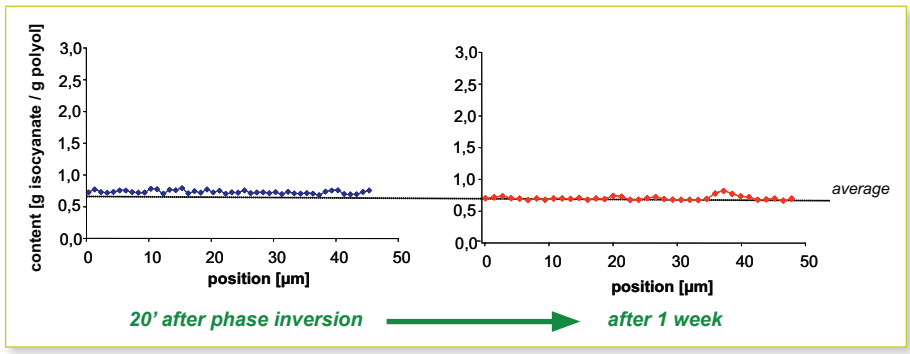

Figure 6—Evolution of the ratio isocyanate/polyol in a dry polyurethane film (case B : good emulsification after phase inversion).

to the part A. To bring the formulation to the desired viscosity for application, water can be added as a last step,.

The quality of the final coating is greatly influenced by the characteristics of the components used in the formulation. One key parameter is the dry content of the polyol, as can be seen in *Figure* 3 where the particle size distribution of the mixture (polyol, polyisocyanate, and water), as recorded by laser light scattering technique for two different initial dry contents of the polyol, are reported.

The differences in the particle size distribution of the initial emulsions may result in differences in the coatings structure that can be detected by IMRS.

Investigation of Film Drying and Composition

When monitoring the polyisocyanate to polyol ratio over time during drying (*Figure* 4), the impact of the initial dry content of the polyol on the film morphology is clearly highlighted. For a formulation prepared with a polyol with an initial dry content of 42% w/w, large heterogeneities of a size up to 20 µm are observed in the film from the very beginning of drying. Within these areas, the content of polyisocyanate is higher than in the surrounding film. During drying, these heterogeneities are free to move in and out of the laser focus. A possible driving force for this could be a lateral mass flow induced by horizontal inhomogeneous film drying which is typical for aqueous dispersions and emulsions.

On the contrary, in the case of pre-diluted polyol (36% w/w) where a narrow distribution of the particles sizes is obtained ("good emulsification"), this effect is not seen and the content of polyisocyanate is close to the theoretical value.

After the phase inversion, the differences observed during water evaporation can still be seen. In the case of a polyurethane film prepared with a nondiluted polyol (case A), a heterogeneous distribution of the polyol and the polyisocyanate through the film thickness is clearly observed, as shown in *Figure* 5. Measurements were made 20 min after the phase inversion so that most of the water has evaporated from the film.

On the contrary, in the case of a pre-diluted polyol (case B), a constant repartition of the components in the dry film is observed, either just after the phase inversion or one week later (*Figure* 6).

If we perform vertical IMRS scans at different horizontal positions of the film (step size horizontal direction = 2 mm, width of the film is 1.8 cm), we can get the composition of a cross section of the film across its total width and thickness (two-dimensional distribution of components in the film). Accumulation of polyisocyanate as well as the relative level of crosslinking can be depicted. *Figure 7* presents the measurements for a one-week-old polyurethane film made with undiluted polyol.

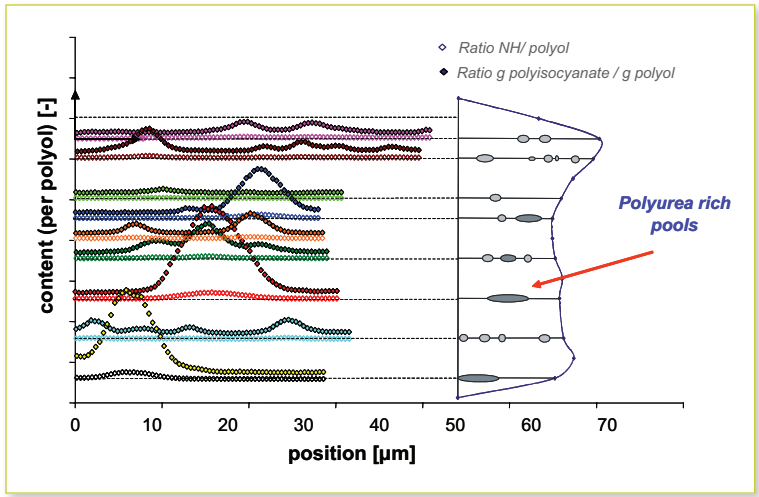

Figure 7—Two-dimensional map of a polyurethane crosslinked film (case A good emulsification with undiluted polyol).

Table 4—Gloss Value of the Films Regarding the Dilution Level of the Polyol

Initial Polyol Concentration (wt %)	Gloss 20° (%)
42	17
38	78
35	89
32	88

In *Figure* 7, high ratio polyisocyanate/polyol areas can be seen along the axis of measurement, indicating a heterogeneous composition of the film. As already highlighted with quantitative measurements, the local value can be twice the average ratio. As far as crosslinking is concerned, the Raman technique cannot distinguish between the NH groups coming from polyurethane and those coming from the polyurea. However, it is remarkable that the higher relative intensity of the NH band coincides with a higher polyisocyanate content. Taking into account the fact that there is a lack of polyol and that two NH bonds are formed with polyurea instead of one for polyurethane, it is likely that these NH rich regions result from urea formation. In a 2D picture of the dried film, indication of high local concentration of polyisocyanate can be plotted as gray zones along the depth of the film (*Figure* 7, right). Black areas indicate where the NH signal is stronger, which can be attributed to the presence of polyurea.

In the case of a good emulsification with diluted polyol, the 2D map of the film shows no indication of high local concentration of polyisocyanate.

These results obtained by IMRS can be compared with the macroscopic application properties of the dry films. Table 4 shows the evolution of the gloss value regarding the initial dilution of the polyol

In the case of the system which has been studied, the large particles size distribution of the emulsion is directly responsible for heterogeneities in the dried film. As a consequence, the gloss of the coating is also affected by the dilution level. This is the reason why particular attention should be paid to the ease of mixing of the hydrophilic polyisocyanate to ensure optimum properties of 2K waterborne polyurethane coatings.

CONCLUSIONS

Inverse Micro Raman spectroscopy has been proven to be a very efficient tool in the investigation of both drying and crosslinking of 2K waterborne polyurethane formulations. It can provide detailed information on the composition and heterogeneities of the film both during the drying process and the curing process. IMRS can be considered as a helpful tool to understand the impact of the ingredients and to finely tune the formulation. GT

References

1. Zhou, X., Tu, W., and Hu, J., *Chinese J. Chem. Engin.* (2006).
2. S. Ito, Tawa, *Colloid & Polym. Sci.*, Vol. 283, No. 7, 731-737 (2005)
3. Cakic, S., Lacnjevac, C., Rajkovic, M.B., Raskovic, L., and Stamenkovic, J., *Sensors 2006*, 6, 536-545 (2006).
4. Ludwig, I., Schabel, W., Castaing, J.C., and Ferlin, P., *American Institute of Chem. Engin. J.*, Vol. 53, 549-560 (2007).
5. H Moritz, H. and VD Ingenieure, V.D., *VDI Verlag* (1999).
6. Schlünder, E.-U., *Drying Technology*, Vol 22, 1517–1532 (2004)

AUTHORS

Philippe Olier—Perstorp, Perstorp Research Center of Lyon, 85 rue des frères Perret, F-69192 Saint Fons Cedex.

Imke Ludwig, **Mathias Kind**, **Wilhelm Schabel**, **Joachim Krenn**—Institut für Thermische Verfahrenstechnik, Universität Karlsruhe (TH), Kaiserstrasse 12, D-76128 Karlsruhe.

Steve Meeker, Rhodia, Research & Technologies Center of Aubervilliers, 52, rue de la Haie Coq, F-93308 Aubervilliers.