ESRF	**Experiment title:** In situ investigation of solvent absorption and desorption in soft polyurethane-base coatings	**Experiment number**: SC 5411
Beamline: BM26	**Date of experiment**: from: 07/06/2023 to: 12/06/2023	**Date of report**: 09/10/2023
Shifts: 9	**Local contact(s)**: Martin Rosenthal	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Gabor Ersek

*Zhang, Yongsheng

*Ilaria Squillante

*Daniele Torbidoni

Prof. Giuseppe Portale

Physical Chemistry of Polymeric and Nanostructured Materials Group, Rijksuniversiteit Groningen, Zernike Institute of Advanced Materials, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Report:

Abstract
The aim of this proposal was to study in-situ the structural evolution that water-based colloidal polymeric coatings undergo during exposure to various solvents by Grazing Incidence Small-Angle X-ray Scattering (GISAXS). The systems under study were polyacrylate- and polyurethane-based films that closely resemble resins used in real everyday applications. The films entail different chemistry and architecture and hence are expected to show different responses to the solvent characteristics. The effect of film composition, solvent nature and exposure time were examined. The results elucidates the relationship between the coating architecture and the solvent resistance and provide useful insights for the community to better design coatings with improved barrier properties.

Goals of our experiments
During our beamtime SC 5411 at DUBBLE we were aiming for the following:

1) To follow the phase rearrangement during solvent exposure and (re)drying
2) To elucidate the appearance and evolution of the structural heterogeneities, across the whole film thickness during solvent exposure (both in the plane and across the thickness)
3) To reveal the impact of the coating architecture on the barrier properties of the films.

Performed experiments

The following film compositions were tested:

- Polyurethane film
- Polyurethane/Polyacrylate hybrid film with 50/50 weight ratio between the components
- Polyurethane/Polyacrylate hybrid film with 70/30 weight ratio between the components
- Polyurethane/Polyacrylate hybrid film with 90/10 weight ratio between the components

In a typical in-situ experiment: a thick colloidal film was mounted in an aluminium humidity chamber. Then the film was exposed either to water vapor or EtOH vapor. The air flow rate was set at 20 l/h. The swelling of the material was ongoing for ~70 min followed by drying with the same dry air flow rate for additional ~70 min. The swelling and deswelling of the material was followed with GISAXS using 6 different angles (0; 0.06°; 0.09°; 0.12°; 0.2°; 0.5°) in order to gain insights about the materials' morphology at different penetration depths.

Moreover we have tested also the following ex-situ samples:

- Polyurethane films, that were casted under various environmental conditions; before and after water exposure
- Polyurethane/Polyacrylate hybrid film with 50/50 weight ratio between the components, that were casted under various environmental conditions; before and after water exposure
- Polyurethane/Polyacrylate blended film with 50/50 weight ratio between the components, that were casted under various environmental conditions; before and after water exposure

Results

1) Generally, the experiments were all successful. We have been able to follow the structural changes upon swelling. Also, the experimental set-up allowed us to gain information simultaneously on both the bulk and the surface of the film. It was shown that in case of the PU the EtOH vapor significantly damages the surface of the film. When PAc is present, the film quality also get worse and the PAc domains' spacing changes but no significant surface damage occurs.

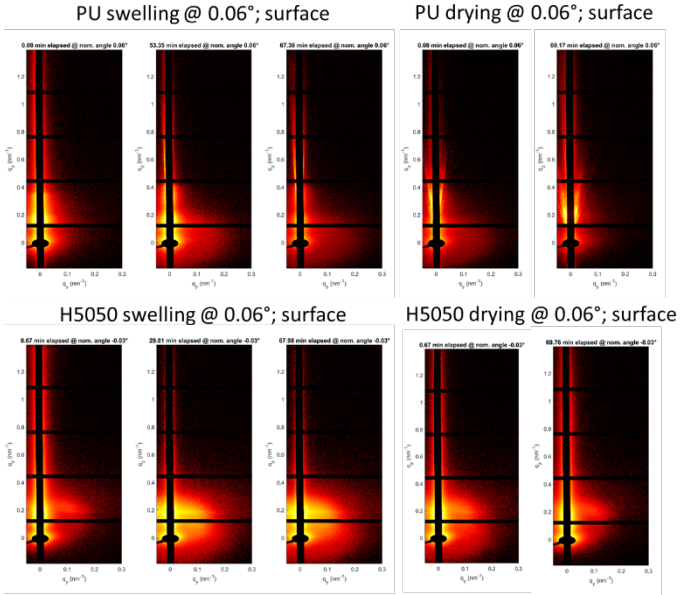

Figure 1: set of images obtained during EtOH exposure, and subsequent drying

2) It was shown that the extent of surface damage upon water exposure is influenced by the preparation (drying) conditions of the PU films.

3) We observed that in the hybrid and blended films structural rearrangement occurs upon solvent exposure. Moreover, the films' behaviour is influenced by the film casting conditions.

Conclusions

The aim of the proposal was achieved. Successful measurements of the effect of water and EtOH swelling on the surface structure of soft PU-based coatings were performed. Further analysis of the data is currently ongoing

which will allow us to extract more information about the systems. We foresee that thiese data will be part of a future publication and will be inserted in the PhD thesis of Gabor Ersek.

Additional comments

During the in-situ experiments we observed that the total intensity of the images change during the electron injection process (refill). Figure 2 shows the total image intensity normalized by the incoming beam intensity as obtained without any samples in the beam, namely only measuring the air background. The jump in intensity occurred at the time of the injection and could not be normalized. Moreover after the jump the intensity does not stay constant, but a slow decay can be observed. This may point to a problem with the photodiode used in the beamstop or the ionization chamber. We will work closely with the beamline staff to address this problem in the future.

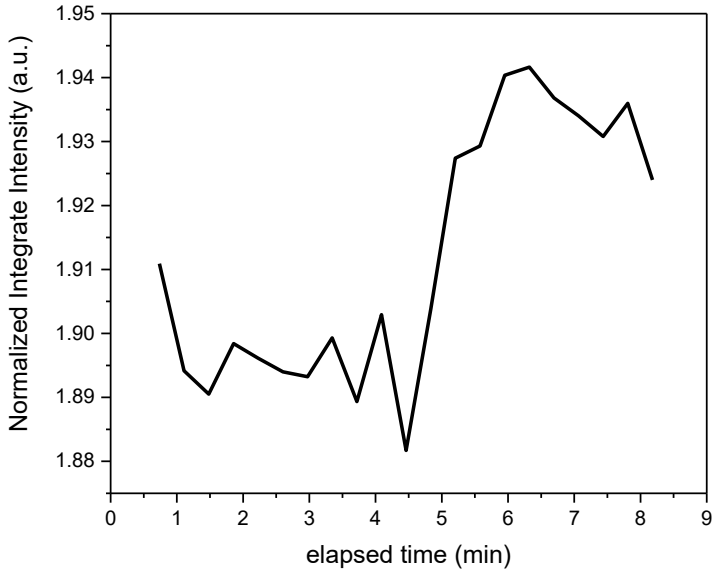

Figure 2: Normalized intensity change upon injection in an air background measurements.