ESRF

Experiment title:

Real-time investigation of film formation in colloidal waterborne coatings

Experiment number:

A26-2 921

Beamline:

BM26

Date of experiment:

from: 08/10/2021 to: 12/08/2021

Date of report:

25/03/2022

Shifts:

12

Local contact(s):

Daniel Hermida Merino

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Gabor Ersek

Razieh Mehrabi

Prof. Giuseppe Portale

Report:

Aim of the proposal

The aim of this proposal was to perform in-situ study of the structural evolution during film formation in water-based colloidal polymeric particles (latexes). We utilized Gracing Incidence Small-Angle X-ray Scattering (GISAXS) to follow the particle coalescese and gain insight about the stucture of the final films. The systems under study were polyacrylate- and polyurethane-based colloids that closely resemble resins used in real life applications. The latexes entailed different chemistries and structural properties. The effects of composition and latex architecture were examined.

Goals of our experiments

During our beamtime A26-2 921 at DUBBLE we were aiming for the following:

1) To follow the particle aggregation and coalescence during drying.

2) To study the appearance and evolution of the structural heterogeneities, across the whole film thickness from the analysis of the eventual residual scattering signal in the late stage of drying.

3) To reveal the impact of the different particle composition and structure (hybrids/blends) on the particle packing/coalescence stage and on the size and concentration of the final film defects, under the two different relative humilities and air flow used (different drying rates).

4) To elucidate the distribution of the heterogeneities in the dry state in the direction normal to the substrate, by varying the incident angle (penetration depth).

Overall, our aim is to unravel the correlation between the characteristics of the polymer particles, drying conditions on the film formation behaviour of waterborne colloidal suspensions.

Performed experiments

The following environmental parameters were tested:

- Air flow: uncontrolled, low (20 l/h) and high (100 l/h)
- Humidity: uncontrolled, high (85+ %), low (15 %)
- Temperature: 22 °C, 35 °C

The following latex compositions were tested:

- Polyurethane
- Polyacrylate
- Polyurethane/Polyacrylate hybrid latex with 50/50 weight ratio between the components
- Polyurethane/Polyacrylate blend latex with 50/50 weight ratio between the components

The experimental cell was a custom made environment-controlled cell (Figure 1). The windows of the cell were covered with Kapton™ tape. The humidity was set by applying cc. LiCl and cc $(NH_4)_2SO_4$ solutions.

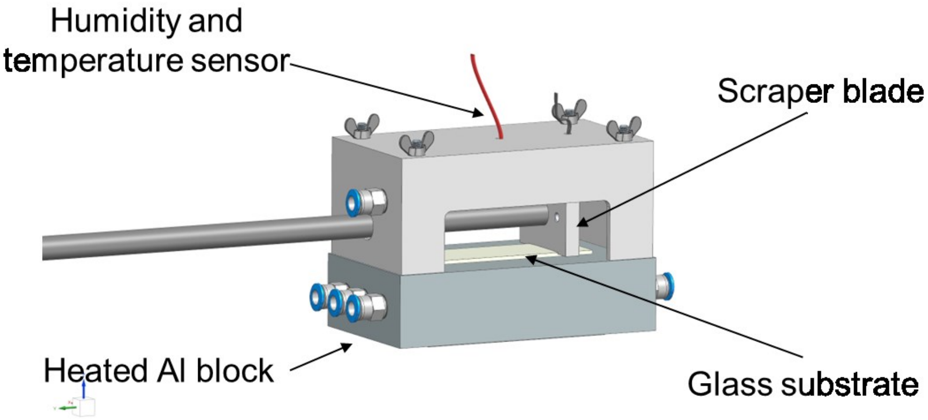

Figure 1: Environment-control cell used for the drying experiments.

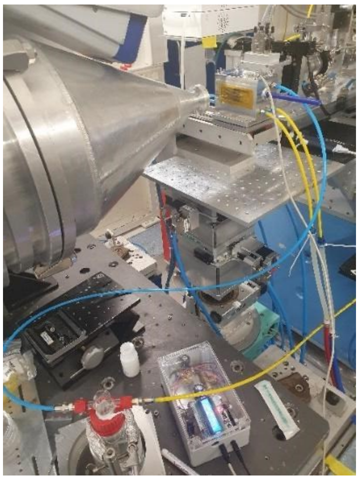

Figure 2: The cell mounted to the beamline.

In a typical experiment:160 µl of latex was casted on the top of a sodalime glass wafer by spreading the suspension with the scraper blade. After then, the system was tilted to 0.12° incident angle in order to perform the in-situ GISAXS measurements. We followed the stuctural evolution for 120/180 min.

Results

1) Following the particle aggregation and coalescence during drying. This goal was achieved by analysing the change in intensity, position and shape of the diffraction peak related to the interparticle distance occurring in the first part of drying. The development of the GISAXS signal of a drying PU film is shown on Figure 3.

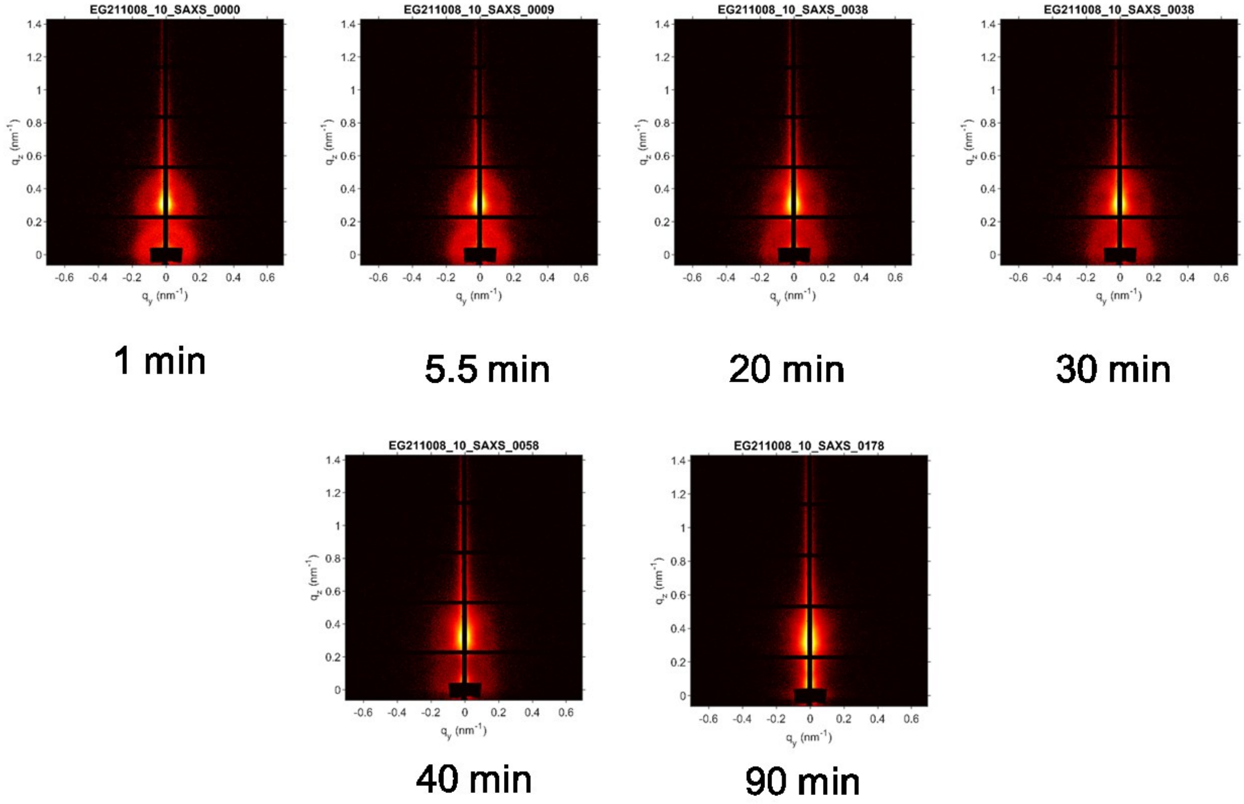

Figure 3: Evoltion of GISAXS singal in case of drying PU film. Drying conditions: 85+ % RH, 20 l/h gas flow.

We could understand the particle aggregation and coalesecence through analysing the q_y cuts of the obtained images at the Yoneda level. The effect of various environmental factors can be understood as the speed of the particle coalesence can be followed, moreover the interphase distance can be quantified through the drying process. From the results we concluded that the humidity and the air flow do not alter the film formation mechanism but greatly affect the onset for particle coalescence.

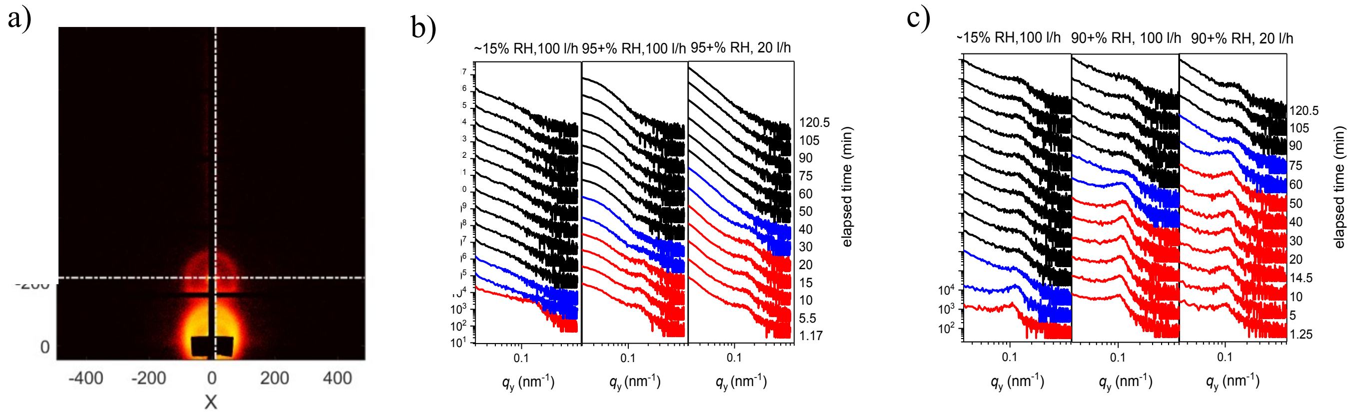

Figure 4a) calibrated GISAXS image of Polyurethane/Polyacrylate hybrid latex with 50/50 weight ratio between the components 1.5 min after casting. $\alpha_i > \alpha_c$ The dashed line indicates the postions of the q_y and q_z cuts. b),c) q_y cuts at the Yoneda level of the drying systems – red curves represent packing pacrticles, blue curves represent the particle coalescese, black curves represent the signal from the final film.b) PU films c) hybrid latex films.

Also by analysing the position of the Yoneda peak, it was observed that in the early period of the dying the incident angle changes from 0.12° to 0.2° (inclination of the beam) due to the self leveling of latex formulation.

Further analysis of the data is currently ongoing which will allow us to extract more information about the systems.

2) To study the appearance and evolution of the structural heterogeneities, across the whole film thickness from the analysis of the eventual residual scattering signal in the late stage of drying.

The analysed films were good film-forming materials, therefore no void formation was expected. However, analysing the images at the late stage of drying we could get information about the matrix.

It is shown that the mechanism of structural rearrangement during drying of PU films and the final structure of the coating depend on the speed of the drying process. A heterogeneous matrix is formed when high humidity and low flow rate are applied in the drying chamber. However, high evaporation rate results in a homogeneous nanostructure.

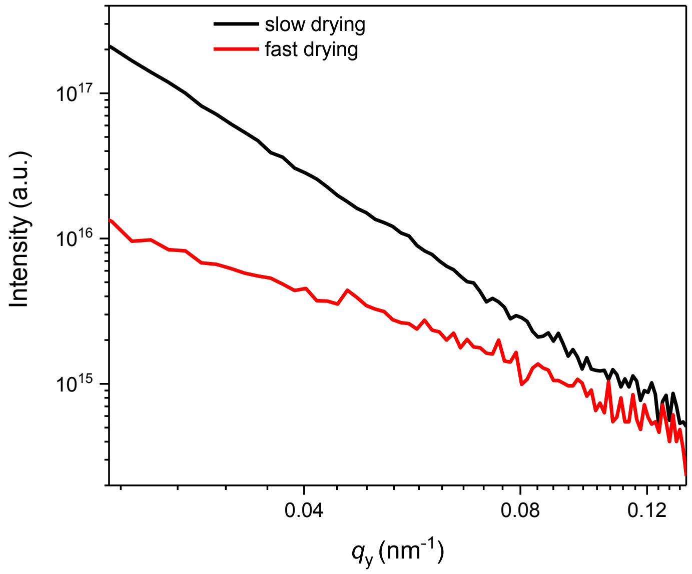

Figure 5: qy cuts at the Yoneda level of the drying PU system. Fast drying = 15% RH, 100l/h flow rate; Slow drying = 85% RH, 20 l/h flow rate.

Further analysis of the data is currently ongoing which will allow us to extract more information about the systems.

3) To reveal the impact of the different particle composition and structure (hybrids/blends) on the particle packing/coalescence stage and on the size and concentration of the final film defects, under the two different relative humilities and air flow used (different dry rates).

Table 1: Time elapsed till the particles are fully coalesced.

	100 l/h flowrate 15% RH	100 l/h flowrate 85% RH	20 l/h flowrate 85% RH
Polyurethane latex	~5 min	~ 30 min	~40 min
Hybrid PU/PAc 50/50 latex	~10 min	~ 50 min	~75 min
Blended PU/PAc 50/50 latex	~ 15 min	~ 65-70 min	-

Table 1 shows the effect of the introduction of the hydrophobic PAc to the hydrophilic PU matrix on the particle coalescence. We found that the particle coalescec is hindered as presence of hydrophilic PAc restricts the water diffusion to the surface. The effect is greater in case of blend latex architecture.

Further analysis of the data is currently ongoing which will allow us to extract more information about the systems.

4) To elucidate the distribution of the heterogeneities in the dry state in the direction normal to the substrate, by varying the incident angle (penetration depth).

To achive this goal we performent GISAXS scan of the dried films at various angles. We found that the structure is changing towards the bulk of the material. Figure 6 and Figure 7 gives an exaple of the achived results.

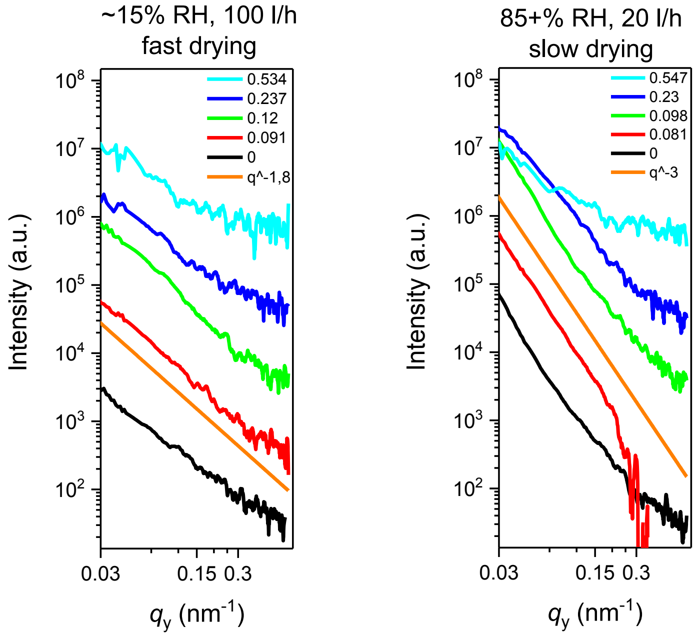

Figure 6: Angle dependent GISAXS measurement of the freshly dried PU films.

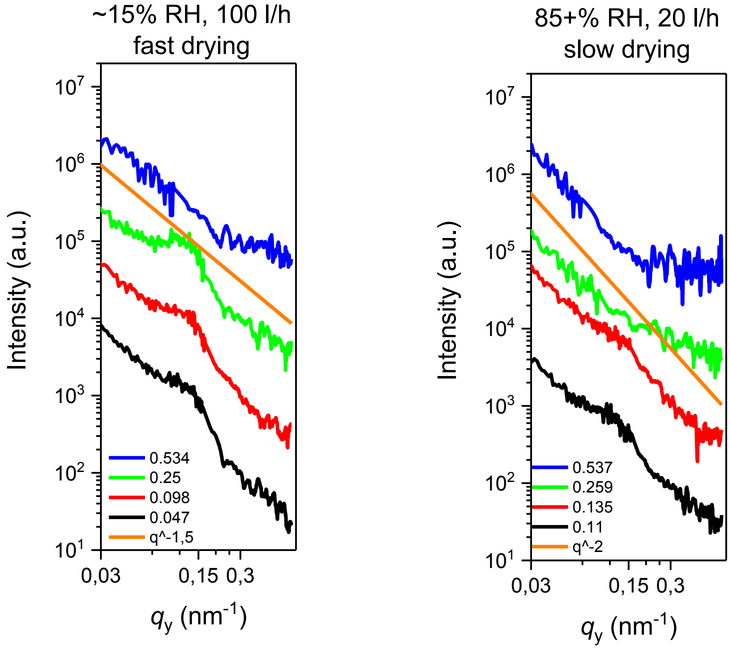

Figure 7: Angle dependent GISAXS measurement of the freshly dried hybrid films.

Further analysis of the data is currently ongoing which will allow us to extract more information about the systems.

Conclusions:

The beamtime was successful. The beamline perfomed nicely and the technical support by the local contact, technician and engineering was great. All the goals have been acheived. The data are of sufficient quality to be inserted in the PhD thesis of Gabor Ersek and we expect to publish these data in 2022/2023. Also, based on the promising results, and the good performances of the environmental cell, we expect to submit new proposals to explore differmet drying conditions and different systems.