Optical Technology to Analyse Film-Formation

H. Dihang(*), L. Brunel(*) and C. Tisserand (*)

(*) Formulaction

10, impasse Borde Basse, 31240 L'Union (France)

Presented at the 14th International Coating Science and Technology Symposium,

September 7-10, 2008, Marina del Rey, California[1]

1. Introduction

Control and understanding of film formation remain of great importance for coating manufacturers and raw material suppliers. They have to innovate constantly to provide new products of high performance to comply with the recent environmental legislations. These new formulations are based on different chemistries, hence undergo different film-formation processes compared to the classic solvent-based formulas, leading to different final properties of the coating. A wide range of characterization techniques have been used for research on coating drying, curing and film formation of latex (microscopy techniques, spectroscopy scattering and optical, thermal analysis, physical testing methods). For more routine analyses, the BK Drying Recorder is often used by paint manufacturers to extract characteristic drying times such as set-to-touch, tack-free, or dry-hard times. Each of these above mentioned techniques provides very useful information on film formation and drying processes. However, most of them are not capable of measuring the build-up of properties under realistic conditions of solvent evaporation and/or on the appropriate substrate. We present here a new optical technique based on Multispeckle Diffusing-Wave Spectroscopy (MS-DWS) to study film formation of coatings. We have studied a latex and correlated the film-formation kinetics with gravimetric analysis.

2. Experimental

The MS-DWS measurements were carried out using the Horus® Film Formation analyser from Formulaction. Weight loss measurements were simultaneously performed on the same coating. The weight loss measured with the balance was converted to volume fraction of latex as a function of time. The wet content (52%) was assumed to be the value at T=0 for the gravimetric analysis, and the assumption was made that all water had disappeared when the

balance showed a constant value. All experiments were performed in duplicate in order to average the times and improve the accuracy. Results reported in this paper were performed on a commercial coating based on an acrylic latex Tg -4°C, density 1.04 g/mL, solid content 48% and particle size of 100nm. It was spread manually using a stainless steel applicator (Doctor Blade type) giving a wet thickness of 120 microns. The coating was applied on a glass panel and the measurements were carried out at a relative humidity level of 40 ± 5%, and a temperature of 20 ± 1°C.

3. Results and Discussion

The film-formation process of a water-based latex coating, sample A, was studied using our MS-DWS technique and correlated to gravimetric analysis. The kinetics obtained are shown in figure 2.

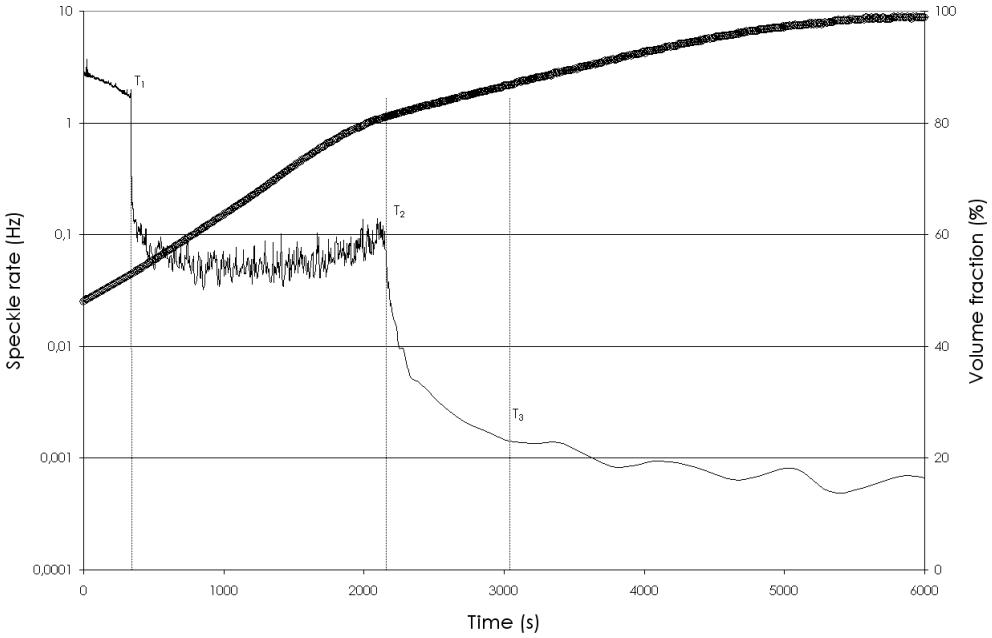

Figure 2. MS-DWS kinetics (solid line) and gravimetric analysis (circles) for latex coating.

The film-formation profile of sample A shows a film-forming process in four main steps (figure 2). Over the first 5 minutes (phase I), the signal remains high (> 1 Hz) indicating fast motions inside the film. The signal decreases slowly as the water content goes from 52 wt.% to 43 wt.%. The volume fraction of latex is lower than 64%, indicating that the particles are free to move. This first phase corresponds to an **evaporation stage**, *i.e.* the water evaporates from the film surface, water molecules migrate from the liquid to the atmosphere generating currents, hence fast Brownian motion of latex particles.

At the beginning of phase II, a clear change appears on the kinetics with a sharp decrease of the signal, characteristic of an important increase of the viscosity of the system. This time, T_1, fits well with the definition of the open time, which is described by Keddie as the stage where the viscosity reaches a critical value. It also correlates well with manual measurements of the open time. Phase II is characterised by accelerations and decelerations of the speckle rate up to T_2=35 minutes. During phase II, the water content continues to decrease from 43 wt.% to 11 wt.%. The volume fraction of latex increases up to 83 %, which fits with the formation of a close-packing array with deformable particle. The turbulent signal and the high concentration in solid indicate that particles start to interfere in the motion of each other; the particles rearrange and organize. The phase II can be defined as a **packing stage**.

At the beginning of phase III, the signal decreases sharply indicating a drastic reduction of the viscosity. We can assume that the water content (11 wt.%) corresponds only to interstitial water remaining in the film. The drastic reduction of the mobility can be attributed to the disappearance of the bulk water, close-packing of particles being reached. This is also consistent with literature, where the third stage of the latex film formation described as the **particle deformation** stage is closely linked to the visco-elastic properties of the latex.

The continuous reduction of the signal after the total evaporation of water in phase IV indicates a continuous increase of the film coherence. It can last days. The phase IV observed on the kinetics of sample A can be defined as a **interdiffusion** stage.

Film formation of latex coatings have been intensively studied over the past twenty years, but the complete mechanism is still subject to interrogations and different theories are proposed to attempt to explain the film-formation of such systems. Current understanding of film formation from latex coatings consists in 4 stages: (i) the first stage is described as an evaporation stage where particles are still free to move, (ii) the second stage corresponds to the particle ordering or packing stage, *i.e.* particles immobilize by multiple contacts with one another when solvent evaporates, (iii) the third stage consist in compaction or deformation of particles to fill the voids left by water evaporation, *i.e.* elimination of pore spaces by progressive flattening and rearrangements of particles, (iv) the final stage is a 'coalescence' stage, *i.e.* fusion of particles due to interdiffusion of the polymer through particle-particle boundaries. The different phases of the MS-DWS kinetics of sample A indicate that signal seems to correlate well with what is described in the literature. The figure 3 gives a schematic representation and our interpretation of the different phases observed on the kinetics: (I) concentration upon bulk water evaporation, (II)

rearrangement and packing of particles, (III) particle deformation by evaporation of interstitial water, and (IV) interdiffusion / coalescence processes between the latex particles. Work in still in progress to complete this view with further correlations with various analytical techniques.

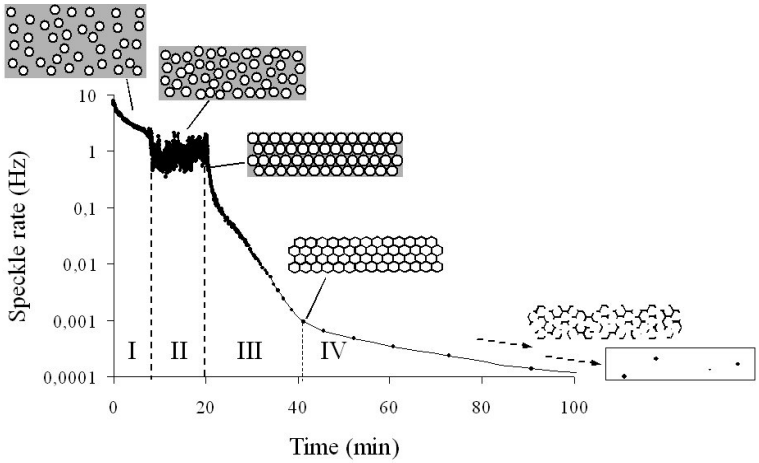

Figure 3. Film formation for latex coating.

4. Conclusion

have presented a new optical technology, based on Multispeckle Diffusing-Wave Spectroscopy, to study film formation from coatings. This technology monitors and displays in real time the motion of scatterers (particles, droplets, interfaces…) inside the sample as a function of time. Measurements have been performed on a water-based formulation and have been compared with gravimetric analysis. Four phases are systematically observed on the film-formation kinetics of water-based coatings and have been identified as evaporation (I), packing (II), particle deformation (III) and interdiffusion (IV) phases, as described in the literature. The different changes in slope and shape observed on the kinetics could be related to changes in the film structure. The measurement is simple to perform: the coating is drawn on a substrate (any kind of coating can be used), placed under the laser beam and the measurement is started without any required calibration nor set-up parameters to enter. This new MS-DWS technique coupled to our A.S.I.I. processing appears then as an original and non intrusive tool to investigate film formation processes in representative conditions, providing a unique and complementary information compared to existing techniques and determining objectively open-time, on appropriate substrates.