Determination of the Film Formation Properties of Clay-Microgel-Nanocomposites via Grazing Incidence Small-Angle X-ray Scattering

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Previously, the structure of clay-microgel-nanocomposites in dispersion, consisting of the microgel PVCL/AAEM (Poly(N-vinylcaprolactam-co-acetoacetoxyethyl methacrylate)) and the synthetic clay laponite, were analysed via USAXS [1]. In addition to the investigation of the nanohybrids, films of the composite particles with 0, 2.5, 8.75 and 20 wt.% laponite were prepared by spin coating on a silicon wafer. Roughness of such films was already measured in an earlier work by atomic force microscopy [2]. However, no information about the inner structure of the films has been available so far.

Measurements via grazing incidence small-angle x-ray scattering (GISAXS) were performed at beamline BW4 with a sample-to-detector distance of 1600 mm. The photon energy was set to 8.980 keV, corresponding to a wavelength of 1.381 Å. The incidence angle was varied between 0.3 and 0.7°. Fig. 1 shows the scattering patterns for microgel films with different amounts of clay at an incidence angle of 0.5°. Intensities are normalized to the measurement time and the DORIS current. Scattering patterns of films with 8.75 and 20 wt.% clay loading (Fig. 1c)+d)) show Kiessig oscillations in qz-direction, which indicate the formation of a closed film. For microgel with 2.5 wt.% laponite, the oscillations are distinctively weak, indicative of a defect-rich film. For the microgel without clay, no oscillations are observed at all. Furthermore, it can be noticed that the amount of diffuse scattering decreases with increasing clay amount (Fig. 1). However, for the sample with 20 wt.% laponite, much more diffuse scattering appears in contrast to the film with 8.75 wt.% clay loading. We interpret this as due to the formation of laponite aggregates, fostered by the high clay loading.

Scattering curves in qy- and qz-direction are displayed in Fig. 2. The scattering curves of the clay-microgel films in qz-direction at qx=qy = 0 (Fig. 2a) are similar, whereas the scattering curve for the film without clay shows different features, for example the Yoneda peak of the silicon wafer. The appearance of the Yoneda peak provides evidence for large areas of the wafer not being covered by microgel particles. This interpretation is in agreement with the very high amount of diffuse scattering (Fig. 1a)). Scattering curves in qz-direction at qz = 0.151 1/Å (Fig. 2b) show characteristic lengths which correspond to the mean distance of two microgel particles, indicated by the arrows. The determined lengths are (189±25) nm for microgel particles without clay, (118±20) nm and (71±11) nm for microgel with 2.5 wt.% and 8.75 wt.% laponite, respectively. For microgel with 20 wt.% clay, it is not possible to determine such a characteristic length, consistent with the formation of laponite aggregates which dominate the scattering contrast.

In summary, the tendency to film formation increases with clay loading until 8.75 wt.%, which is confirmed by the AFM images shown in Fig. 3. For a very high clay loading of the microgel (20 wt.%), the scattering contrast appears dominated by laponite aggregates. For quantitative analyses of the scattering data, simulations with the software package FitGISAXS [3] are planned.
Figure 1: Scattering patterns of microgel films with a) 0, b) 2.5, c) 8.75 and d) 20 wt.% clay loading [4].

Figure 2: Scattering curves of clay-microgel films: a) parallel ($q_z = 0.151 \, 1/\text{Å}$) and b) perpendicular ($q_x=q_y=0$) to the sample surface [4].

Figure 3: AFM images of clay-microgel films with 0, 2.5, 8.75 and 20 wt.% clay loading (from left to right) [4].

References