ESRF	**Experiment title:** Gradient contrast variation SAXS measurements of multiphase polymer nanoparticles for coating applications	**Experiment number**: A26-2 922
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Report:

Abstract

The proposal aimed to study the fine details of the architecture of waterborne multiphase polyurethane/polyacrylate colloids using gradient contrast variation SAXS. The studied latexes entailed different chemistry and structural properties (defined by the particle composition, the glass transition temperature of the polymer, the crystallinity of the phases, and the way of addition) which have effects on their behavior in case of coating application. Depending on the chemistry of the two polymers and how the synthesis is conducted, core@shell, dispersed embedded nanodomains (occlusions), and multilobed morphologies were expected.

Goals of our experiments

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

1) understanding the internal structure and density of the PU/PAc nanoparticles
2) getting an overview of how the structure changes depending on their composition
3) analyze what kind of effect the different addition processes have
4) getting to know the effect of the glassy and rubbery state of the polyacrylate phase.

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Performed experiments

The following latex compositions were tested with static contrast variation:

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

We also tested a novel experimental procedure to fine-tune the contrast during the measurement. We layered 1wt% latex suspension solutions with 0 and 40 v/v % sucrose content on each other in a rectangular glass capillary. After 1h, the diffusion of the sucrose led to a continuous range of contrast around the contact point of the two initial suspensions. By performing a raster scan around this point we could collect in a relatively short timespan an extensive data set of complementary scattering curves.

Issues

We could not travel to ESRF due to the COVID-19 pandemic restrictions, so we needed to mail in our samples. However, we faced issues with the mail-in service. A lot of the capillaries were broken during transport which caused a delay in the measurements, as we needed to reprepare and resend multiple samples.

Some of the collected data had poor quality. In Figure 1A it can be seen that the signal shows multiple spikes/reflections. Also, as Figure 1B) suggests, the intensity of the background at high q-values was very high which covered the high q region of the signal (Porod signal of the colloids). Being the experiment performed in mailing-in mode, we could not check the data during acquisition, so we figured out this problem only after the experiments were performed.

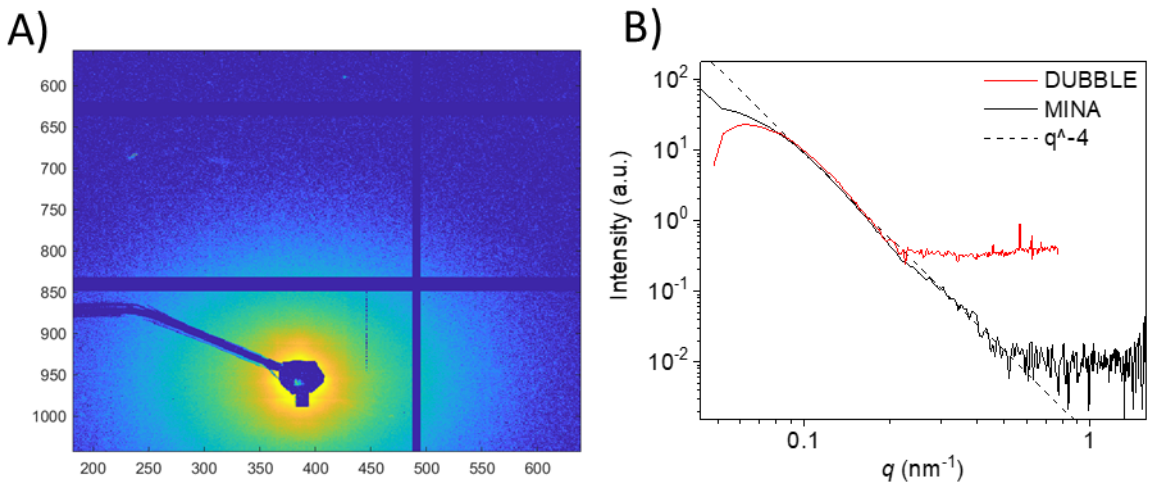

Figure 1A) 2D SAXS image of a polyurethane colloid sample measured in a glass capillary. B) Comparison between the 1D SAXS signal obtained during the run at DUBBLE and the signal measured at the MINA diffractometer (rotating Cu anode, 8 keV) in Groningen.

We tested the gradient contrast variation method, although the collected data's quality was poor. During the background measurement, we faced reproducibility issues (possibly) due to the mixing of the two suspensions.

Bemaline support

The level of support was great, if we considered that this was a mailing-in experiment during the COVID time and the experiments were performed by the beamline staff.

Results

Nevertheless, some good experimental results were acquired.

- Our data show that the polyurethane particle has multiphase structure.

- The collected data suggests that the PAc@PU system with a 50/50 and 70/30 weight ratio has core-shell architecture, and the system with a 90/10 weight ratio shows the presence of PAc occlusions.

Conclusions

The proposal's aim was not achieved fully due to poor data quality and problems with the samples. Successful measurements provided us with insights into the particle's architecture, but the gradient contrast variation measurements need to be further optimized. Further analysis of the data is currently ongoing which will allow us to extract more information about the systems. We foresee that these data will be inserted in the Ph.D. thesis of Gabor Ersek and hopefully in a publication. However, the acquired good-quality data are not enough to be used in a single publication mainly focused on the results of this beamtime.