



Autumn 2005

Welcome to the Raman Update, produced by HORIBA Jobin Yvon's Raman Team, to provide our customers, colleagues & friends with up-to-date information in the field of Raman Instrumentation and Application.

See us next at:

**Fullerene  
Nanotubes General  
Symposium**  
7th - 9th Jan '06  
Japan

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## Concentration profile measurements in polymeric coatings during drying by means of Inverse-Micro-Raman-Spectroscopy (IMRS)

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There are many important industrial applications for solvent and waterborne coatings such as foils for LCD panels, varnishes, adhesives, paper coatings and even bio-medical applications such as transdermal patches. Coatings on these products and devices are often formed from dissolved coating components that are applied to the substrate material and then subsequently dried to create the desired end material.

The drying process of the coating often determines the performance and quality of the resulting product. In order to design and control such coating and drying processes, online moisture and solvent profile measurements during the coating formation become of significant interest.

The University Karlsruhe (TH) has applied a measuring technique called Inverse-Micro-Raman-Spectroscopy (IMRS) to a Confocal Raman Spectrometer (LabRAM INV - HORIBA Jobin Yvon) which was manufactured whereby the standard upright LabRAM microscope was replaced by an Inverted Microscope sampling system (in this case an Olympus IX50). With this arrangement, a free space was created above the sample which

allowed a greater flexibility in sampling orientation and in the accommodation of environmental control cells. In this case a special cell incorporating an air flow channel was installed to enable the characteristics and kinetics of the drying of a polymer coating to be studied in-situ.

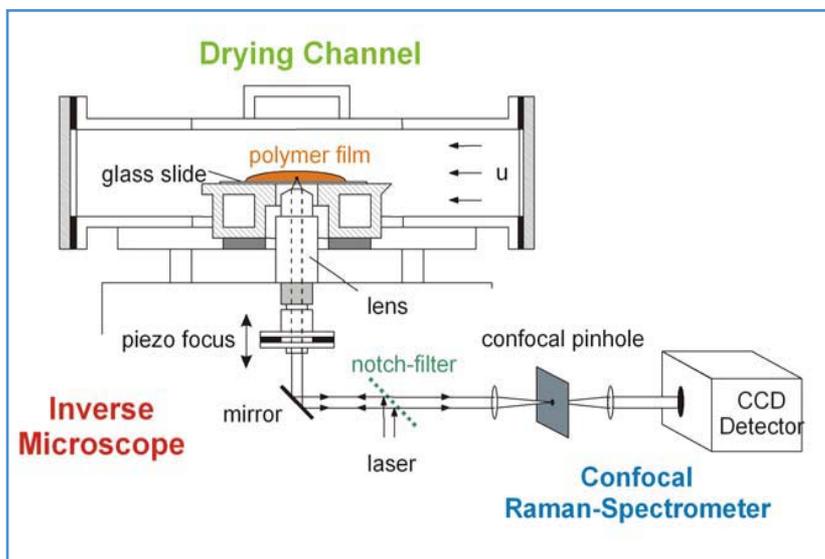


Figure 1 Inverse-Micro-Raman-Spectroscopy (IMRS), a new technique to measure concentration profiles in polymer coatings and films, e.g. during a drying process.

The preliminary work obtained in this collaboration showed many advantages in the use of Raman spectroscopy for the study of drying characteristics in coating materials. Subsequently this has led to a much larger project funded by the DFG (German Research Foundation) on "Thin-Film-Drying".

The work has most recently revealed that the IMRS technique enables the measurement of solvent content within thin films online, in-situ and with a high spatial resolution of up to 1  $\mu\text{m}$ . Temporal and kinetic resolution of up to 0.5 s is also obtained through this method and quantitative measurements can be acquired by the use of specific calibration procedures.

### Instrumentation

The modified LabRAM INV used in these studies utilises the standard backscattering Raman geometry whereby the laser beam is transferred through the optical microscope and irradiates the sample. The backscattered light is then collected with the same objective and transmitted into the integrated spectrometer. Since the inverted geometry is provided by the LabRAM INV, the sample is illuminated from below with the focused laser spot moved into the sample volume by means of a piezo Z-axis nano-positioning system. Translation of the piezo device enables data to be collected at a depth of up to 200 microns.



Figure 2 The HORIBA Jobin Yvon LabRAM INV

The design of the rest of the system is then the same as that for the more conventional Raman microscope with the scattered light directed through a holographic notch-filter to remove the Rayleigh scattered light and transmitting the Raman signal and the spectrometer with a air cooled detector CCD.

The confocal pinhole within the system is responsible for the control of the spatial filtering and ensuring that only light

from a controlled and desired sampled volume be detected. The use of such a precise spatial and depth control mechanism is important with such measurements. Without such a device spectral artifacts and components from scattered light that is generated from above or below the desired position within the sample would also be detected and degrade the quality of data.

The difference in the refractive index (RI) caused by the air gap between sample and objective is minimised by using an objective with a high NA and an immersion oil (placed between the glass cover slip and objective). The immersion oil has the same refractive index as the glass and a similar one to the polymer and so minimises the differences in the refractive indices for these media. The closer the refractive indices of immersion oil, glass and sample, the better is the spatial resolution one obtains inside the polymer film.

For the sample preparation a liquid polymer solution is cast on a thermostated copper plate with a glass slide in the centre of the plate. Detailed information of this procedure can be found in reference [1,2].

### Investigations with solvent borne coatings

In figure 3 the Raman spectra in different layers of a solvent borne polymer coating during drying are shown.

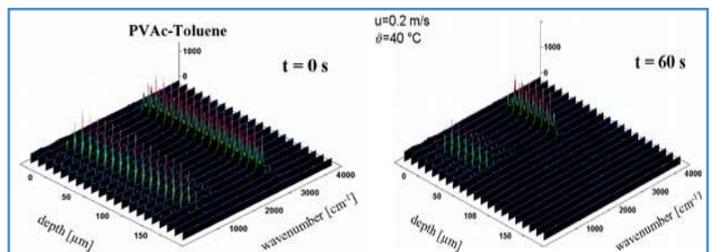


Figure 3 Raman spectra at different depths of a polymeric solvent coating (polyvinylacetate-toluene) during the drying process, measured with the IMRS-technique

(left): at the beginning of a drying process ( $t = 0\text{ s}$ , initial film thickness: 150  $\mu\text{m}$ )

(right): after  $t = 60\text{ s}$  of drying. The solvent ( $\approx 1010\text{ cm}^{-1}$ ) evaporates and the film shrinks to 50  $\mu\text{m}$ .

In order to obtain quantitative solvent content data, calibration measurements are needed. A calibration can be easily performed by acquiring Raman spectra of a calibration set of samples prepared with different but known concentrations in sealed optical cells. The calculated solvent concentration profiles from measured data (like the ones displayed in figure 3) are shown in figure 4. The symbols indicate the locally determined solvent content (gram solvent per gram polymer) in the film during the drying process. The lines are simulation results from drying

model calculation. Simulation results can be fitted to the measured values in order to predict the drying behaviour of technical processes.

In addition, the shrinkage of the coating surface is also plotted. Towards the end of the drying process, steeper concentration profiles could be measured as a dry skin at the surface is formed. The diffusion of the solvent through this skin controls the entire drying process and even after 3 days of drying a significant solvent content underneath the film surface could still be measured. This phenomenon, in the coating industry, known as "skinning", could be shown here for the first time experimentally in thin film coatings. Further investigations with the measurement technique and more detailed information about the results can be found in reference [3].

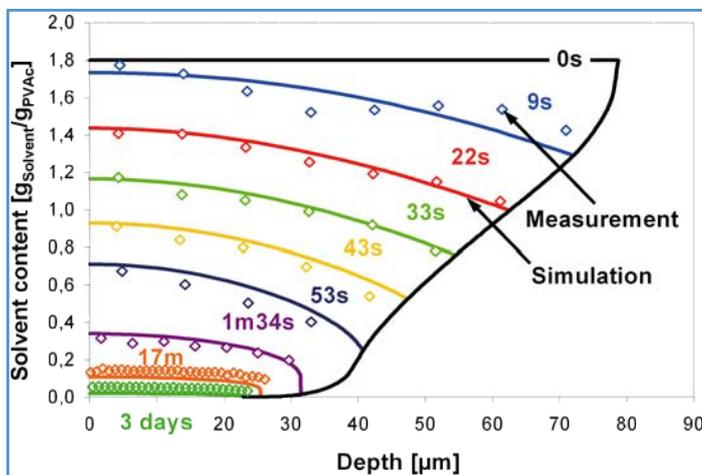


Figure 4 Measured concentration profiles in a polymer solution (polyvinylacetate-toluene) during the drying process (symbols). The quantitative solvent contents (g solvent/g polymer) in the film are determined from the raw data (e.g. figure 3) by using a measured calibration factor [1].

### Investigations with Water based Coatings

A major issue for the coating industry is to develop new waterborne latex systems to replace the more common solvent based polymeric coatings. Large scale applications such as paints, adhesives and other applied coatings would benefit from the use of systems with a lower environmental impact, but which match the properties and drying behaviour (shown in figure 4) of solvent-based polymeric films. Waterborne decorative topcoats generally still show inferior application properties compared to solvent-based paints and the quality of the final polymer film is often characterised by a poorer finish, or micro-cracking, and poorer resistance to dissolution by water.

A variety of physicochemical parameters such as a polymer's glass transition temperature ( $T_g$ ), the composition of

the latex dispersion and a polymer's physical characteristics are likely to influence the application and final film properties in such a coating. To date, the specific effects of these parameters in waterborne systems is largely unknown. In this programme of research some of the very first experimental data on factors influencing the application properties and final film quality have been obtained using the IMRS technique. As an example, figure 5a, 5b show re-dispersion experiments of dry latex films with different glass transition temperature  $T_g$ . The soft latex (fig. 5a) has formed a smooth and non-porous film structure, which makes water intrusion impossible, whereas for the harder latex (fig. 5b) film formation is incomplete and water can diffuse into the film and even accumulates at the film-substrate interface.

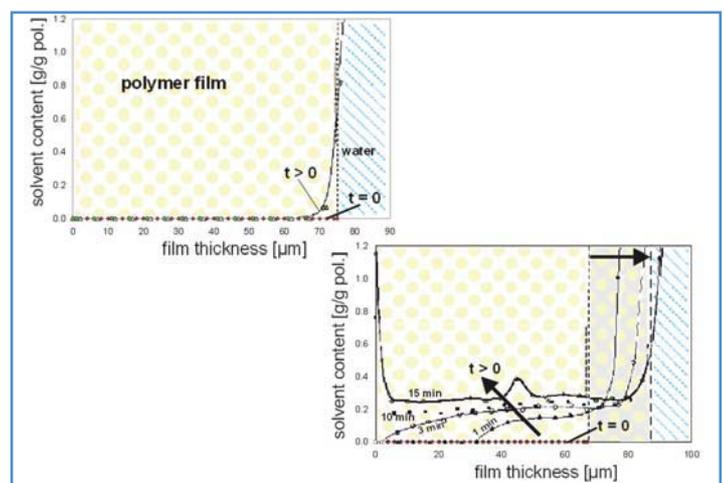


Figure 5 Redispersion experiments of a dry polymer film (latex dispersion) with water. Measurements performed with IMRS.

a) from "soft" latex (low  $T_g$ )      b) from "hard" latex (high  $T_g$ )

In summary, the coupling of the power of confocal Raman microscopy to the inverted sampling geometry has enabled detailed investigations to be made of solvent and water based coating systems, providing important information on the processes and chemistry that occurs at the coating interface and within.

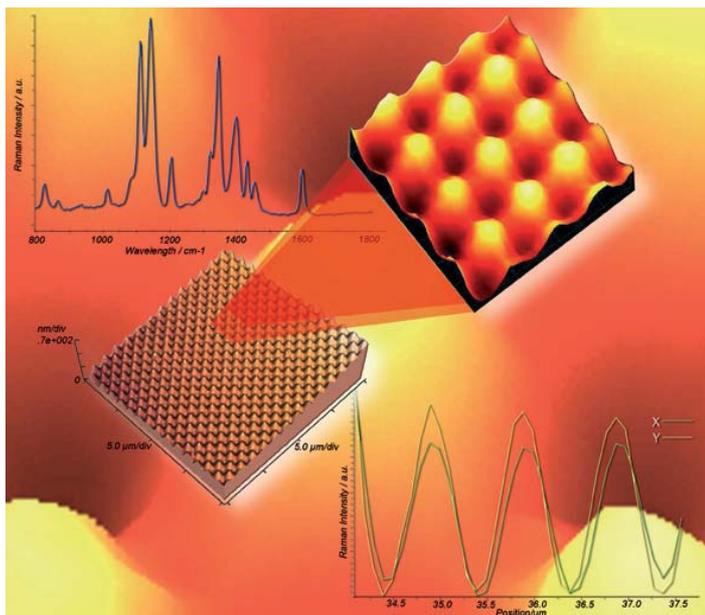
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- Schabel W., Ludwig I., Kind M.; Measurements of Concentration Profiles in Polymeric Solvent Coatings by Means of an Inverse-Confocal-Micro-Raman-Spectrometer - Initial results, *Drying Technology*, Vol. 22, Nos. 1&2, 285-294, 2004
- Schabel W.; Inverse Mikro Raman Spektroskopie - eine neue Messmethode zur Untersuchung lokaler Stofftransportvorgänge in dünnen Filmen, Folien und Membranen, *Chemie Ingenieur Technik*. 2005
- Schabel W., Scharfer P., Müller M., Ludwig I., Kind M.; Messung und Simulation von Konzentrationsprofilen bei der Trocknung binärer Polymerlösungen; *Chemie Ingenieur Technik*, vol 75, Heft 9; p. 1336-1344, 2003

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## Raman Imaging Gallery

HORIBA Jobin Yvon continues to acknowledge the often ground breaking research of its customers, and launched a Raman Imaging Competition in May. The prize was a digital camera and their Raman Image on the front of the international magazine Microscopy and Analysis.



HORIBA Jobin Yvon would like to thank everyone for the high number of quality contributions to the competition, making the task of selecting a winner difficult. We are proud to announce the winner as F. Lagugné-Labarthe and D. Talaga from the University of Bordeaux I in France with their contribution of a Raman and AFM image very fitting and a good illustration of an exciting and developing aspect of the Raman technique.

On the website of HORIBA Jobin Yvon a new Raman Image Gallery has been created where you can discover

## Contact Details

For further information on any of the articles within this newsletter, or should any of your colleagues wish to be part of our mailing list, or should you have queries or comments, please contact [Joanna.Mason@jobinyvon.fr](mailto:Joanna.Mason@jobinyvon.fr) or any of the following addresses :

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