X-RAY DIFFRACTION

Dehydration study of microgel thin films using non-ambient X-ray reflectometry

Application Note 624

The physical properties of surfaces, ultra-thin films, and multilayer coatings are of paramount importance in modern technology. X-Ray Reflectivity (XRR) is a unique analysis technique for the non-destructive and calibration-free investigation of the structural properties of thin films down to the sub-nanometer scale. These properties include layer thickness, roughness, mass density, and chemical composition regardless of whether the films are amorphous, liquid, polycrystalline, or epitaxial. In this application note, we report the temperature dependent deswelling of microgel thin films. Microgels, mostly consisting of spherical colloidal networks of intramolecularly crosslinked hydrophilic polymer chains, have the ability to store large amounts of water. This is associated with a large increase in volume [1]. Consequently, at ambient conditions, the microgel is expected to be in the swollen state due to humidity. Subsequent heating of the film should lead to dehydration of the gel accompanied by a decrease of its layer thickness. Non-ambient XRR can precisely track these thickness changes and determine at which temperature the film is entirely dehydrated. This allows drawing conclusions about the amount of water the film can effectively store, i.e. a water storage figure of merit.

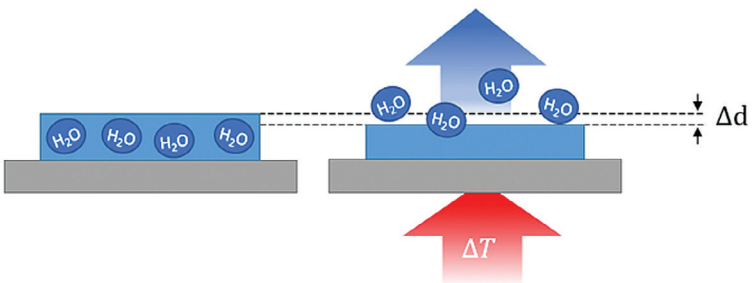


Fig. 1 A hydrated microgel film (left side) is heated up and its thickness reduced through dehydration (right side).

Sample and instrument configuration

For this application note, a microgel film of approximately 70 nm thickness was deposited on a single-crystalline silicon wafer. The sample, with the size of 15 x 15 mm², was stored at ambient conditions. The measurements were carried out on a D8 diffractometer, equipped with a Cu radiation sealed ceramic tube. The incident beam was conditioned by a Goebel mirror producing a highly parallel beam with a divergence of less than 0.023°. The beam width was limited using a 0.05 mm slit. To reduce the angular acceptance of the detector, an anti-scatter slit of 0.1 mm was placed in front of a 0.1 mm detector slit. A Bruker AXS TC-REFLECTOMETRY non-ambient chamber was mounted in the center of the goniometer. This chamber allows to reach sample temperatures up to 800°C [(1)]. It features a motorized and software-controlled Knife Edge Collimator (KEC) to properly define and dynamically optimize the irradiated area on the sample. Also the sample tilt and sample height are motorized and software-controlled, which allows for an accurate sample alignment at different temperatures.

Experimental details

In order to track changes in the film thickness with increasing temperature, a measurement sequence was set up using the DIFFRAC.WIZARD plugin of the DIFFRAC. MEASUREMENT CENTER. The sample temperature was successively increased from 40°C to 100°C, in steps of 10°C. After each temperature step and before each measurement, the temperature was held constant for 2 minutes. The programmed temperature profile can be seen in the picture below. The yellow hatched regions indicate the measurements where there is a locked coupled 2Theta/Theta scan from 2θ = 0° - 3° in steps of 0.005° and a time per step of 0.5 s is set up, resulting in a total measurement time of 5 minutes.

Fig. 2 and 3 A TC-REFLECTORMETRY non-ambient chamber center is mounted on a vertical goniome-ter of a D8 diffractometer (left side). The right side shows the sample heater (adjustable in height) and the motorized knife-edge collimator on top of the sample holder.

(1) Alternatively, using a low temperature accessory kit, the accessible temperature range can be changed to –180°C, … , +450°C .

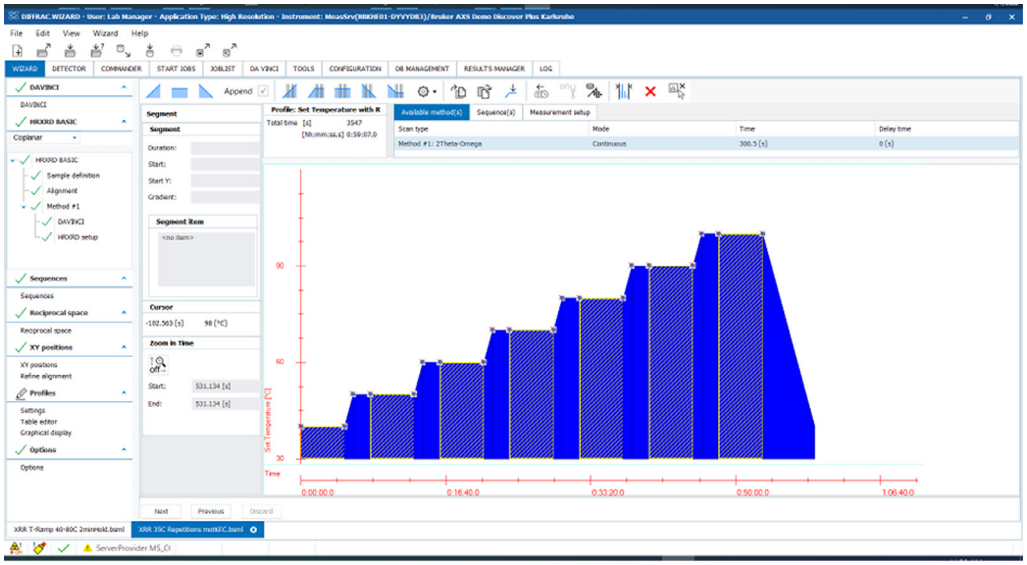
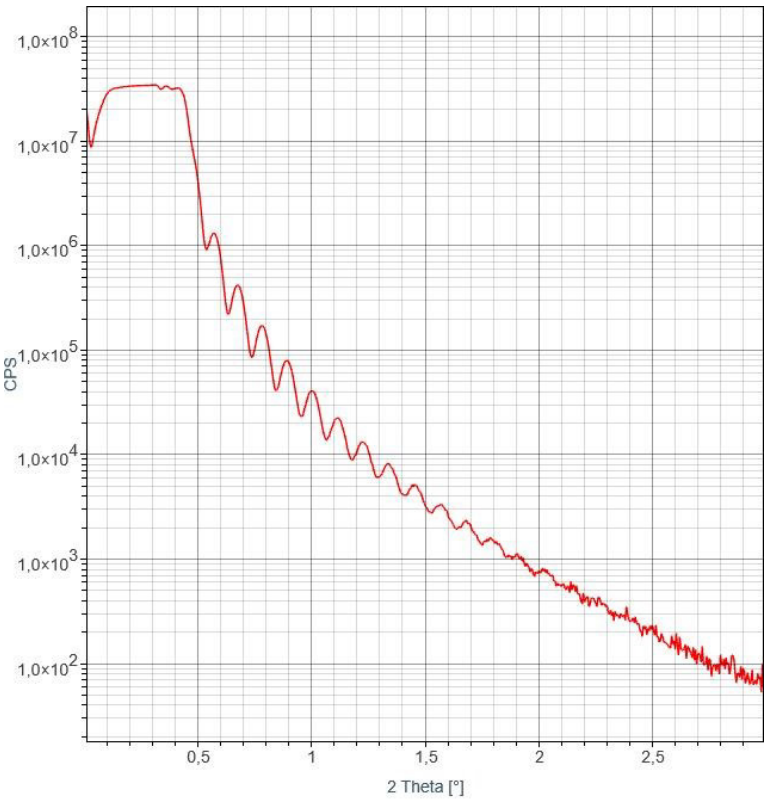


Fig. 4 A temperature profile was set up in DIFFRAC.WIZARD to perform XRR measurements between 30°C and 100°C. After reaching 100°C, the sample is cooled down to 30° again.

In XRR measurements, it is crucial to align the goniometer axes with respect to the surface normal of the sample and the sample height. As a change in temperature can affect both the sample height and the sample inclination within the goniometer coordinate system, an automatic sample alignment needs to be performed before every measurement. To improve the quality of the XRR measurements, the motorized Knife Edge Collimator (KEC) of the TC REFLECTOMETRY chamber was set to a sample-to-knife distance of 20 µm. The KEC limits the beam spill at low angles as it acts as a virtual slit at the sample position. Consequently, the footprint effect is very limited, and the total external reflection plateau is already reached at a 2θ angle of 0.2°, which allows a proper analysis of the critical angles.



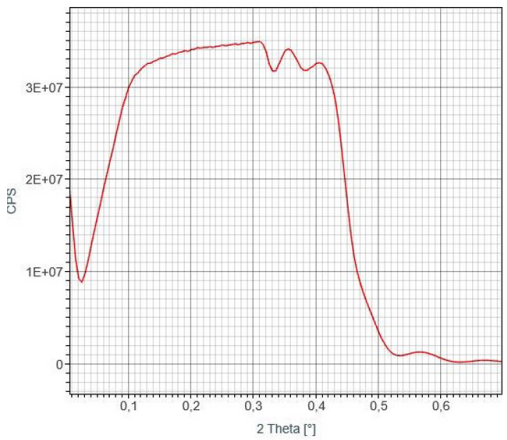


Fig. 5 and 6 The measured XRR curve exhibits a few distinct features: First, the low angular part is governed by half of the direct beam bypass-ing the sample, followed by the footprint effect. Around 2θ ≈ 0.2° all photons hit the surface, lead-ing to the formation of a total external reflection plateau. A first critical angle is observed at about 0.32°, followed by a second one at 0.44°. In between, a single Kiessig fringe is apparent. For better visibility, the region around the critical angles is depicted in the inset on a linear scale.

Data analysis and results

The first critical angle can be attributed to the organic top layer while the latter one originates from the silicon substrate. After the critical angle, Kiessig fringes stemming from the organic layer are observed up to only about 2.2°, indicating a large roughness of the air-organic interface. A full profile fit using a two-layer model is performed to extract the density and thickness of the organic layer. Additionally, the roughness parameters of the interfaces air-layer and layer-substrate are evaluated.

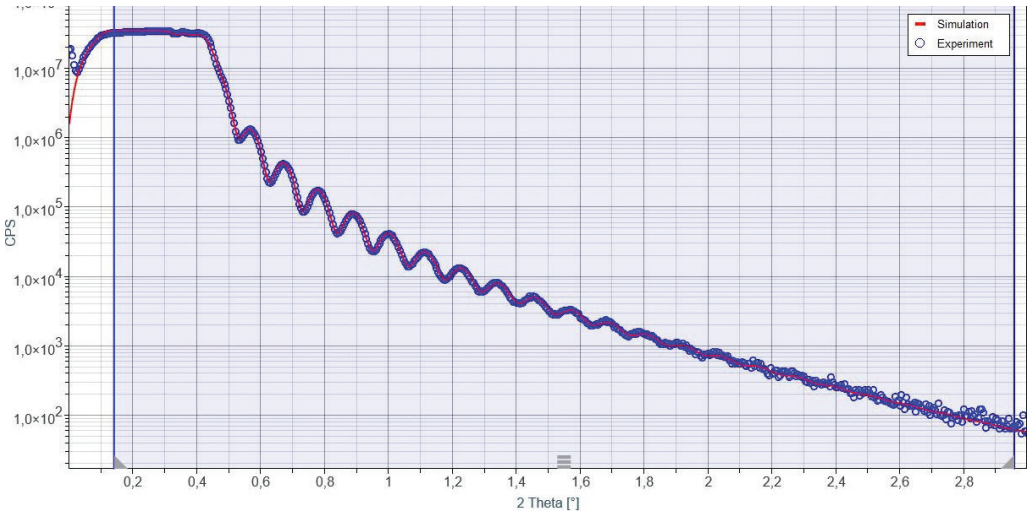


Fig. 7 Analysis of the XRR measurement taken at room temperature. A single layer on substrate model was used to fit the data. Measurement (open circles) and simulated curve (red line) are in excellent agreement.

As the temperature dependency of the layer properties are studied here, several scans at different sample temperatures have to be evaluated in the same manner. DIFFRAC.XRR offers a workflow designer that allows for a batch evaluation of such series of measurements, in this case, a temperature series. The sample is modeled, and a fit is generated at one curve, while all user actions are recorded by the workflow designer. Subsequently, the recorded workflow is executed on all scans within the measurement series. Such workflows can also be saved and applied to any other similar data set. This feature of DIFFRAC.XRR significantly simplifies routine analysis of mea-surement series or even single measurements and allows for the integration of DIFFRAC.XRR into automated XRD solutions.

[Completed]

Index	Temp [°C]	Proces...	Workflow State
1	40.4359	40.4359	✓
2	50.3361	50.3361	✓
3	60.2812	60.2812	✓
4	70.0616	70.0616	✓
5	79.9967	79.9967	✓
6	89.9983	89.9983	✓
7	100	100	✓

Fig. 8 Batch mode of DIFFRAC.XRR: Series of measurments can be analysed by applying a single recorded workflow to each of the XRR curves.

Besides the individual fits, the evolution of fitted layer properties can be conveniently displayed in graphs. Shown below is the thickness of the organic layer versus sample temperature. Starting at 73.25 nm, a steady decrease of the layer thickness is observed up to 80°C. Further heating to 100°C does not reduce the thickness any further. Therefore, it can be concluded that at 80°C the layer is fully dehydrated.

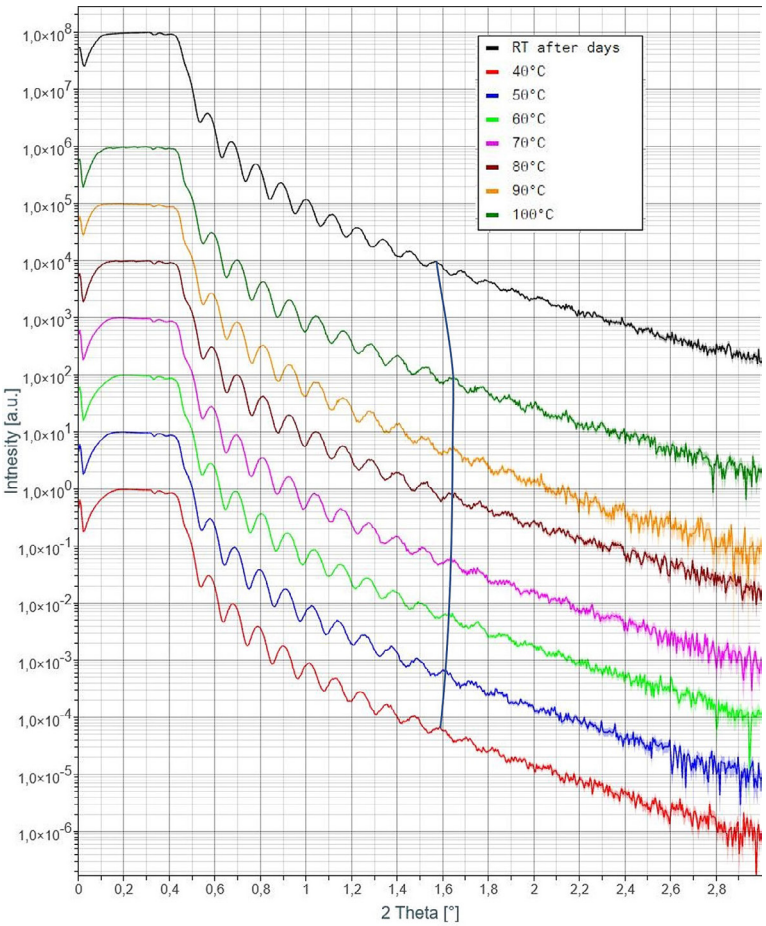


Fig. 9 A series of XRR measurements was taken from an ≈ 70 nm thin microgel film. The sample is heated up from 30°C to 100°C in steps of 10°C. In the range of 40° — 80°C a continuous reduction of the film thickness can be observed. At temperatures higher than 80°, the film thick-ness does not decrease any further indicating the complete dehydration of the film. After exposing the sample to ambient conditi-on for several days (black curve), the initial film thickness is reached again.

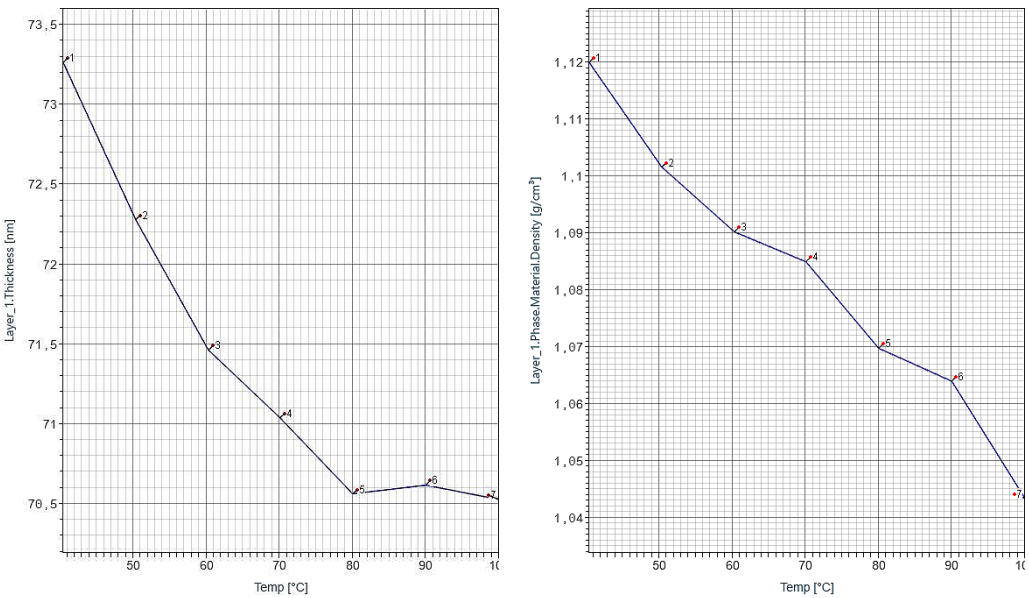


Fig. Thickness (left side) and mass density (right side) of the microgel film as a function of the temperature: The film thickness decreases continuously with increasing temperature. Beyond 80°C, the film thickness remains stable at about 70.6 nm. This indicates that the microgel is completely dehydrated and cannot release any further water.

Summary and Conclusion

In this application note, the temperature dependent dehydration of a microgel thin film was investigated using non-ambient X-ray reflectometry:

- A D8 diffractometer equipped with a TC-REFLECTOMETRY stage was used to measure XRR curves at different temperatures reaching from 30°C up to 100°C.
- DIFFRAC.XRR was used to consistently analyze the entire series of measurements in automated mode: A single microgel layer on top of a silicon substrate was chosen as sample model and film thickness, density, and roughness were fitted to XRR measurements.
- The analysis revealed that the film thickness, as well as the mass density, decreases with increa-sing temperature: The film thickness reduces by 3.7% up to 80°C and remains contant at higher temperatures. The density continuously decreases by 6.8% over the entire temperature range.
- When exposing the dehydrated film to ambient condition for a couple of days, the film thickness and the electron density return to their original values. This indicates that water molecules are embedded again into the film.

The D8 diffractometer with TC-REFLECTOMETRY stage is a powerful solution for the study of thin films using non-ambient X-ray reflectometry and can be used to take series of XRR measurements. This solution allows for automated sample alignment and, equipped with the Knife-Edge collimator, for excellent data quality. DIFFRAC.XRR is a powerful and easy-to-use software for the automated analysis of such XRR measurement series.

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[1] Hydration and Solvent Exchange Induced Swelling and Deswelling of Homogeneous Poly (N-isopropylacrylamide) Microgel Thin Films, Langmuir 2019, 35, 16341–16352

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