Structure and dynamics in PVCL/AAEM microgel glasses

S. Schipmann¹, M. Widera¹, O. Faley¹, R. Schröder², M. Sprung³, A. Pich² and U. Klemradt⁴

¹II. Physikalisches Institut B, RWTH Aachen University, 52056 Aachen, Germany
²DWI an der RWTH Aachen e.V., RWTH Aachen University, 52056 Aachen, Germany
³DESY, 22607 Hamburg, Germany

We analysed microgel glasses based on a PVCL/AAEM (Poly(N-vinylcaprolactam-co-acetoacetoxyethyl methacrylate) microgel, which consists of a PAAEM rich core and a thermoresponsive shell dominated by PVCL. Below their transition temperature of 32 °C, these microgels are swollen in water; above this temperature, the polymer chains collapse due to the destruction of hydrogen bonds [1]. Structure and dynamics of a high viscous microgel suspension and an almost solid sample were measured. The microgel concentration in water was about 18 wt.% and 22 wt.%, respectively.

Measurements were performed at beamline P10 with an energy of 8 keV and a sample-to-detector distance of 5 m. Data were taken by a Maxipix detector during the cooling processes between 41°C and 1°C. In order to reduce beam damage of the sample, the beam size was set to 40x40 µm², and an exposure time of 0.1 s as well as a delay time of 0.9 s were chosen.

Scattering curves of both samples are shown in Fig. 1a,b). For the collapsed state of the microgel particles, similar scattering curves are measured for both samples. For the sample with 18 wt.% microgel, no significant change of the interparticle structure can be observed well below the transition temperature in contrast to the higher concentrated sample. A comparison of the maximum position of the structure factor (Fig. 1c) indicates an increasing distance between the microgel particles with decreasing temperature due to their swelling properties. For the sample with 22 wt.% microgel, swelling is strongly limited as particles are in a jammed state.

Figure 1: Scattering curves of samples with a) 18 wt.% and b) 22 wt.% microgel. c) Interparticle distance for both samples.

Figure 2: Two-time correlation functions for sample with a) 18 wt.% microgel at \( q = (0.0024 \pm 0.0001) \text{ Å}^{-1} \) and b) 22 wt.% microgel at \( q = (0.0027 \pm 0.0001) \text{ Å}^{-1} \).
Figure 3: Temperature-dependent results of a) $1/\Gamma$ and b) $\beta$ for $g(\tau)$ at $q = (0.0024 \pm 0.0001) \, \text{Å}^{-1}$ and $q = (0.0027 \pm 0.0001) \, \text{Å}^{-1}$, respectively.

Figure 4: q-dependent results of a) $\Gamma$ and b) $\beta$ for $g^{(2)}(q, t)$ at $T=1 \, ^\circ\text{C}$.

For evaluating the dynamics, two-time correlation functions are calculated by

$$G(q, t_1, t_2) = \frac{\langle l(q, t_1)l(q, t_2) \rangle_\Phi}{\langle l(q, t_1) \rangle_\Phi \langle l(q, t_2) \rangle_\Phi}.$$

Results are displayed in Fig. 2. In order to quantify the dynamics, a Kohlrausch-Williams Watts form was fitted to the one-time correlation function (Fig. 3)

$$g^{(2)}(q, t) = \langle G(q, t_1, t) \rangle_{t_1} = 1 + Ae^{-2[\Gamma t]^\beta}.$$

Above the transition temperature, the relaxation time $1/\Gamma$ is comparatively slow and increases with decreasing temperature. For the sample with 18 wt.% and 22 wt.% microgel, the fastest dynamics are observed at 21 °C and 11 °C, respectively. Below these temperatures, further slowing down of the dynamics occurs. Analysis of the relaxation time also shows a q-dependence of $q \propto \Gamma$ (Fig. 4). The KWW exponent yields values $\beta \sim 1.2 – 2.2$ for all temperatures and decreases slightly with rising q-value. These results are in agreement with measurements made for colloidal fractal gels and aerogels by other groups [2,3].

In conclusion, our measurements show that the temperature dependence of the structure and dynamics varies with microgel concentration. For further study of the glass transition, a measurement of concentration-dependent series between 10 wt.% and 25 wt.% with a higher time resolution would be required.

References