Investigation of Inhomogenous Drying of Aqueous Latex Dispersions

I. Ludwig[(*)], W. Schabel[(*)], J.-C. Castaing[(**)], P. Ferlin[(**)] and M. Kind[(*)]

[(*)] Institut für Thermische Verfahrenstechnik, Universität Karlsruhe
Kaiserstraße 12, 76128 Karlsruhe, Germany
Tel.:+49 721 608 6978, E-mail: imke.ludwig@ciw.uka.de

[(**)] Rhodia Recherches et Technologies, Aubervilliers, France

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Abstract: Experimental evidence is given for a mechanism of film formation from industrial water-borne latices. Perpendicular to the substrate (vertical direction) drying is gas-side controlled, indicated by measured uniform water concentration profiles. These findings are supported by model calculations. In horizontal direction (parallel to the substrate) inhomogeneous drying is observed. Water concentration gradients lateral across the film are the result of horizontal mass fluxes towards the edge of the film and the formation of a drying front.

The technique of Inverse-Micro-Raman-Spectroscopy (IMRS), which is used in this work, provides the high space and time resolution needed to measure water concentration profiles within thin films in vertical and horizontal direction during drying.

Keywords: **Latex, film formation, concentration profiles, dispersion, Raman spectroscopy**

INTRODUCTION

Due to stricter environmental regulations, aqueous latex dispersions, among others like e.g. aqueous polyurethane emulsions and alkyd emulsions, are considered to be a better choice of the future for coatings and paints compared to solvent-based formulations. Industry has invested significant time and effort into the development of water-based systems, that show a drying behaviour comparable to that of established solvent-based formulations. This requires a fundamental understanding of the film formation mechanism from colloidal dispersions. Although researchers have often dealt with the question of latex film formation, there is still no consensus on the details of this mechanism. This is also due to a lack of experimental methods, which have a space and time resolution required to follow film drying. No measurements can be found in the literature which show drying in the film at a comparable accuracy as obtained by IMRS.

Aim of this work is the investigation of inhomogenous drying in horizontal direction of the film using the technique of Inverse-Micro-Raman-Spectroscopy (IMRS) and the development of a model to decribe the experimental findings.

LATEX FILM FORMATION

There exist different models and theories regarding the film formation process and the forces which are responsible for film formation. Review articles on this topic can be found in the literature [1], [2], [3]. Common understanding is that the process of film formation is described by a mechanism which includes four consecutive stages: (1) constant loss of water with time and the concentration of the latex dispersion, (2) particle contact and ordering, (3) their deformation and (4) the interdiffusion of the polymer chains across the particle boundaries and the formation of a mechanically stable film. In Fig. 1, the different stages of film formation are illustrated.

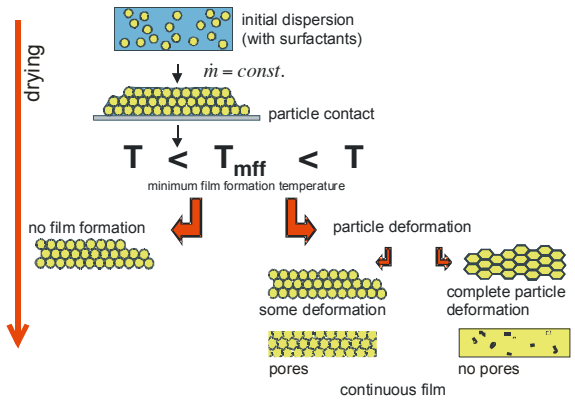

Fig. 1. Mechanism of latex film formation

MEASUREMENT TECHNIQUE AND DATA EVALUATION

A measurement technique, called Inverse-Micro-Raman-Spectroscopy (IMRS), has been developed at Karlsruhe Universtiy in collaboration with a spectrometer company [4] by combining an inverse microscope with a confocal Raman spectrometer (Fig. 2).

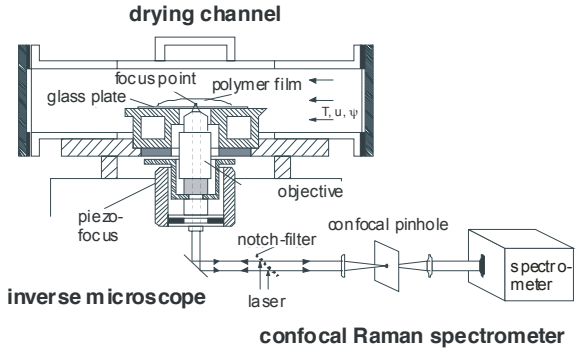

Fig. 2. A representation of the measurement technique of Inverse-Micro-Raman-Spectroscopy (IMRS)

The peaks of the Raman spectrum are characteristic for the different components of the investigated dispersion. With the technique, the local water content within thin latex films can be obtained quantitatively during drying with an optical resolution of $1-2$ µm and a time resolution of ~ 1 s. The method includes the preparation of a sample film within the drying channel and the drying of the film at defined conditions. As shown in Fig. 2, a monochromatic laser beam is focused into the latex film during drying by a system of mirrors and optical lenses. Within the film, a part of the light is scattered - elastically or inelastically - due to the interaction of the monochromatic laser beam with the molecules of the sample. Only the inelastically scattered light - the Raman light - can pass back through the interference pattern of a notch filter. High spatial resolution is achieved by a confocal pinhole, which is optically coupled with the objective's focus. It only allows backscattered light from the plane of focus to be detected by the CCD camera. The technique is well suited to investigate the drying mechanism of both solvent-based polymer solutions [5] and water-based dispersions. A method for calibration and quantitative evaluation of Raman data from solvent-based polymer solutions has been developed using the Raman intensity ratio of solvent and polymer peak. Detailed information on the calibration procedure can be found in [6], [7]. The calibration procedure uses relative Raman intensities of the polymer and water peak taken from the same spectrum. The ratio of these two peaks changes due to evaporation. This is a key issue in order to obtain quantitative data by the IMRS measurement technique. The calibration method is not limited to binary polymer-solvent systems, but can also be used for systems with more than one evaporating component. For latex dispersions scattering effects have to be taken into account [8].

SAMPLE LATEX AND EXPERIMENTAL CONDITIONS

The experiments were performed with a dispersion containing pure acrylic latex. The dispersion of solid content ~ 50 mass % has an average particle size of ~ 100 nm, verified by photon correlation spectroscopy, and a minimum film formation temperature of T_{mff} ~ 20 °C.

The experiments were done at room conditions of T = 25 °C, a relative humidity of φ = 40 % and at conditions of free air convection. At these experimental conditions the drying temperature is close to the polymer's glass transition temperature. Therefore it is expected that the latex particles will not be able to completely deform which will lead to a porous film structure.

EXPERIMENTAL RESULTS AND DISCUSSION

Vertical film drying

Fig. 4 shows the quantitative evaluation of a film drying experiment for a film of acrylic latex dispersion. The film has an initial film thickness of d = 105 µm (determined from the first water profile measuerment at t = 0 min (Fig. 4)) and an initial solvent content of X = 0.93 g water / g polymer and dries at a constant rate. The measurement position for the laser is in the middle of the sample film. Here, the laser focus is moved from the bottom of the film (left side in Fig. 4) to the film surface (right side) in steps of 4 µm. One complete scan through the film takes about 30 seconds. The experimental data are represented by the symbols.

Unlike film drying of solvent-based films, drying of aqueous latex dispersions at ambient conditions is gas-side controlled, indicated by the fact that no steep concentration gradients form in the film during drying which would indicate some kind of film-side diffusion resistance. The experimental data were compared to constant-rate-model (CRM) calculations indicated by the straight lines in Fig. 4. The constant-rate-model uses a gas-side mass transfer coefficient, obtained from a simple Sherwood-correlation for the thin film geometry [9], to calculate the evaporative flow of water from the film. At the beginning model and experiment show excellent agreement. Below a water content of X ~ 0,35 g water / g polymer which marks the onset of particle contact drying seems to be accelerated compared to the calculation. This is the result of horizontal mass flow and lateral inhomogeneous drying as will be discussed below.

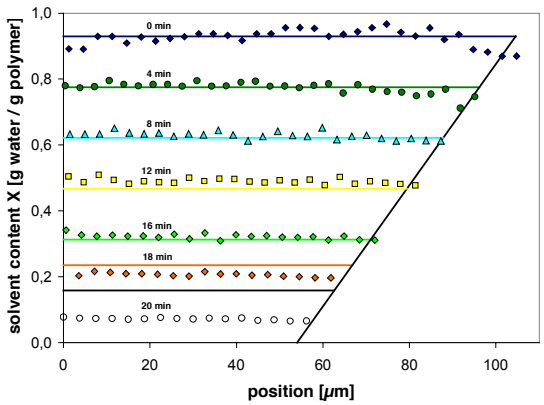

Fig. 4. Vertical concentration profiles of water in a film of acrylic latex during drying.

Horizontal inhomogeneous drying

Horizontal inhomogeneous drying of latex films, where drying starts at the edge of the film and a drying front moves towards the center, has often been observed [10], [11], [12], [13].

Here, the IMRS technique is used to investigate horizontal film drying by measuring the water concentration at different positions horizontally across the film. For the data acquisition (every two minutes), the film is covered by a lid. This considerably slows down drying and allows measurements at different positions during one acquisition time. An evaluation of the data gives the water profiles in vertical and horizontal direction and the film thickness with high accuracy. An illustration of lateral inhomogeneous film drying is given in Fig. 5. The different measurement positions are highlighted.

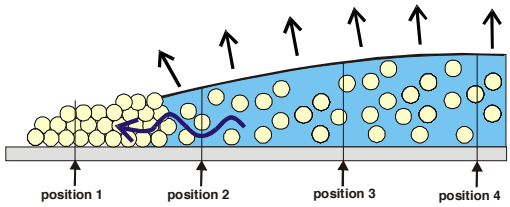

Fig. 5. A schematic view of lateral inhomogeneous latex film drying. The measurement positions are highlighted.

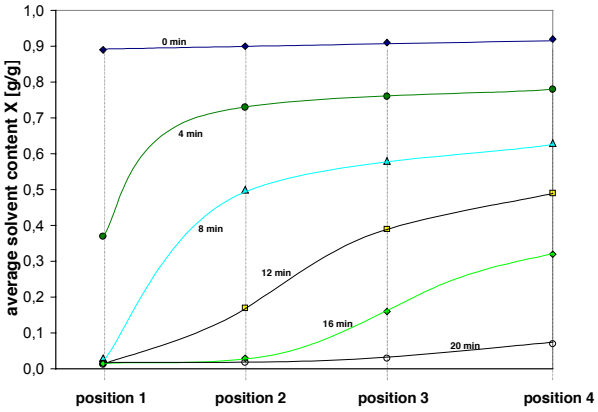

Fig. 6. Horizontal concentration profiles of water in a film of acrylic latex during drying.

Fig. 6 shows, that at the beginning of the experiment the water content is constant throughout the film. Compared to the center of the film drying at the edge is faster due to the larger evaporation area and the reduced film thickness. As shown before, drying in the center can be described by the equations for gas-side controlled evaporation from the film surface (constant-rate-model).

First particle contact takes place at the edge of the film. Assuming cubic closest packing of monodisperse spheres, particle contact would take place at a water content of X = 0.35 g water / g polymer. For random closest packing particle contact would be already at higher X. The closely-packed particles at the edge form capillaries which cause a pressure gradient, resulting in additional horizontal mass flux of water and – at the beginning of drying- particles. Brown [14] calculated analytically the capillary pressure of a triangular pore of three neighbouring particles.

$$p_c = \frac{12.9 \cdot \gamma}{r_{pore}} \qquad (1)$$

The strength of capillary forces is dependent on the water-air surface tension and the pore radius. If throughout the experiment capillary suction is no longer strong enough to keep the water at the film surface, a water front will form and move into the

porous film structure and towards the center of the film. Here, the formation of such a front is first observed after t = 8 min of drying, when the solvent content at the edge decreases to zero and a remarkable decrease of water content is measured at position 2. After t = 12 min the same decrease was observed at position 3. The decrease of water content is the result of the drying front moving towards the center of the film.

Fig. 7 shows the drying curves (= average water content in vertical direction of of the film versus drying time) at different measurement positions (1, 2, 3, 4) across the film. The same conclusions can be drawn as discussed above. Drying at the edge (position 1) is almost doubled compared to the drying rate at the center (position 4). An increase in drying rate at one position is the result of the drying front moving through the measurement spot.

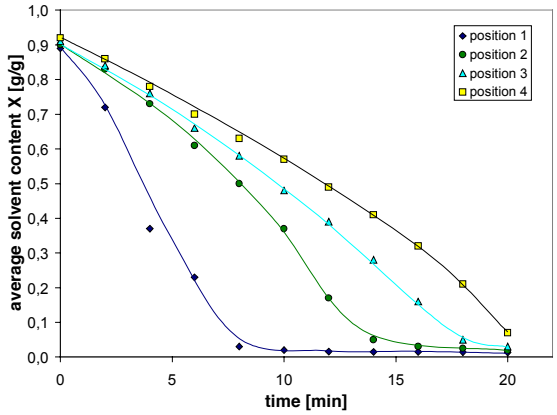

Fig. 7. Drying curves taken at different positions in the film.

CONCLUSIONS AND NEXT STEPS

The investigation of film drying using the technique of Inverse-Micro-Raman-Spectroscopy (IMRS) reveals that no concentration gradients form in vertical direction of a film of aqueous acrylic latex dispersion. Drying at ambient conditions is gas-side controlled. The calculated mass flow from the constant-rate-model (CRM) and experimental values initially coincide very well. Later on, drying is accelerated compared to the model, which is the result of horizontal mass flow due to capillary suction.

In horizontal direction large differences in water concentration can be measured across the film. Drying is faster at the edge of the film due to the greater evaporation area and a reduced film thickness. Water is kept at the film surface by capillary suction. Once the capillary pressure is no longer sufficient to keep water at the film surface, a drying front forms which moves towards the center of the film. The drying front passing through the measurement focus is indicated by an increase in drying rate at the respective position.

In the future, horizontal drying of latex dispersions with different characteristics as e.g. polymer composition and glass transition temperature will be compared. In addition a model will be developed to calculate the horizontal variation of drying rate.

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