ESRF	**Experiment title:** Surface morphology of coatings with segregating block copolymers	**Experiment number**: CH-6006
Beamline: ID10	**Date of experiment**: from: 20-07-2021 08:00 to: 25-07-2021 08:00	**Date of report**: 14-01-2021
Shifts: 15	**Local contact(s)**: Oleg Konovalov	*Received at ESRF:*

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Report:

In this experiment we investigated the surface morphology of polydimethylsiloxane-poly(ethylene oxide) (PDMS-PEO) block copolymers incorporated in a solvent-borne coating formulation. These block copolymers are typically added to coating formulations to functionalize the (liquid) coating surface which is achieved by preferential segregation of the PDMS segments to the film-air interface. The degree of PDMS surface enrichment and change in coating surface properties is strongly dependent on the molecular characteristics of the block copolymer[1]. Furthermore, film drying strongly influences the segregation process and systems can exhibit heavy segregation or even phase separation[2].

X-ray reflectivity (XRR) experiments were performed at the ID10 beamline using a 2D detector. A film application device was positioned on the beamline sample table to allow the scattering experiments to commence directly after drawdown of the liquid coatings (Figure 1). Sample allignment and height adjusment was done between separate XRR measurements to compensate for the decreasing film height during drying. The coating system is a two-component polyurethane formulation solvent-borne in butyl acetate, composed of Macrynal® SM515/70BAC acrylic resin and Desmodur® N 75 BA isocyanate crosslinker. A minor amount (0.001 – 1 wt%) of a PDMS-PEO block copolymer is mixed in the formulation. Details on the coating preparation and block copolymer synthesis can be found in a previous publication[1].

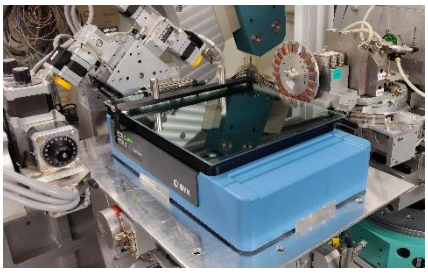

Figure 1 *XRR setup at ID10. A substrate is placed on the glass plate after which the drawdown bar deposits a liquid film which is measured directly after application.*

In a preliminary analysis of our acquired data, we first investigated the optimal settings of the integration window of the signal on the detector. As the beam is spread somewhat in the vertical direction due to small surface undulations, a vertical integration window of 25 pixels on either side of the center pixel of the direct beam yielded the best results (51 pixels high in total). The integration window in the horizontal direction was set to 4 pixels on either side of the direct beam (9 pixels wide in total). Subsequently a background correction

was applied to the XRR data (Figure 2). The background correction simply used an area of 2 pixels wide on the left and on the right of the integration window. The background correction clearly enhances the usable *q*-range significantly. Additionally, the observed slope is not sensitive to the width of the integration window.

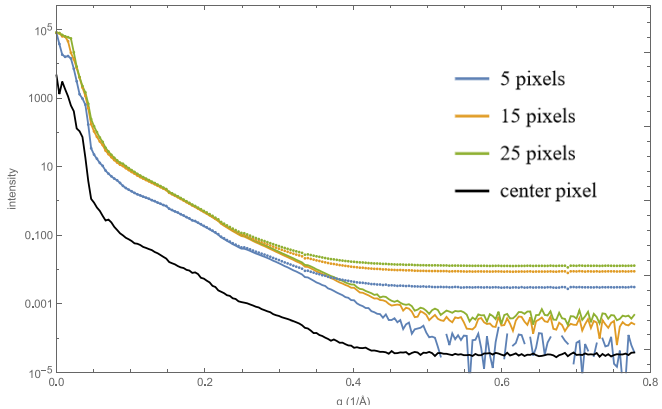

Figure 2 XRR data without (discrete markers) and with background correction (continuous lines) based on different signal peak widths, *of a dried coating containing a PDMS-PEO block copolymer.*

After averaging the different individual measurements performed, the reflectivity curve of a dried coating containing 0.1 wt% PDMS-PEO block copolymer is shown in Figure 3 as an example. The data was fitted to a three-layer model of a top phase composed of air, an intermediate phase of PDMS, and a bottom phase depicting the coating matrix. Relevant x-ray refraction values were taken from literature or estimated based on the atomic composition and assumed density of the materials. The thickness of the PDMS layer and the roughness of the PDMS-air interface were selected as the only fitting parameters.

A PDMS layer thickness of 14.1 Å and a surface roughness of 3.8 Å provided an optimal fit to the XRR data. These values seem reasonable given the length of the relatively short PDMS segment used. Inclusion of a PEO intermediate layer between PDMS and the coating matrix did not improve the fit, indicating that these segments are likely mixed with the underlying matrix polymers.

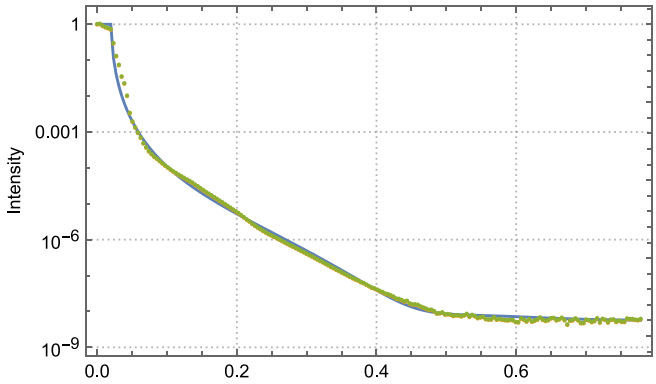

Figure 3 *XRR experimental data (corrected, green) and XRR fit (blue) of a dried coating containing a PDMS-PEO block copolymer.*

Subsequent data analysis will focus on samples containing the respective block copolymer in a different dosage (0.001 – 1 wt%) and will be compared to the other block copolymers investigated, which differ primarily in their PDMS chain length. Previous work[1,2] has indicated that the PDMS surface concentration on the coating surface is strongly affected by both the block copolymer dosage and the molecular characteristics, which we aim to now correlate to the PDMS layer thickness determined using XRR. Following this, we will attempt to perform the same analysis for the reflectivity data obtained on drying films, which hopefully provides information on changes in surface morphology or PDMS layer thickness during the film drying process.

References:

[1] S.P.W. Govers, N. Alexander, M. Al-Masri, J. Omeis, L.G.J. van der Ven, G. de With and A.C.C. Esteves, *Progress in Organic Coatings* **2021**, *150*, 105991

[2] J. Opdam, S.P.W. Govers, J. Melio, L.G.J. van der Ven, G. de With, R. Tuinier and A.C.C. Esteves, *Journal of Colloid and Interface Science* **2022**, *612*, 617-627