Structural, micro and macro-rheological properties of a ternary Silica-Pluronic F127-Starch system

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ABSTRACT

Multiple-particle tracking (MPT) microrheology in combination with classical bulk mechanical rheometry has been used to characterize structural and rheological properties of a ternary Silica-Pluronic-Starch system. Results reveal that the structure in the gel state consists presumably of viscous areas with a characteristic length scale less than 1 µm within an elastic matrix formed of cell-spanning aggregates of silica particles.

INTRODUCTION

Thermosensitive systems find broad applications in many industrial processes and products[1]. Understanding and modelling such systems is of high technical relevance and often the key to solve challenging production issues is to identify the materials microstructure. Indeed, a correlation between microstructure, microrheology and bulk rheology is the key to a rational goal-oriented product design.

In general, mechanical properties of complex fluids are characterized using classical bulk rotational rheology. This latter technique provides an average measurement of the bulk response, but does not allow for local measurements in the system. To address these issues, a new class of microrheology measurement techniques has emerged[2] to probe the material response on micrometer length scales with microliter sample volumes. Microrheology methods typically use embedded micron-sized probes to locally deform a sample.

In this study, we have used the method of multiple-particle tracking. The basic idea of MPT is to monitor the Brownian motion of inert fluorescent tracer particles that are evenly distributed within the fluid by means of digital video microscopy. The resulting particles trajectories are then transformed into mean square displacement (MSD) traces using a track algorithm. Statistical analysis of the MSD distribution provides information about the degree of heterogeneity in the system and local viscoelastic properties with microscale resolution can be extracted following the method of Mason et al.[3]. Up to now, MPT has been frequently used to study biological matter, such as micro-structural and micro-mechanical properties of actin filament network[4], living cells[5], proteins[6], DNA solutions[7], or biological gels[8]. More recently it has also been used to study commercial acrylate thickeners[9] and hyaluronic acid cryogels[10] for application in tissue engineering.

We have used MPT in combination with bulk rheology to investigate structural, micro and macro-rheological properties of three component Silica-Pluronic F127-Starch thermosensitive dispersion at concentrations of 50%-1%-1% respectively. From bulk mechanical measurements, we have determined the sol-gel transition temperature ($T_{sol\text{-}gel}$) of the suspension and characterized macro-viscoelastic properties in both liquid and gel states. MPT has been performed in both states by adding tracer particles of different diameter (0.5 μm and 1 μm), which allows to characterize local viscoelastic and microstructural properties of the system. Additionally, the effect of varying the silica particles concentration on the gelation kinetics, micro and macro-structural and rheological properties has been investigated too.

EXPERIMENTAL

Materials

The three component system investigated consists of colloidal silica particles, Levasil 30/50, kindly provided by AkzoNobel PPC (Bohus, Sweden), temperature-responsive triblock copolymer Pluronic F127 (PEO_{99}-PPO_{67}-PEO_{99}) provided by BASF (Germany) with molecular weight 12600 g/mol and hydroxypropylated and oxidized potato starch Solcoat P55 supplied by Solam (Germany). Polymer concentrations were kept constant-1:1 (2% polymers in total). Dispersions at solid contents of 30%, 40% and 50% silica particles were tested.

Methods

A rotational rheometer Rheoscope 1 (Thermo Electron) equipped with a cone-plate measuring cell (diameter 50 mm, cone angle 1°) was used to perform small amplitude oscillatory shear experiments covering the frequency range from 0.1 to 100 rad.s^{-1}. Strain sweep experiments performed prior to frequency sweeps ensure that the strain amplitude used was sufficiently small to provide a linear material response at all investigated frequencies. The sol-gel transition temperature of the system has been determined performing oscillation temperature sweep tests, varying the temperature from 20 to 35 °C with a heating rate of 0.3 °C/min. A solvent trap was used to avoid evaporation of the sample during the experiments.

MPT experiments were performed using an inverted fluorescence microscope (Axio Observer D1, Zeiss), equipped with a Fluar 100x, N.A. 1.3, oil-immersion lens or a C-Apochromat, 40x, N.A. 1.2, water-immersion lens. We have used green fluorescent polystyrene microspheres of 0.5 and 1 μm diameter (Bangs Laboratories) as tracer particles. The mixture (vol. ~20 μl) containing the investigated fluid including the tracers was injected into a self-build chamber, consisting of a coverslip and microscope glass slide. Images of these fluorescent beads were recorded onto a computer via a sCMOS camera Zyla X (Andor Techology). Displacements of particle centers were monitored in a 127 × 127 μm and 269 × 269 μm field of view respectively, at a rate of 10 frames/s. Movies of the fluctuating microspheres were analysed by a custom MPT routine incorporated into the software Image Processing System (Visiometrics iPS) and a self-written Matlab program based on the widely used Crocker and Grier tracking algorithm.

RESULTS AND DISCUSSION

For the system with 50% silica particle concentration, the variation of the viscoelastic moduli G′ and G′′ as a function of temperature as determined from bulk mechanical rheology is reported in Fig.1.

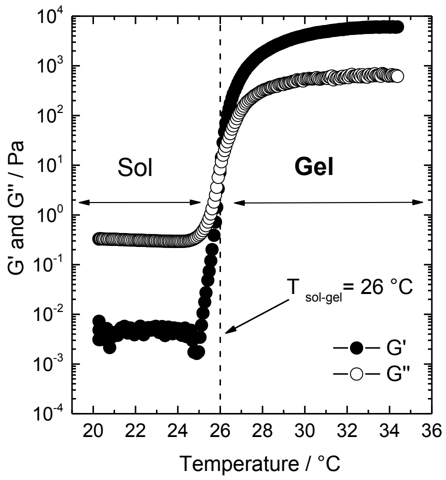

Figure 1. Temperature sweep test for 50% silica particles with 1% PF127 and 1% Starch at $\omega = 10$ rad.s^{-1} and $\sigma = 1\ Pa$.

$T_{sol\text{-}gel}$ has been determined directly from the crossover of G´ and G´´ and has been found to be ~26°C. Oscillatory shear measurements (Fig. 2) performed in the liquid state, at T=20 °C, exhibit a liquid like behaviour with G´´>G´ and variations G´´~ ω and G´~ω^2. In the gel state at T=35°C, the system shows a typical gel like behaviour with G´>G´´ and constant modulus G′=4300 Pa in the whole frequency range investigated.

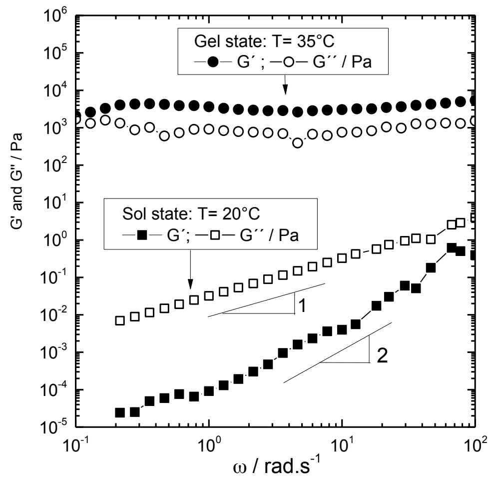

Figure 2. Frequency sweep test for 50% silica particles with 1% PF127 and 1% Starch in the liquid and gel state.

Absolute values of G´ and G´´ moduli obtained from oscillatory shear measurements are in fairly good agreement with those obtained from temperature sweep tests at corresponding temperatures and similar angular frequency ω=10 rad.s^{-1}. Similar experiments have been performed decreasing the silica particle concentration, but keeping constant both pluronic and starch concentrations to 1%. $T_{sol\text{-}gel}$ is not affected by the silica particle concentration decrease, but on the other hand absolute values of G´ and G´´, both in liquid and gel states, decrease as shown in table 1. The main effect is observed in the gel state, where the elastic modulus G´ decreases strongly from 6000, 4061 to 766 Pa as the silica concentration decreases from 50, 40 to 30%, respectively, indicating the formation of much less stiffer gels.

Table 1. G´ and G´´ from the temperature sweep experiments.

	T = 20 °C		T = 35 °C	
[Si]	G’/ Pa	G´´/ Pa	G´/ Pa	G´´/ Pa
30%	0.001	0.045	766	92
40%	0.004	0.081	4061	453
50%	0.005	0.330	5993	628

In addition to bulk mechanical measurements, microstructural and local viscoelastic properties of this system have been investigated by means of multiple-particle tracking. Measurements have been performed both in liquid and gel states after mixing the solution with fluorescent polystyrene particles of different diameter (0.5µm and 1µm). For measurements performed in the sol state with both particle sizes, the ensemble-average MSD trace adopt a power-law behavior as a function of time with a slope β close to 1 $\langle\Delta r^2(\tau)\rangle \sim \tau^{\beta}$ throughout the probed time scales, Fig. 3A. This result indicates that the motion of the

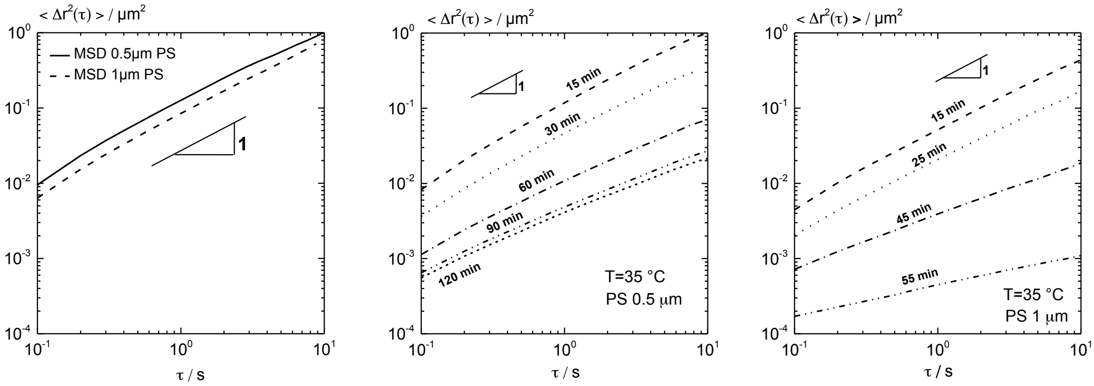

Figure 3. Ensemble-average MSDs for 50% silica, 1% PF127 and 1% starch solution in the sol state at 20 °C (A), in the gel state at 35 °C with 0.5 (B) and 1 μm (C) fluorescent tracers up to one hour

beads is purely diffusive and that the microenvironment surrounding the particles responds like a viscous liquid. The apparent viscosity η_{app} in these viscous micro regions has been determined from MSD traces using the relation $\langle \Delta\, \vec{r}^2(\tau) \rangle = 4D\tau$ in combination with the Stokes-Einstein relation $D = k_B T / 6\pi\eta a$, where D is the diffusion coefficient and a is the tracer particle radius.
We found η_{app}= 24.7 and 20.2 mPa.s for measurements performed with particles of diameter 0.5 and 1 μm respectively. These values are in good agreement with the viscosity value determined from bulk rheological measurements: i.e., η_{Bulk}= 20 mPa.s.

For MPT measurements performed in the gel state, 15 minutes to 2 hours after the sol-gel transition, at T=35 °C and with tracer particles of diameter 0.5 μm (Fig. 3B), the ensemble-average MSD varies almost linearly with time indicating that the motion of the tracers is always diffusive and that essentially all particles explore a viscous environment. At the same time, the MSD absolute value continuously decreases with time indicating an increase of η_{app} in this region from 26 to 714 mPa.s, respectively. This result reflects the presence of a slow kinetic process occurring at a microscale level directly after the gel formation. This latter corresponds probably to a rearrangement of the network formed by the silica particles with a progressive shrinkage of the network mesh size leading to an increase of the polymer concentration within this viscous region as function of time, without ever trapping these 0.5 μm tracer particles during the total duration of the experiment. MPT results obtained in the gel state but with larger particles of diameter 1 μm are shown in Fig. 3C. Here, at times shorter than 45 minutes the ensemble-average MSD varies, as with 0.5 μm particles, linearly with time, but after one hour it exhibits a much weaker time dependence (slope ~0.4) indicating that these particles are elastically trapped presumably in regions, where silica particles bridge-flocculated and interpenetrate in a strong elastic network.

In summary, the variation of the probe size reveals that the structure in the gel state consists supposedly of viscous areas within an elastic matrix and that the size of these areas decreases slowly with time with a characteristic length scale or mesh size less than 1 μm (Fig. 4). The matrix is probably formed of silica particles with adsorbed pluronic molecules on their surface which have aggregated together, thus forming a strong elastic network, while the viscous regions contain probably a mixture of starch and pluronic molecules.

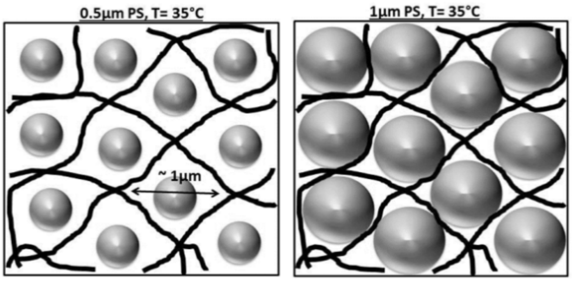

Figure 4. Schematic representation of the gel microstructure according to the MTP results for 0.5µm (left) and 1µm (right) tracers. Black lines represent the elastic network composed of silica particles with adsorbed pluronics, surrounded by viscous solution containing polymers.

CONCLUSIONS

In this work we have used well-established experimental methods: classical rotational rheology and MPT to get new insight into structural and dynamical properties accompanying the sol-gel transition of a ternary Silica-Pluronic F127-Starch thermosensitive system.

For a solution of composition Silica 50%-Pluronic1%-Starch1%, we have determined a sol-gel transition temperature of ~26°C and a kinetic of gel formation less than 2 minutes. Additionally, decreasing the silica particle concentration in the system does not affect gelation time and sol-gel transition temperature, but on the contrary it has a significant effect on G′ in the gel state where a strong decrease in elasticity is observed.

MPT results performed in the sol state shows that tracer particles, independently of their diameter, have a purely diffusive behaviour indicating that the micro-environment surrounding the particles responds like a viscous liquid. In the gel state, the variation of the probe size reveals that the structure of the system consists presumably of viscous micro-areas with a characteristic length scale or mesh size less than 1 µm within an elastic matrix built of cell-spanning aggregates of silica particles and that the size of these areas decreases slowly with time.

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