EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In-situ formation and annealing in waterborne polymer coatings	**Experiment number**: 26-02-875
Beamline:	**Date of experiment**: from: 22/June/2018 to: 25/June/2018	**Date of report**:
Shifts:	**Local contact(s)**: Daniel Hermida-Merino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

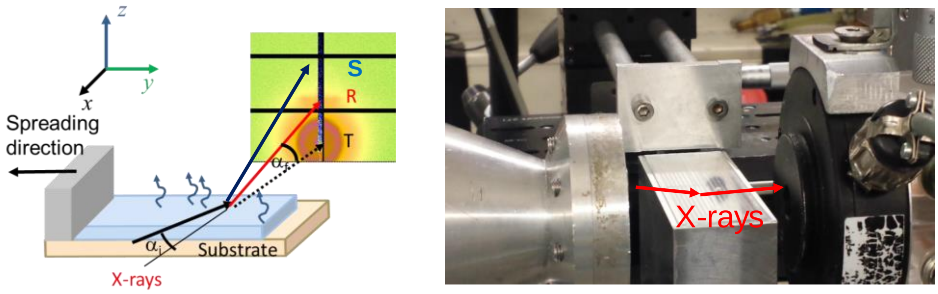
Giuseppe Portale (Uni Groningen)

Apostolos Vagias (Uni Groningen)

Jingjin Dong (Uni Groningen)

Report:

A system to allow in-situ GISAXS during slot-die coating (Fig. 1) of waterborne coatings was successfully tested during this beamtime at BM26B.
The great performances of the beamline allowed high quality data to be acquired with second time resolutions.



Automated slot die coating apparatus (DUBBLE BM26B, ESRF, Grenoble & MINA, RUG)

Figure 1. Experimental setup used for in-situ slot die coating experiments.

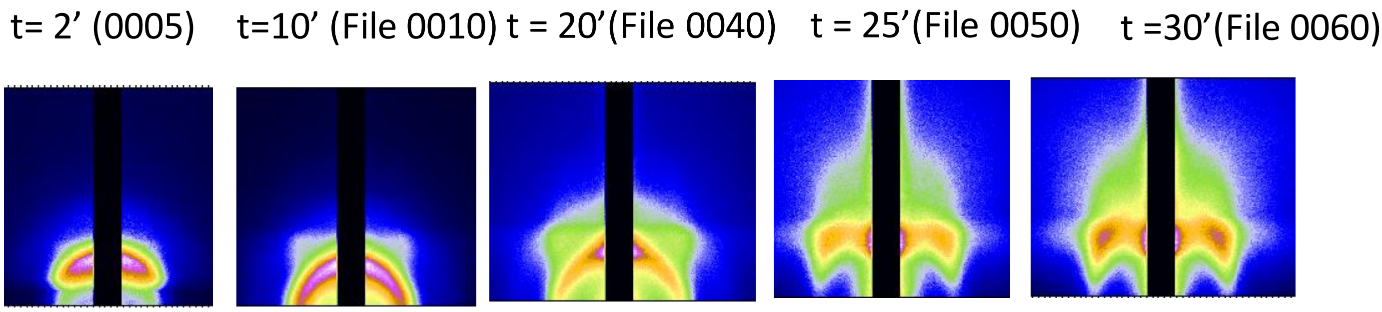


Figure 2. (left) GISAXS patterns at selected time for the hard (top row) and the soft (bottom row) investigated polyacrylic coatings. (right) Time evolution of the scattered intensity for the two studied coatings as revealed by in-situ GISAXS. Drastic intensity rise is related to formation of a "well defined" solid/air interface.

Several formulations were investigated. Some of them showed nice signals others not. One of the successful experiments is reported in Fig. 2. We will use these preliminary results as the basis for an upcoming proposal on in-situ.
Part of this beamtime was also dedicated to a full investigation of ex-situ depth resolved analysis.
These static results are necessary to be acquired in preparation to a successful in-sittu study.
We have published these results in the following manuscript. Abstract is also attached.

Vagias, Apostolos, et al. "Investigation of the Nanoscale Morphology in Industrially Relevant Clearcoats of Waterborne Polymer Colloids by Means of Variable-Angle Grazing Incidence Small-Angle X-ray Scattering." ACS Applied Polymer Materials 1.9 (2019): 2482-2494.

Abstract
Soft polymer colloidal water suspensions are extremely important formulations for industrial applications such as water-based environmental-friendly coatings, paints, and adhesives. Homogeneity of the final coating at the micrometer and nanoscale is a crucial factor for optimal coating performance, such as barrier properties against solvent permeation. Here, we investigated the remnant nanostructure in slot-die-coated micrometer-sized thick clear coating films (clearcoats) of three different waterborne polymer colloids (pure soft, pure hard, and soft/hard multiphase), commonly utilized as primers in paint formulations [Mader et al. Prog. Org. Coat.2011, 71, 123–135], using variable-angle grazing incidence small-angle X-ray scattering (GISAXS) complemented with cross-sectional atomic force microscopy (cs-AFM). After complete macroscopic drying, the coating films exhibit the presence of residual nanostructure with characteristic distance (d*) smaller than the original particle size and even smaller (≪d*) heterogeneity dimensions. These nanostructural heterogeneities (i) develop due to partial particle coalescence, (ii) are preferentially located close to the air–film interface and (iii) demonstrate the tendency to align perpendicular to the air–film interface, implying vertical gradient in hydroplasticization effects having occurred earlier during film formation. The extent and size of the nanostructural heterogeneities, driven by the slot-die coating application, strongly depend on the polymer chemistry (glass transition temperature, Tg) and the colloidal architecture. Last, solvent exposure has a significant impact on the nanostructure, causing the removal of these heterogeneities and leading to a more strongly coalesced film.