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Multiple-Particle Tracking (MPT) Measurements of Heterogeneities in Acrylic Thickener Solutions

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Abstract In this study the method of multiple-particle tracking (MPT) is used to quantify the degree of structural and mechanical micro-heterogeneity of two polymeric thickener solutions finally aiming at a better understanding of the contribution of microheterogeneities, which commonly occur in solutions of many synthetic as well as bio-polymers, on bulk rheology. We have chosen the commercial polyacrylate ester Sterocoll FD and Sterocoll D (BASF Aktiengesellshaft) as model systems. For the Sterocoll FD solution the ensemble-averaged mean square displacement (MSD) is almost linear in time, as expected for such a weakly elastic fluid and relatively similar to that observed for a homogeneous aqueous glycerol solution, used as a reference system. However, the MSD distribution is broader than for the glycerol solution and their statistical analysis clearly reveals a heterogeneous structure on the μm length scale. For the Sterocoll D solution, the average MSD exhibits a subdiffusive behavior, typical for highly elastic solutions. Moreover, the displacements of microspheres at different locations within the solution display a wide range of amplitudes and time dependences. The MSD-distribution is very broad/bimodal and the statistical analysis indicates a degree of inhomogeneity slightly higher than for the Sterocoll FD solution.

Keywords Acrylic thickeners · Microheterogeneity · Microrheology · Multiple-particle tracking

Introduction

Synthetic acrylic polymers are frequently used as thickening agents in water-based coatings and adhesives or personal care products. Typically, these commercial alkaliswellable acrylates (as well as various other polymeric thickeners) form inhomogeneous partly aggregated or cross-linked solutions. Inter- and/or intramolecular aggregation is due to hydrophobic groups randomly distributed along the chains and can be varied through the solvent quality [1–3]. Crosslinking can be induced either thermally or by adding appropriate crosslinking agents during synthesis. Accordingly, such thickener solutions cover a wide range of rheological behavior, ranging from weakly elastic, almost Newtonian to highly elastic gel-like. Despite its high technical relevance, little is known so far about the contribution of the micro-scale inhomogeneities to the bulk viscoelastic properties [4]. Here we use the method of MPT, which was originally described by Apgar et al. [5] and Ma et al. [6], to quantify the degree of structural and mechanical microheterogeneity of such acrylic thickener solutions. Up to now MPT is frequently used for the study of microheterogeneity of actin filament network [7–10], living cells [11–15], proteins [16, 17], DNA solutions [18] or biological gels [19, 20]. The principle of MPT consists of monitoring the thermally driven motion of inert microspheres that are evenly distributed within the solutions and to statistically analyze the distribution of

mean square displacements, from which information about the extent of heterogeneity can be extracted. In order to calibrate our MPT set-up we first investigated a mixture of glycerol/water solution, viscous liquid sample known as perfectly homogenous, even at length scales much smaller than the radius of the microspheres used for the MPT experiments. We also systematically compared the rheological properties derived from MPT measurements with those obtained from classical mechanical rheometry.

Materials and Methods

Samples

The acrylic thickeners were donated by the BASF-Aktiengesellschaft (Ludwigshafen, Germany). These acrylate esters are co-polymers with a typical composition of about 50% methacrylic or acrylic acid and 50% ethylacrylate and eventually a small amount of crosslinking agent [3]. They are made from emulsion polymerization and delivered as milky liquids with a solids content of 25–30% and pH $\gg$ 2.5. Thickening properties in aqueous environment are recovered upon neutralization when the acid groups dissociate and the polymer chains get soluble. In our study the polymer concentration for both Sterocoll FD and Sterocoll D was 1 wt. %. Solutions were stirred at room temperature for 48 h and adjusted to pH = 8 slowly adding 1 N NaOH. Polymer concentration was determined thermo-gravimetrically after neutralization. Subsequently samples were equilibrated for at least 24 h prior to testing. No further change of pH and viscosity was observed within 3 months. A mixture of glycerol/water with 85% glycerol content and a zero shear viscosity of 0.1 Pa s at 20 °C was also investigated as a perfectly homogeneous reference system comparable in viscosity to our thickener solutions.

Mechanical Rheology Measurements

Steady and oscillatory shear measurements were performed at a temperature of 20 °C with a Rheo-Stress RS150 rheometer (Haake) using a Couette cell geometry for the glycerol and Sterocoll FD solutions and a cone-plate geometry (60 mm in diameter, 1° cone angle) for the Sterocoll D.

Multiple-Particle Tracking

In our study we have used green fluorescent polystyrene microspheres of 0.5 μm diameter (Bangs Laboratories: USA, lot Nr FC03F/7049) as tracer particles. The mixture (total volume: ∼ 20 μl) containing the sample solution including the tracers (volume fraction around 1%) was injected into a self build chamber, consisting of a coverslip and microscope glass slide. The sample thickeness

was ∼ 150 μm and the microscope was focused roughly halfway into the sample to minimize wall effects. Images of the fluorescent beads were recorded onto a personal computer via a progressive scan camera (Allied Vision Technology: Pike F-100B, 2/3″ CCD, 1000 × 1000 square pixels (7.4 μm), up to 60 fps) mounted on an inverted fluorescence microscope (Axiovert 200, Zeiss), equipped with a C-Apochromat 40×, N.A. 1.2, water-immersion lens combined with a 2.5× optovar magnification changer. Movies of the fluctuating microspheres were analyzed by a custom MPT routine incorporated into the software Image Processing System (Visiometrics iPS). Statistical analysis of the trajectories was done using Enthought Microrheology Lab software (Austin, USA) based on the Crocker, Wirtz and Weitz calculations [21–23]. The displacements of the particle centers were simultaneously monitored in a 75×75 μm² field of view, for 100 or 200 s at a rate of 10 f/s. For each experiment a total of 100 to 150 particles was tracked.

Results and Discussion

Trajectories and MSDs

Typical trajectories of microspheres (0.5 μm diameter) dispersed in glycerol and in acrylic thickeners solutions are reported in Fig. 1. The extent of displacement is reduced by approximately a factor 2 for the Sterocoll FD solution (Fig. 1B) compared to the glycerol solution (Fig. 1A). This result corresponds to a higher viscosity of the Sterocoll FD solution. For the Sterocoll D sample, the magnitude of particle displacement is much lower (Fig. 1C) compared to both glycerol and Sterocoll FD solutions. This limited particle motion already indicates a higher viscosity but also suggests the presence of high elasticity in the system. From these trajectories the coordinates of the particles centroids were transformed into MSD traces [22]. For the glycerol and Sterocoll FD solutions the MSD traces adopt a power-law behavior as a function of time with a slope close to 1 $\left(\left\langle \Delta r^2 \left(\tau \right) \right\rangle \propto \tau \right)$ throughout the probed time scales (Figs. 2A and B). We conclude that the motion of the beads in glycerol and Sterocoll FD is purely diffusive and that the microenvironment surrounding the particles responds like a viscous liquid. Interpreting the data leads to a measure of viscosity η using $\left\langle \Delta r^2 \left(\tau \right) \right\rangle \propto 4D\tau$ in two dimension where the Stokes–Einstein equation gives $D = k_{\mathrm{B}} T / 6\pi \eta a$ and a is the tracer particle radius. At long time scales (larger than 10 s), the profile of the MSD traces are affected by slight convection of the solutions, which is difficult to avoid for low viscosity fluids. In Sterocoll D the beads move significantly differently, as shown in Fig. 2C. Particle motion weakly depends on time for $\tau < 100$ s, indicating that particles are highly constrained by the surrounding solution. The motion is subdiffusive with a power-law having slopes well below one $\left(\left\langle \Delta r^2 \left(\tau \right) \right\rangle \propto \tau^\alpha \right.$ with $\alpha < 1 \right)$

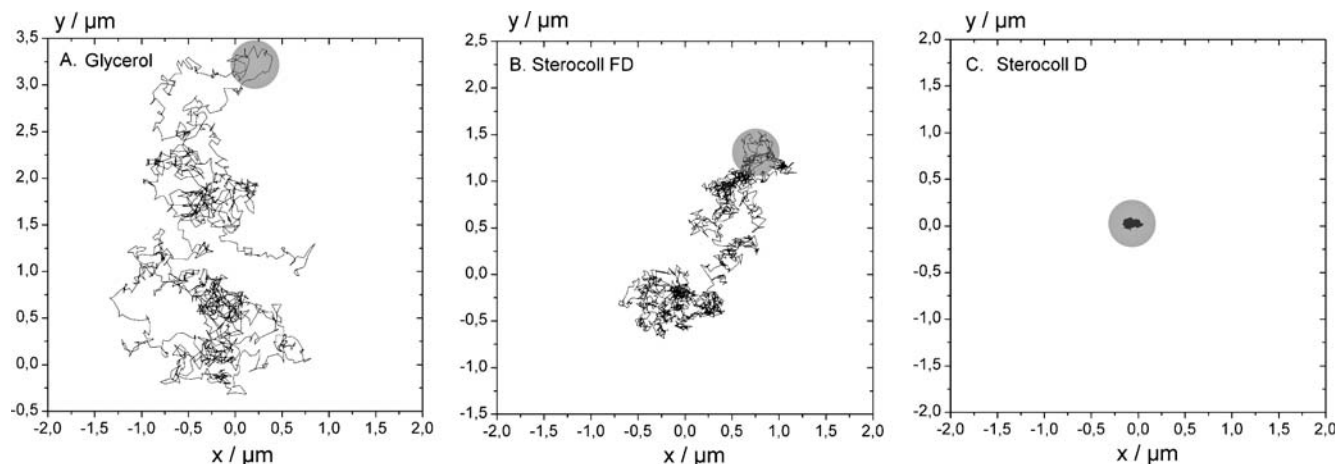**Fig. 1** Typical trajectories of a 0.5 μm diameter, fluorescent polystyrene microsphere (represented by a *sphere*) embedded in a solution of glycerol 85% (**A**), Sterocoll FD 1% (**B**) and Sterocoll D 1% (**C**). The total acquisition time was 100 s, with an interval of 100 ms between consecutive frames
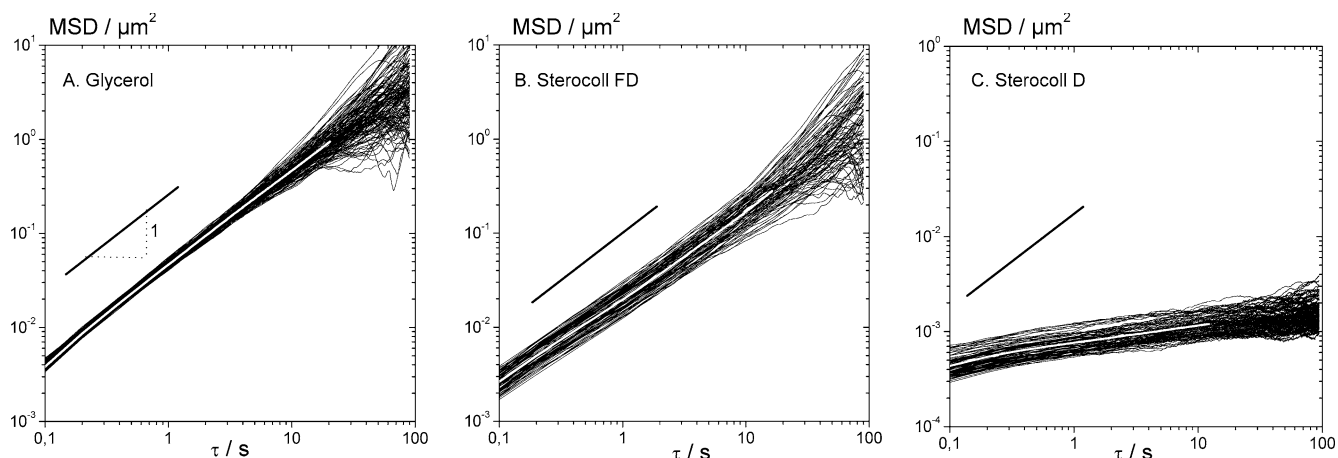

Fig. 2 Mean square displacement of individual microspheres dispersed in solution of glycerol 85% (**A**), Sterocoll FD 1% (**B**) and Sterocoll D 1% (**C**). The *white curve* is the ensemble-average MSD

that is the signature of elastic trapping of the beads by the mesh of the Sterocoll D solution. Another observation concerning the MSD traces is that the range of displacement at a given time scale is narrow for the glycerol/water mixture, but much wider for the two acrylic thickener solutions. To derive the macroscopic properties of each solutions, the ensemble-average MSD and ensemble-average diffusion coefficient were calculated from the individual MSDs. The ensemble-average diffusion coefficient decreases slightly from 1.17×10^{-14} m^2/s (glycerol 85%) to 0.5×10^{-14} m^2/s (Sterocoll FD). In comparison the same microsphere has a diffusion coefficient of 0.86×10^{-12} m^2/s in water at 20 °C.

MSD Distributions and Statistical Analysis

To quantify the level of inhomogeneity in the different solutions we generated the MSD distributions from the MSD

traces, normalized by the ensemble-average MSD. For the glycerol solution the MSD distribution is symmetric about the mean (Fig. 3A), as expected for a homogeneous liquid. For the Sterocoll FD solution, the distribution is also fairly symmetric (Fig. 3B), however it is significantly broader compared to the glycerol mixture. Finally, the MSD distribution further broadens and becomes even asymmetric (Fig. 3C) for the Sterocoll D solution.

By analyzing the contribution of the 10, 25, and 50% highest MSD values to the ensemble-average MSD at a time scale of 1 s (Fig. 4), we find that for the glycerol solution these parameters are close to those expected for a perfectly homogeneous liquid (10, 25, and 50%), for which all MSD values should theoretically be similar. For the Sterocoll FD, despite the fact that this solution behaves mostly like a liquid, it displays a much higher degree of heterogeneity than the glycerol solution (Fig. 4). The contributions of the 10, 25 and 50% highest MSD
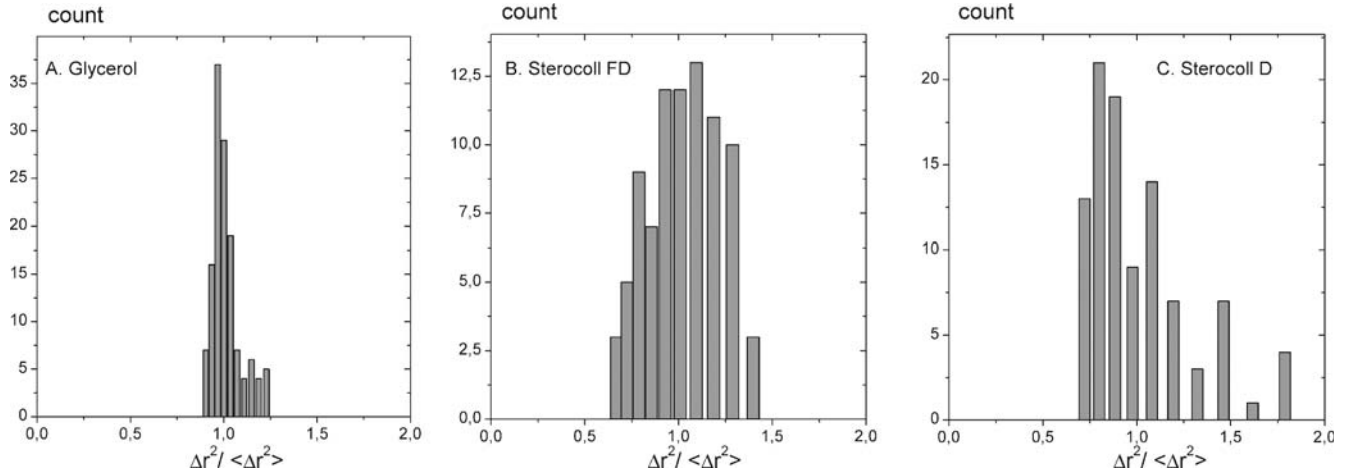
Fig. 3 MSD distributions measured at time lag of 0.1 s, normalized by the corresponding ensemble-average mean, for a solution of glycerol 85% (**A**), Sterocoll FD 1% (**B**) and Sterocoll D 1% (**C**)
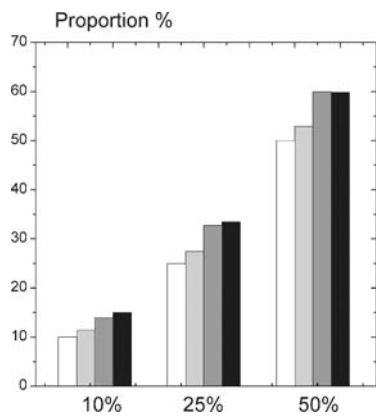

Fig. 4 Contributions (in %) of the 10, 25, and 50% highest MSD values to the ensemble-average MSD at a time scale of 1 s. Note that the contributions predicted for a perfectly homogeneous solution should be exactly 10, 25, and 50% respectively (*first column*). The *second column* represents the solution of glycerol 85%, the *third column* Sterocoll FD 1% and *fourth column* Sterocoll D 1%

values are (14, 32.7, 59.9%) respectively. For the Sterocoll D solution the contribution of the highest MSD values are slightly larger (15, 33.4, 59.8%) than those for Sterocoll FD (Fig. 4). This results indicate a slightly higher degree of heterogeneity for this system.

Van Hove Correlation Function

In order to perform the statistical analysis we examined the distribution of displacements at lag time τ, known as van Hove correlation function [25, 26]. The equation expression is given by:

$$G_s(r, \tau) = \frac{1}{N} \sum_{i=1}^{N} \langle \delta(r_i(\tau) - r_i(0) - r) \rangle = \frac{N(r, \tau)}{N} ,$$

where $r_i(\tau)$ is the distance traveled by a particle i in a time τ. $N(r, \tau)$ is the number of particles that move a distance between r and $(r + \mathrm{d}r)$ in a time interval τ, and N is the number of particles. To a first approximation $G_s(r, \tau)$ has a Gaussian form but deviations from this form reflect the presence of heterogeneities. Such deviations can be characterized by the non-Gaussian parameter [27]

$$\alpha = \frac{\langle r(\tau)^4 \rangle}{3 \langle r^2(\tau) \rangle^2} - 1 .$$

This quantity is zero for a Gaussian distribution, while broader distributions result in large values of α. The van Hove correlation functions for the glycerol, Sterocoll FD and Sterocoll D solutions are shown in Fig. 5A–C respectively. The solid line represents the Gaussian fit to the distribution. For the glycerol solution the ensemble-averaged data fits well to a Gaussian over several order of magnitude (Fig. 5A), as expected for a homogeneous, purely viscous fluid. The α value is 0.04, a strong indicator for the homogeneity of the solution. By contrast, in Sterocoll FD (Fig. 5B) and Sterocoll D (Fig. 5C) the α values are 0.225 and 0.283 respectively. This deviation of the ensemble-averaged distribution from Gaussian behavior indicates and confirms the heterogeneity of those systems.

Viscosity and Moduli

The variation of the viscoelastic moduli as a function of frequency has been determined as well as by MPT and standard oscillatory rheology. For MPT, the rheological properties were extracted from the MSD measurements following the method of Mason et al. [22]. After Laplace transformation of the MSD traces and the use of the generalized Stockes–Einstein relation (GSER), a complex modulus was calculated, from which frequency dependent elastic and viscous moduli, $G'(\omega)$ and $G''(\omega)$ respectively
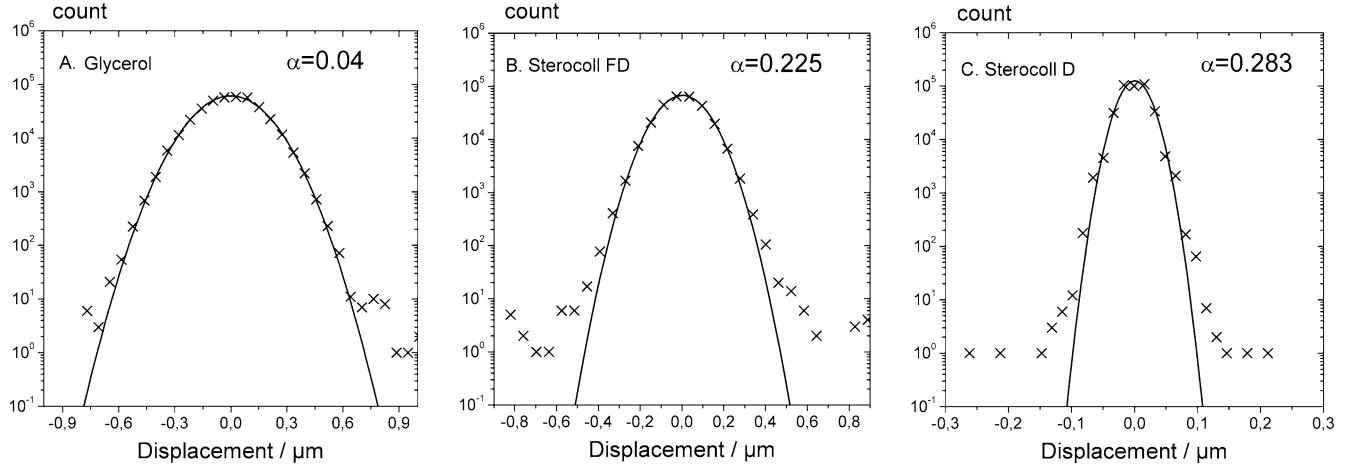
Fig. 5 Van Hove correlation functions for the ensemble-average particles, at time lag 1 s, moving in glycerol 85% (**A**), Sterocoll FD 1% (**B**), Sterocoll D 1% (**C**). The ensemble-average data is fit by a Gaussian distribution. α value is a measure of the fit of the curve to the data, with 0 being a perfect fit
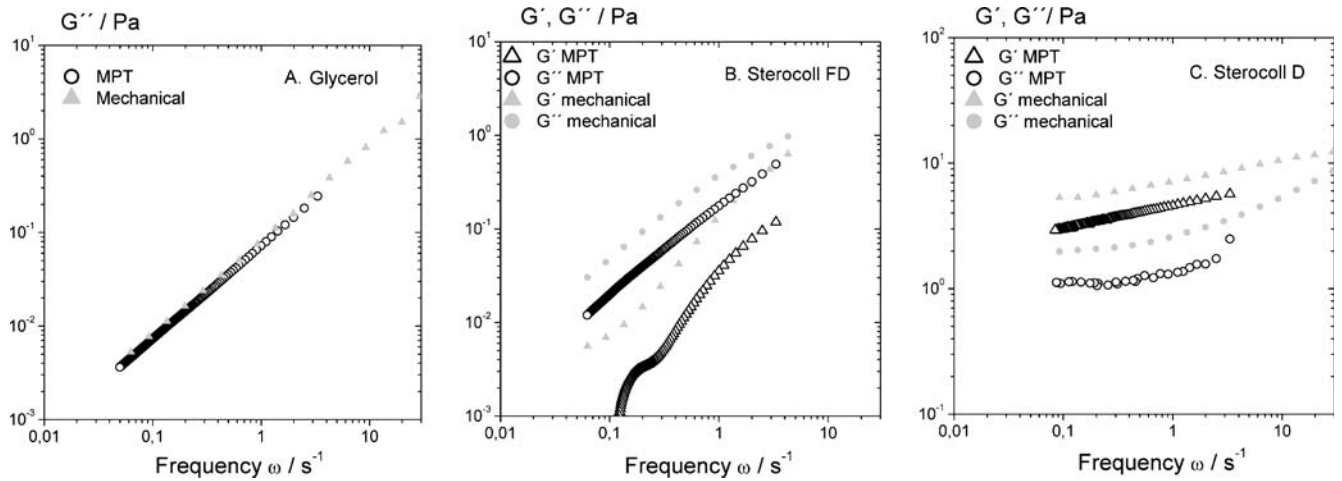

Fig. 6 Frequency-dependent elastic modulus G' and viscous modulus G'' of solution of glycerol 85% (**A**), Sterocoll FD 1% (**B**), Sterocoll D 1% (**C**). *Open symbols* were obtained with MPT, *solid symbols* with mechanical rheology

were extracted. For each sample the zero shear viscosity η_0 has been determined performing steady shear measurements. $\eta_0 = 0.1 \pm 0.01$ Pa s for glycerol/water mixture and 0.24 Pa s for the Sterocoll FD solution. The Sterocoll D solution is strongly shear thinning with a viscosity of 10 Pa s at a shear rate of 0.1 s^{-1}. The glycerol solution exhibits no measurable elasticity modulus G', but only a viscous modulus G'' that increases linearly with the frequency, as expected for this Newtonian liquid (Fig. 6A). The viscosity value determined from mechanical rheometry is $\eta = 0.084 \pm 0.005$ Pa s. From particle tracking measurement $\eta = 0.073 \pm 0.007$ Pa s using $\langle \Delta r^2 (\tau) \rangle \propto 4D\tau$ with $D = k_B T / 6\pi\eta a$ and $D = 1.17 \times 10^{-14}$ m^2/s. The errors introduced here are the standard deviations of repeated measurements on the same sample and refer to the repro-

ducibility of the measurements. The Sterocoll FD solution (Fig. 6B) shows both G' and G'' moduli with $G'(\omega) < G''(\omega)$ confirming a mostly viscous behavior. On the contrary, the Sterocoll D solution (Fig. 6C) shows a significant degree of elasticity with $G'(\omega) > G''(\omega)$ and constant modulus $G' = 10$ Pa in the whole frequency range investigated. The comparison between the rheological properties obtained from the two different techniques shows very good agreement for the glycerol solution, but in the case of the Sterocoll FD and Sterocoll D solutions the viscoelastic moduli are underestimated by a factor ~ 2. We believe this difference could be due to dynamical errors coming from the particle motion during the finite exposure time required for imaging. This error increases with the viscosity of the medium [24].

Conclusions

In this study, we have investigated the mechanical microenvironments and microheterogeneity of acrylic thickeners solutions using the MPT method and compared the results with those obtained for a glycerol/water mixture, characterized as a homogeneous fluid on the length scale of our tracer particles. For the Sterocoll FD solution, the MSD traces varies almost linearly with time, as expected for a predominantly viscous liquid. The MSD distribution exhibits a symmetric shape, however the histogram of MSD values as well as the van Hove analysis clearly reveal the heterogeneity of the system. For the Sterocoll D solution the MSD traces reach a quasi-plateau at time scales up to 100 s, consistent with an elastic trapping of tracer particles in a gel-like environment. For this system, the MSD distribution is highly asymmetric and the statistical analysis shows stronger heterogeneity than for the Sterocoll FD solution. Concerning the rheological quantities there is a fair agreement between MPT and mechanical measurements with in a factor of two, nevertheless improvement of our experimental set-up and calculation process is necessary for quantitative determination of bulk viscoelastic properties of solutions in the viscosity range > 0.1 Pa s.

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