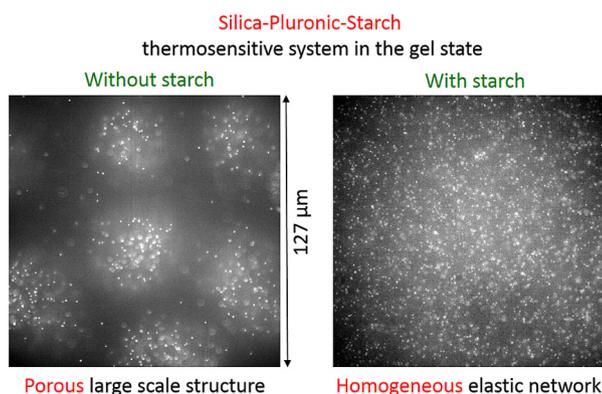Regular Article

# Structural, microrheological and kinetic properties of a ternary silica-Pluronic F127-starch thermosensitive system

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GRAPHICAL ABSTRACT



Silica-Pluronic-Starch
thermosensitive system in the gel state

Without starch

With starch

127 μm

Porous large scale structure

Homogeneous elastic network

ARTICLE INFO

ABSTRACT

*Hypothesis:* The sol-gel transition in aqueous suspensions consisting of silica particles and thermosensitive polymer is controlled by inter-particle forces and solution properties of the polymer. Addition of a second non-thermosensitive polymer may affect the transition. The purpose of this work was to characterize the kinetics of the sol-gel transition and to understand the effects of a second non-thermosensitive polymer on the microstructure, using a combination of classical rheology and microrheology.
*Experiments:* Classical rotational rheology as well as two microrheology methods, Multiple Particle Tracking (MPT) and Diffusing Wave Spectroscopy (DWS), were used to investigate the sol-gel transition of a ternary silica-Pluronic F127-starch thermosensitive system.
*Findings:* Classical rheometry and DWS indicated sol-gel transition temperature ~25 °C at 1 wt% Pluronic, independently of the concentration of the other components. DWS showed a fast gelation process, less than two minutes for all samples, beside a second slow kinetic process. In the gel state, MPT indicated micro-structural and micro-viscoelastic differences compared to rotational rheology. This was explained by formation of an elastic matrix of silica and polymers in combination with assembly of silica particles in large macroporous agglomerates. Presence of starch led to breakdown of the macroporous network, leaving the homogeneous elastic network left.

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## 1. Introduction

Recently, there has been a strong interest for stimuli-responsive colloidal systems [1–4]. The transition from a low-viscosity liquid to an elastic gel in thermosensitive polymer solutions upon heating is an unusual phenomenon, since a numerous types of structured complex fluids often tend to decrease in viscosity with increasing temperature [4]. Thermosensitive systems might find a broad application in many industrial processes and drug delivery [4–6]. Understanding the colloidal stability and the liquid-solid transition in thermosensitive suspensions is of high importance, not only from a fundamental point of view, but also in relation to technological processability and possible applications. Good knowledge of these properties would be helpful in designing new high value products in e.g. the paper industry [7].

Intelligent temperature-sensitive packaging which monitors temperature changes and displays information on quality as well as 3D printing have already strengthened their positions in the packaging and printing industry [5,8], but still there are not enough information regarding the kinetics of sol-gel transition as well as the microrheology and microstructures in thermosensitive coating dispersions and their possible advantages.

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (PEO-PPO-PEO), known as Pluronics or Poloxamers, are well-known to possess thermoreversible properties and one of the most widely studied Pluronic is the Pluronic F127 (PF127), see e.g. Bohorquez et al. [9] and Jalaal et al. [10]. The structure in aqueous solutions of PF127 has been studied in details by various techniques and different phases depending on temperature and polymer concentration have been reported [9,11,12]. At low concentrations and temperatures, the amphiphilic character of PF127 leads to formation of spherical micelles, while with increasing the temperature and the concentration, the micellization tendency is strongly enhanced, which results in rapid increase in the volume fraction of spherical micelles and thermogelling occurs. For pure PF127 solutions, the sol-gel transition occurs with a minimum pluronic concentration of ∼15 wt% and at a temperature of ∼40 °C. Latter temperature decreasing as the pluronic concentration increases [11,13]. Therefore most of the studies and real implementations of PF127 have focused on concentrated systems. Beside studies on pure Pluronic systems, hybrid systems composed of Laponite [14] and/or silica [15,16] nanoparticles mixed with Pluronic have been investigated too. In latter studies, essentially rotational rheology and small angle neutron scattering (SANS) have been used to characterize the evolution of the structure and interaction of nanoparticles and Pluronic through the variation of temperature. In particular, authors discussed the adsorption of Pluronic on nanoparticles surface as well as the aggregation mechanism induced by depletion interaction between particles. They also report that a relatively low PF127 concentration (∼1 wt%) is required [14,16] to get a sol-gel transition as compared to the one-component Pluronic system. Despite large interests on these systems, it still remains to understand the complex interplay of interparticle forces and their microstructures. In the present study, we focus on a ternary silica-PF127-starch system. Latter has already been investigated by Petkova-Olsson et al. by performing macrorheological measurements from which structural properties [17,18] as well as the effect of temperature on interactions between starch and Pluronic F127 [3] have been characterized. The aim of our study is to characterize for the first time the kinetic of the sol-gel transition and to understand the effects of the addition of a second non-thermosensitive polymer, namely starch, on the microstructure and agglomeration mechanism. This might open up future possibilities, related to immobilization of active compounds into a paper coating dispersion analogical to target drug- delivery systems. To achieve these purposes we have used a combination of classical rotational rheology and two new microrheology [19,20] techniques namely: Multiple Particle Tracking (MPT) [21,22] and Diffusing Wave Spectroscopy (DWS) [23,24]. Both techniques provide structural, rheological and dynamical informations of the material on a local scale (0.1–10 μm). In the first part of this paper, we have compared the sol-gel transition temperature $T_{sol-gel}$ as determined from bulk rheological and DWS measurements. Then for the first time, DWS has been used to determine the kinetic of the complete gelation process. In the second part, MPT measurements have been performed both in the liquid and gel states by adding tracer particles of different diameter (0.5 and 1 μm), in order to characterize local viscoelastic and microstructural properties of the system. Finally, the effect of varying starch concentrations in the sample composition on the gelation kinetics, structural and rheological properties has been investigated too.

## 2. Experimental

### 2.1. Materials

Colloidal spherical silica particles, Levasil 30/50 (here denoted SP), were kindly provided by AkzoNobel PPC (Bohus, Sweden) and supplied as an aqueous dispersion at 50% solids by weight. The $\zeta$ -potential of the silica particles used is negative over the region of pH 2–pH 10, indicating that the silica particles carry a net negative surface charge over this pH range. The density of the particles is assumed to be 2.2 $g/cm^3$ [25], the BET surface area is 40 $m^2/g$ and particle diameter is 75 nm according to dynamic light scattering measurements. The same initial batch of aqueous suspension of silica particles was used for all the experiments performed in this study.

Pluronic F127 (PF127), a $PEO_{98}$-$PPO_{67}$-$PEO_{98}$ triblock copolymer was kindly provided by BASF-SE (Germany), it is classified as a non-ionic surfactant with molecular weight of 12,600 g/mol according to the manufacturer and was used without further purification. PF127 is a thermosensitive polymer, which becomes insoluble in water when heated due to its lower critical solution temperature (LCST).

Hydroxypropylated and oxidized potato starch Solcoat P55 (Solam, Germany) was used here. This starch has a degree of substitution (DS) with respect to hydroxypropyl groups of around 0.1, a pH of approx. 7 in aqueous solution and a viscosity value of around 30 mPa ∗ s at 20% (Brookfield LVDV 100 rpm at 50 °C) when jet cooked in accordance with the supplier's instructions. The same starch quality was used in all experiments, since the necessary amount of starch was gelatinized and solubilized in a jet cooker (Raisio Chemical, Finland) at approx. 122 °C and pressure of 2 bar and later freeze-dried. The freeze-dried powder was cold-water soluble. All other chemicals were analytical grade and were used without further purification. In all experiments, Milli-Q quality water (Direct-Q 3UV-R, Merck) with a resistivity at 25 °C of 18 MOhm ∗ cm has been used for solution and suspension preparation.

### 2.2. Methods

#### 2.2.1. Sample preparation

Since a thermosensitive PF127 was used in this study, all ternary suspensions of SP, PF127 and starch were mixed at controlled temperature conditions in order to avoid uncontrolled gelation, by using a cold-water bath of approx. 10 °C. Initially, the silica particle concentration was adjusted to 20, 30, 40 or 50 wt%, by 10 mM NaCl solution. Then Pluronic F127 was added to the suspension,

resulting in a total concentration of 1 wt% PF127 in the bulk solution prior to any adsorption, and the mixture was let to homogenize in a cold water bath for two hours. Finally, the cold-water soluble starch powder was added in concentration 0, 1 or 2.5 wt % in the bulk solution and the suspensions were mixed for two more hours. Also 20 wt% PF127 solution in 10 mM NaCl was prepared at low temperature as described for the ternary mixtures. All suspensions were stored in refrigerator and stirred for a few minutes before experiments.

### 2.2.2. Rotational rheometry

A rotational rheometer (Rheoscope 1, Thermo Haake), equipped with a cone-plate measuring cell (diameter $d_{CP} = 50$ mm, cone angle $a_{cone} = 1°$), was used to perform oscillation temperature sweep tests (heating rate 0.3 °C/min) and for determining the sol-gel transition temperature when the gelation took place in the measuring cell. Additionally, small amplitude oscillatory shear experiments covering the frequency range from 0.1 to 100 rad * $s^{-1}$ have been performed. 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. However, to characterize the kinetic of the sol-gel transition two experimental procedures have been used. In the first one, the sample stored at 20 °C was directly placed on the lower plate of the measuring system preheated at 35 °C, then the upper cone was brought into contact and we measure the variation of viscoelastic moduli as a function of time (Section 3.1.2, Fig. 4). In the second procedure, the sample was first squeezed between the cone and plate and then the temperature was increased from 20 to 35 °C (Supplementary information, Fig. S1). A solvent trap was used to avoid sample evaporation during experiments. For rotational rheometry experiments, a relative experimental error of 10% was estimated.

### 2.2.3. Multiple-particle tracking

Multiple-particle tracking experiments were performed using an inverted fluorescence microscope (Axio Observer D1, Zeiss), equipped with a Fluar 100×, N.A. 1.3, oil-immersion lens or a C-Apochromat, 40×, N.A. 1.2, water-immersion lens. In this study we have used green fluorescent polystyrene microspheres with 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 with height ~150 μm. Images of these fluorescent beads were recorded onto a computer via a sCMOS camera Zyla X (Andor Technology). 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 analyzed by a custom MPT routine incorporated into the software Image Processing System (Visiometrics iPS) and a self-written Matlab program [26] based on the widely used Crocker and Grier [27] tracking algorithm. For MPT experiments, a relative experimental error of 5% was estimated.

### 2.2.4. Diffusive wave spectroscopy

DWS experiments were performed using a DWS RheoLab instrument (LS Instruments AG, Fribourg, Switzerland). In our experiments no tracer particles have been brought into the sample instead we have used the silica particles of diameter 70 nm already existing in the solution as scattering centers. The sample was filled in standard glass cuvettes (Hellma) with a path length of 5 mm and a width of 10 mm. The temperature was controlled within ±0.1 °C using a temperature control chamber. A 200 mW single frequency laser (Torus 532, Laser Quantum) operating at a wavelength λ = 532 nm was used to illuminate a circular ground glass mounted

on a two phase stepper motor allowing for more efficient ensemble averaging. We collected the transmitted light coming from the ground glass and focused it onto the sample with a spot size diameter of roughly 5 mm. The scattered laser light was then collected using single-mode optical fiber and single photon counting detector with high quantum efficiency and subsequently analyzed by a digital correlator. Due to the Brownian motion of particles, the detector records the intensity fluctuation from which the intensity autocorrelation function (ICF) $g_2(\tau) - 1 = \frac{\langle I(t).I(t+\tau)\rangle}{\langle I^2\rangle} - 1$ can be calculated. Changes in the variation of the ICF when increasing the temperature from 20 to 35 °C allows for determining the sol-gel transition temperature as well as the kinetic of this transition process. More details about the DWS device and data processing can be found in Oelschlaeger et al. [28]. For DWS experiments, a relative experimental error of 5% was estimated.

## 3. Results and discussion

### 3.1. Macrorheological characterization

#### 3.1.1. Sol-gel temperature determination: Rheology vs DWS measurements

Firstly, $T_{sol-gel}$ was determined using a rotational rheometer by performing oscillatory shear measurements at a constant angular frequency of 10 rad * $s^{-1}$, while the temperature increased from 20 to 35 °C at a heating rate of 0.3 °C/min. Fig. 1A shows the variation of both storage modulus G′ and loss modulus G″ as a function of temperature for a 30%Si-1%PF127-1%Starch suspension. $T_{sol-gel}$ was determined as the point where G′ and G″ cross each other and a value of $T_{sol-gel} = 25 ± 0.6$ °C was obtained. In addition to temperature sweep tests, frequency sweep tests (Fig. 1B) were performed both in the liquid and in gel states corresponding to temperatures of 20 °C and 35 °C, respectively. At T = 20 °C, the system exhibits a liquid like behavior with G″> G′ and variations G″ ~ ω and G′ ~ ω². In the gel state at T = 35 °C, the system shows a typical gel like behavior with G′ > G″ and constant modulus G′ = 3000 Pa in the whole frequency range investigated.
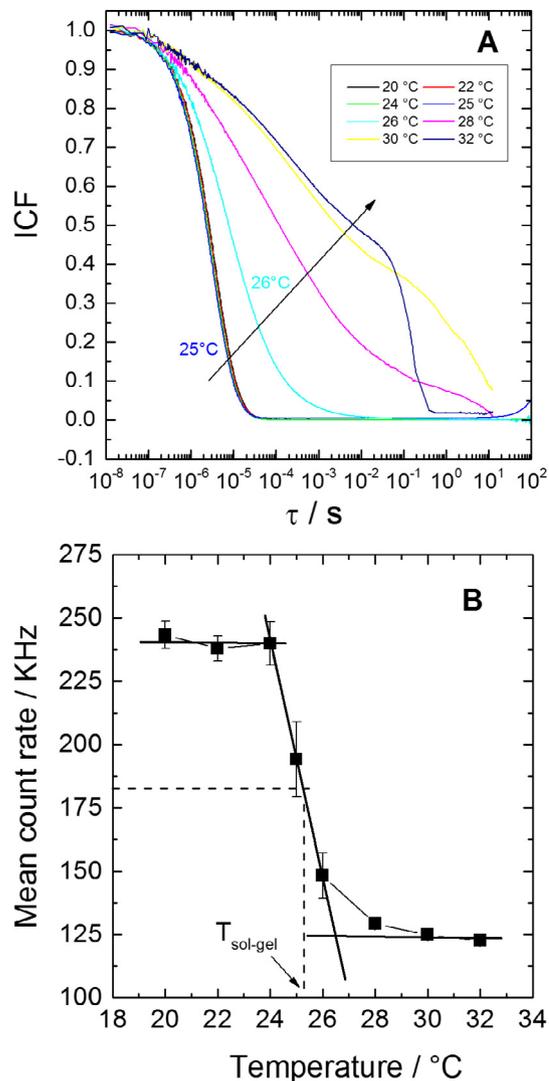
Absolute values of G′ and G″ moduli obtained from oscillatory shear measurements (red symbols in Fig. 1A) are in fairly good agreement with those obtained from temperature sweep tests at corresponding temperatures and similar angular frequency ω = 10 rad * $s^{-1}$.

Secondly, Diffusing Wave Spectroscopy (DWS) was used to determine $T_{sol-gel}$. This scattering technique is an ideal tool for the characterization of particle motion in a media with strong multiple scattering, as it is the case for samples investigated in this study, by treating the transport of light as a diffusion process. With this technique, we have obtained quantitative information about the microscopic dynamics all the way from the liquid state to the final gel, thereby covering the whole sol-gel transition. In these experiments, no additional tracer particles were added to the suspension, instead one of the components of the ternary system (SP) were adopted as a tracer. DWS was used to investigate the same sample as in Fig. 1. The variation of the intensity autocorrelation function (ICF) as a function of lag time (τ) measured at different temperatures between 20 and 32 °C is shown in Fig. 2A. Up to 25 °C, all ICFs show a similar behavior with a fast decay from 1 to 0 corresponding to a fast motion of the sample structure in the liquid state. For the ICF at 26 °C, we observe a deviation with a much slower decrease reflecting a slowdown of the dynamics due to the gelation. From these measurements, we have identified the gel point as being between 25 and 26 °C. For a better accuracy of the $T_{sol-gel}$ value, we have plotted the variation of the average scattered intensity as function of temperature (Fig. 2B). In latter case, $T_{sol-gel}$ has been determined as the temperature obtained at
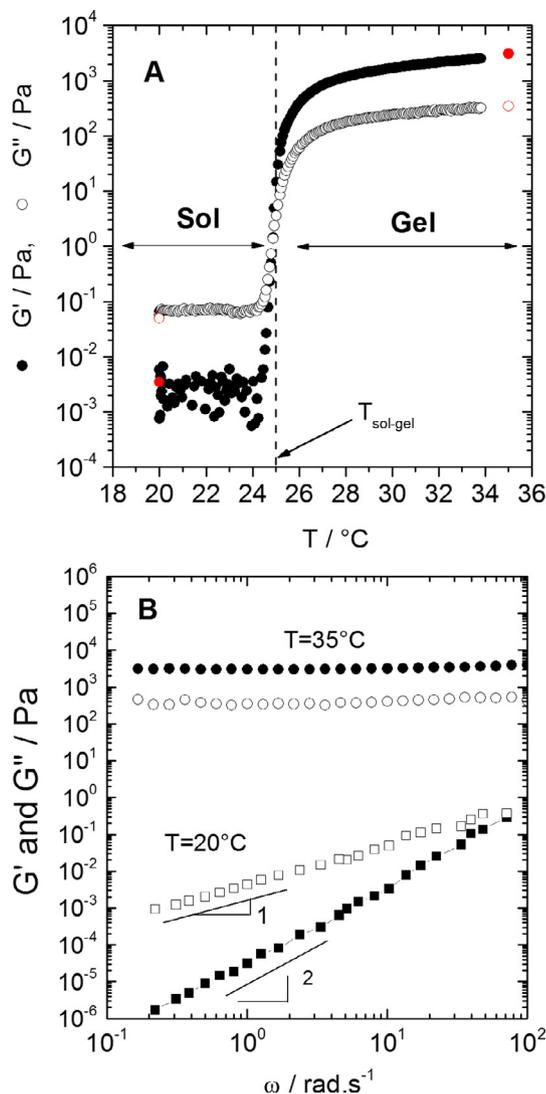
**Fig. 1.** (A) Variation of viscoelastic moduli G′ (closed circles) and G′′ (open circles) of a 30%Si-1%PF127-1%Starch suspension as a function of temperature at a constant stress of 1 Pa and constant angular frequency of 10 rad * s$^{-1}$. Heating rate of 0.3 °C/min. (Red symbols) are obtained from frequency sweep experiments performed at 20 and 35 °C. (B) Variation of G′ and G′′ as a function frequency for T = 20 °C (G′: closed squares, G′′: open squares) and T = 35 °C (G′: closed circles, G′′: open circles) Error bars are as large as the size of the different symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** (A) Variation of the intensity autocorrelation function (ICF) for a 30%Si-1% PF127-1%Starch suspension as a function of lag time at different temperatures between 20 and 32 °C. (B) Variation of the average scattered intensity of the same suspension as in 2A as a function of temperature.

half height of the intensity decrease and has been found to be 25.5 ± 0.6 °C. This value is in a good agreement with that obtained from bulk rheological measurement (25 ± 0.6 °C). Table 1 shows, for all samples investigated, a comparison of $T_{sol-gel}$ values determined from rheological and DWS measurements. In all cases, good agreement has found between both techniques within the experimental errors. In addition, we observe that all values of $T_{sol-gel}$ are constant and equal to ~25 °C. The common point between the samples is that the Pluronic concentration was constant and equal to 1 wt%. This indicates that the Pluronic concentration controls the gelation, independently of silica and starch concentrations. Indeed, Wanka et al. [12,29] reported that the gel temperature for pure aqueous solutions of PF127 decreases with increasing polymer concentration. The value of $T_{sol-gel}$ for the pure PF127 aqueous solution at 20 wt% obtained from our rotational rheometry was equal to 21.5 °C, in rather good agreement to the value of approx. 20 °C as reported by Wanka et al.. In the here studied ternary system, the

sol-gel transition occurs at much lower concentrations of PF127 (as low as 1 wt% in the bulk phase), which is a feature that can provide cost-effective thermosensitive systems in areas such as heat-based coating.

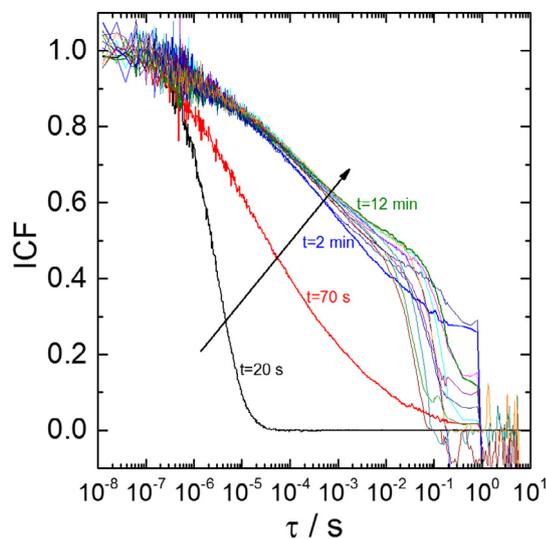### 3.1.2. Kinetics of the sol-gel transition

In addition to the determination of the gelation temperature, we have also monitored the kinetic of this transition process. This latter could not easily be determined by classical rotational rheometry; mainly because the process is fast (quasi-instantaneous), but also because of the risk of structural changes in the sample when lowering the upper plate of the measuring geometry to the contact measuring point. These changes in sample structure made it difficult to get reliable results, at least at very short times. In order to avoid this "squeeze" effect, we have used the DWS technique and monitored the variation of the ICF as a function of time for a sample previously stored at 20 °C in a closed cell and then directly placed in the DWS sample holder preheated at 35 °C (Fig. 3).

Each ICF was averaged during 20 s, which was the minimum time needed for a sufficiently good resolution. The fast decrease of the ICF curve observed a t = 20 s indicates that the sample is still

**Table 1**
$T_{sol-gel}$ determined from rotational rheology (oscillation temperature sweep tests) and DWS measurements.
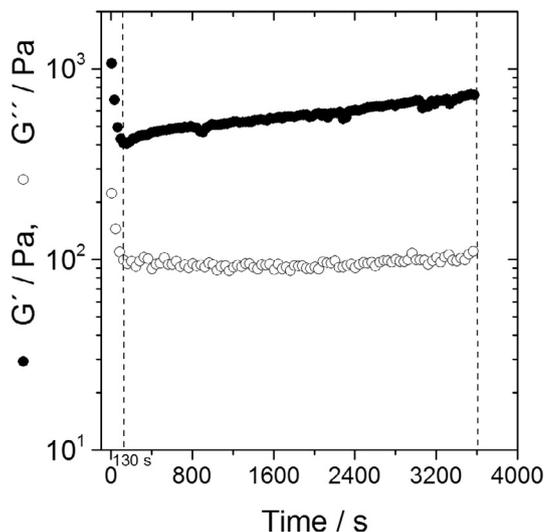
| Si/wt% | PF 127/wt% | Starch/wt% | $T_{sol-gel}$/°C Rotational rheology | $T_{sol-gel}$/°C DWS |
|---|---|---|---|---|
| 20 | 1 | 1 | 25.5 ± 0.6 | 25.0 ± 0.6 |
| 30 | 1 | 0 | 25.5 ± 0.6 | 24.8 ± 0.6 |
| 30 | 1 | 1 | 25.0 ± 0.6 | 25.5 ± 0.6 |
| 30 | 1 | 2.5 | 24.3 ± 0.6 | 24.0 ± 0.6 |
| 40 | 1 | 1 | 26.0 ± 0.7 | 25.5 ± 0.6 |
| 50 | 1 | 1 | 25.1 ± 0.6 | 26.5 ± 0. 7 |



**Fig. 3.** ICF variation as a function of time evolution for a 30%Si-1%PF127-1%Starch suspension at T = 35 °C.



**Fig. 4.** Variation of G′ and G′′ as a function of time for a 30%Si-1%PF127-1%Starch suspension at T = 35 °C at a constant angular frequency of 10 rad * s⁻¹ and stress of 0.1 Pa. Error bars are as large as the size of the different symbols.

### 3.2. Microrheological characterization

#### 3.2.1. MPT in sol and gel states

In addition to bulk mechanical measurements, microstructural and local viscoelastic properties of the 30%Si-1%PF127-1%Starch system were investigated by means of multiple-particle tracking (MPT) microrheology. Measurements were performed both in liquid and gel states after mixing the suspension with fluorescent polystyrene particles of different diameter (0.5 and 1 μm). For measurements performed in the sol state (Fig. 5A), the ensemble-average mean squared displacement (MSD) trace adopt a power-law behavior as a function of time with a slope β close to 1 throughout the probed time scales, where β is given by the relation $\langle \Delta r^2(\tau) \rangle \sim \tau^\beta$. This result indicates that the motion of the beads is purely diffusive and that the microenvironment surrounding the particles responds like a viscous liquid. The apparent viscosity $\eta_{app}$ has been determined from MSD traces using the relation $\langle \Delta \bar{r}^2(\tau) \rangle = 4D\tau$ 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 $\eta_{app}$ = 4.10 and 4.00 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., $\eta_{Bulk}$ = 3.7 mPa * s.

For MPT measurements performed in the gel state at T = 35 °C, 5 min to 1 h after the sol-gel transition and with tracer particles of diameter 0.5 μm (Fig. 5B), the ensemble-average MSD varied also linearly with time indicating that the motion of the tracers was always diffusive and that essentially all particles explored a viscous environment. However, at the same time, the MSD absolute value decreased by almost a factor three, which corresponds to a $\eta_{app}$ increase from 5 to 11 mPa * s, respectively. This result confirms the presence of a slow kinetic process occurring at a microscale level directly after the gel formation. It was only after 80 min that the MSD exhibited a much weaker time dependence (slope ∼0.5) indicating that the movement of these particles is restricted. All these results can be explained by the formation at short time (t < 2 min) of a network formed by the silica particles with a mesh size much larger than the tracer particle diameter (0.5 μm), so that the tracer particles only explore viscous regions. Then the network rearranges with a progressive shrinkage of the

in the liquid state, but the deviation observed at t = 70 s corresponding to a slowdown of the diffusion indicates that the gelation process has already started. The rapid change in the slope of the ICF curves ended after 120 s. This fast kinetic transition from a liquid to a gel was similar for all samples investigated independently of the composition. In addition to this fast process, we also observed at longer times (t > 120 s) that ICFs did not stay constant but on the contrary continued to evolve slowly over time, at least up to 12 min, which indicated a permanent motion of the structure of the gel leading in a strengthening of the network.

This second slow kinetic process was also observed during bulk rheological measurements. Fig. 4 shows variations of G′ and G′′ as a function of time for a sample stored at 20 °C and then directly placed on the lower plate of the rheometer preheated at 35 °C. At short times less than 130 s, which corresponds to the gelation time, both G′ and G′′ decrease strongly. This decrease is probably due to the destruction of part of the gel due to the closing of the upper plate as already mentioned previously. Then from ∼100 s up to 1 h, G′ increases of about 85% from 400 to 740 Pa while G′′ stays constant at a value of 100 Pa. This continuous G′ increase indicates that the structure of the gel network is not stable; it is constantly reorganizing and strengthening itself, thus confirming the presence of the second slow kinetic process as observed from DWS experiments. Another type of rheological experiment, where the sample was first squeezed between the plates and then heated, also confirmed the second slow kinetic process (Supplementary information, Fig. S1). In latter case, the absolute value of the storage modulus increases by approximately 50% from 1.7 to 2.5 kPa.
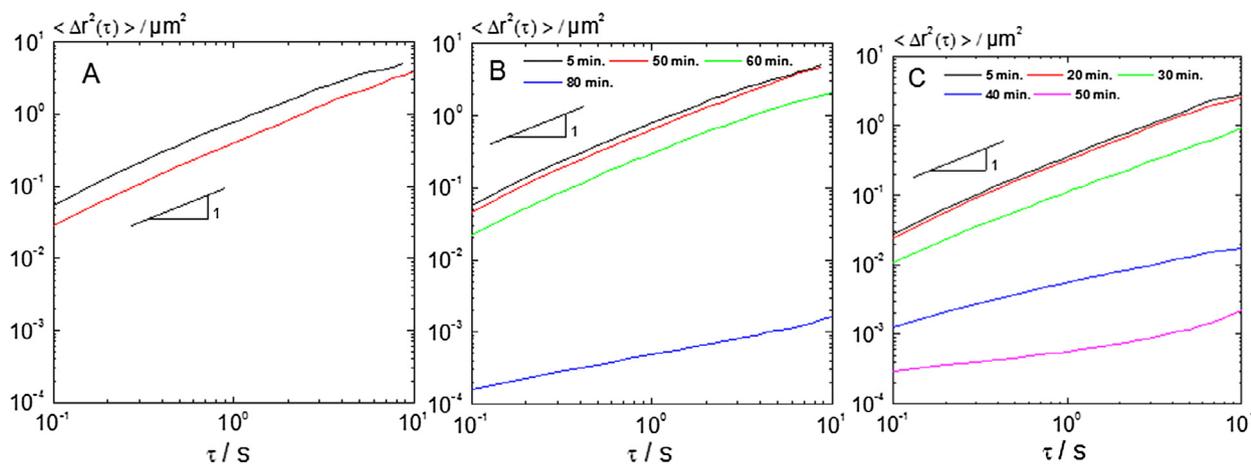
**Fig. 5.** Ensemble-average MSDs for 30% silica - 1% PF127 - 1% starch suspension in the sol state at 20 °C with 0.5 (black line) and 1 μm (red line) tracer particle diameter (A), in the gel state at 35 °C with 0.5 (B) and 1 μm (C) fluorescent tracers up to more than one hour after gelation.

mesh size leading to an increase of the polymer concentration within viscous regions until the particles are completely trapped at longer times. Similar results are obtained with larger tracer particle of diameter 1 μm with however one difference (Fig. 5C): the MSD exhibited an almost time independent behavior already after 50 min.

In summary, the variation of the probe size revealed that the structure of the system consisted presumably of viscous micro-areas within an elastic matrix built of assembled silica particles and that the size of these areas decreased slowly with time with a characteristic length scale or mesh size less than one μm. The matrix was probably formed of silica particles with adsorbed PF127 on their surface as previously described [3,17], which have aggregated together, thus forming a strong elastic network. On the other hand, the viscous regions contained probably a polymer mixture of starch and PF127 molecules. This result was different from that obtained for a pure Pluronic 20 wt% solution where tracer particles (0.5 μm in diameter) were already trapped 10–15 min after the gelation which indicated the formation of a more homogeneous and elastic network in latter case (see Supplementary information, reference system, Fig. S2).

### 3.2.2. Silica concentration effect: Bulk rheology, DWS and MPT

In this section, we investigated the effect of Si concentration on rheological properties while keeping constant both Pluronic and starch concentrations to 1 wt% each. Table 1 has already shown that the sol-gel transition temperature is independent of Si concentration for concentrations between 20 and 50 wt%. However, rotational measurements shows a dependence of absolute values of $G'$ and $G''$ as a function of Si concentration both in liquid and gel states as shown in Table 2. Main effects were observed in the gel state, where $G'$ and $G''$ increase strongly from 504 to 5993 Pa and 53 to 628 Pa, respectively, as the silica particle concentration increases from 20 to 50 wt%. This result indicates the formation of much stiffer and elastic gels when the Si concentration increases, presumably due to a strengthening of the network formed by the assembled silica particles. Concerning MPT measurements, results obtained for samples with Si concentrations of 40 and 50 wt% are almost similar to those obtained with 30 wt%; i.e. MSDs vary linearly with time up to 40–50 min after the gelation process thereafter they flatten indicating trapping of the tracer particle in the network matrix. This result indicates no huge structural and kinetic differences between samples on a micro level; probably for the case of higher particle concentration, the network

**Table 2**

G' and G'' values in both liquid and gels states from temperature sweep tests, where the stress was 0.1 Pa for 20 wt% Si and 1 Pa for 30, 40 and 50 wt% Si, frequency 10 rad $* s^{-1}$ and the heating rate used was 0.3 °C/min. The raw data of the measurements can be find in the Supplementary file, Fig. S3.

| [Si]/wt% | T = 20 °C (liquid state) | T = 35 °C (gel state) | |
|---|---|---|---|
| | G''/Pa | G'/Pa | G''/Pa |
| 20 | $0.025 \pm 2.5 \times 10^{-3}$ | 504 ± 50 | 53 ± 5 |
| 30 | $0.069 \pm 7.0 \times 10^{-3}$ | 3050 ± 30 | 391 ± 39 |
| 40 | $0.081 \pm 8.1 \times 10^{-3}$ | 4061 ± 41 | 453 ± 45 |
| 50 | $0.330 \pm 3.3 \times 10^{-2}$ | 5993 ± 60 | 628 ± 62 |

becomes stronger and stiffer which is responsible for the increase in the elastic moduli $G'$.

### 3.2.3. Starch concentration effect: 30%Si-1%PF127-Starch system

In this section, we investigated the effect of varying starch concentration by keeping constant Si and Pluronic concentrations to 30 and 1 wt%, respectively.

Bulk oscillatory shear measurements were performed on three different samples containing starch concentration of 0, 1 and 2.5 wt% (Fig. 6) in the gel state at T = 35 °C. Results demonstrated similar viscoelastic properties in the three cases; i.e. a strong gel-like behavior with a plateau modulus $G_0 = 2.8 \pm 0.6$ kPa within the experimental errors. Results from MPT measurements performed in the gel state and with tracer particle of diameter 1 μm are shown in Fig. 7. For all suspensions independently of starch concentration at 30 min after the sol-gel transition, the variation of the MSD shows a similar behavior (Fig. 7A–C): i.e. a linear time dependence indicating that the microenvironment surrounding the particles responds like a viscous liquid. However a viscosity increase is observed from 3.3, 17 to 34 mPa ∗ s for suspensions with starch concentration 0, 1, 2.5 wt%, respectively. This increase is probably not only due to the increase of starch concentration in the aqueous phase, since for a pure aqueous 2.5 wt% starch solution the viscosity is less than 2 mPa ∗ s.

Presumably, the interactions between non-adsorbed Pluronic and starch formed inclusion complexes that were responsible for this viscosity increase. In a previous study, Petkova-Olsson at al. [3] have shown the formation at elevated temperatures of such PF127-starch complexes by performing surface tension titration and quartz crystal microbalance measurements. Gruber and Konish [30] also reported the ability of starch to form inclusion complexes with hydrophobic moieties of cellulose ether, latter being responsible of a viscosity enhancement.
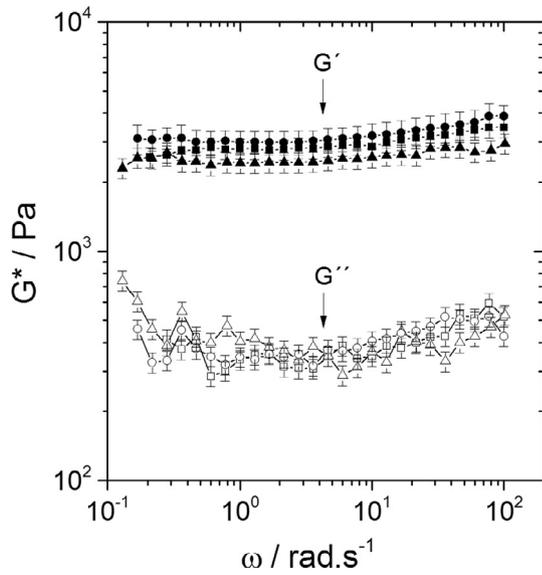
**Fig. 6.** Frequency sweep tests for suspensions 30% silica-1% PF127 with 0% (square), 1% (circle) and 2.5% (triangle) starch concentration in the gel state at 35 °C. G' (closed) and G''(open) symbols. 10% error bars for all symbols.

A different behavior was observed at slightly longer times (40–50 min). For the sample without starch (Fig. 7D), even 50 min after the gelation, the MSD varied linearly with time indicating that particles sense the same viscous region as at short times with nevertheless a slight viscosity increase from 3.3 to 6 mPa ∗ s. Whereas, for both samples containing starch concentrations of 1 and 2.5 wt% (Fig. 7E and F), the MSD showed a time-independent behavior after 50 and 40 min, respectively. These differences in microrheological behavior can be related to differences in microstructural properties.

Optical microscope images performed on the three samples containing tracer particles before the thermogelling process starts and up to one hour after the gelation process are shown in Fig. 8.

For the sample without starch, 10 min after the sol-gel transition (Fig. 8A) the particle repartition is very homogeneous similar as in the liquid state at T = 20 °C (results not shown), then becomes slightly heterogeneous after 30 min. (Fig. 8B) and finally strongly heterogeneous after 60 min. (Fig. 8C). In the latter case, the particles represented by white dots are located in round pores of diameter 60–70 μm separated from each other by black areas of thickness ~30–50 μm, with no tracer particles in it. Latter areas presumably correspond to a network formed of agglomerated silica particles with a large number of particles defining the thickness of the network lamella, between 40 and 100 particles as one particle has a diameter of 0.75 μm. White areas represents viscous regions that might contain Pluronic residues, which have not been
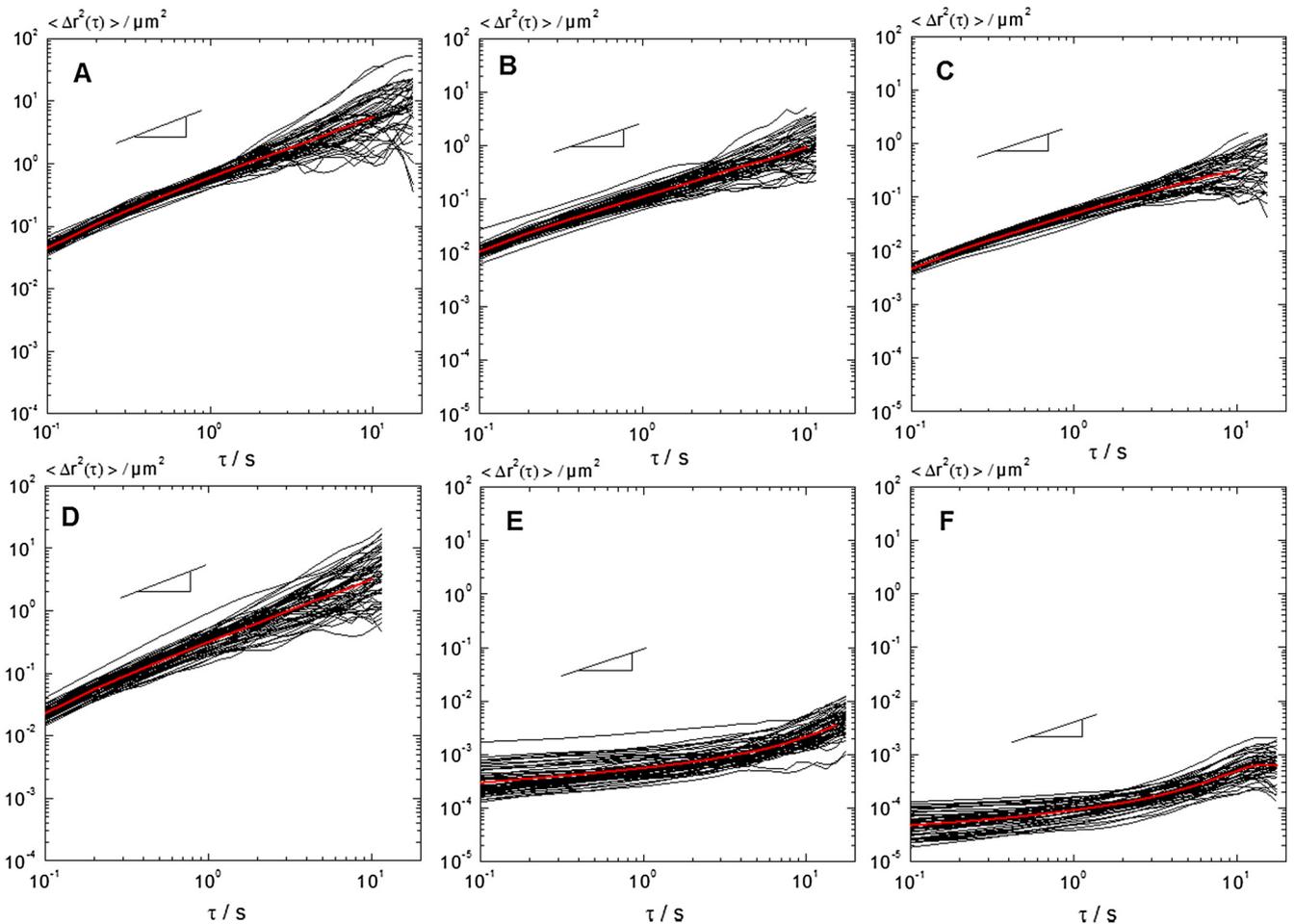


**Fig. 7.** MSDs of individual polystyrene microspheres of diameter 1 μm dispersed in suspensions of 30% Silica-1% PF127-**0%** starch, after 30 min (A) and 50 min (D) in the gel state at 35 °C; **1%** starch, after 30 min (B) and 50 min (E) in the gel state at 35 °C, and **2.5%** starch, after 30 min (C) and 40 min (F) in the gel state at 35 °C. The red curve is the ensemble-average MSD.
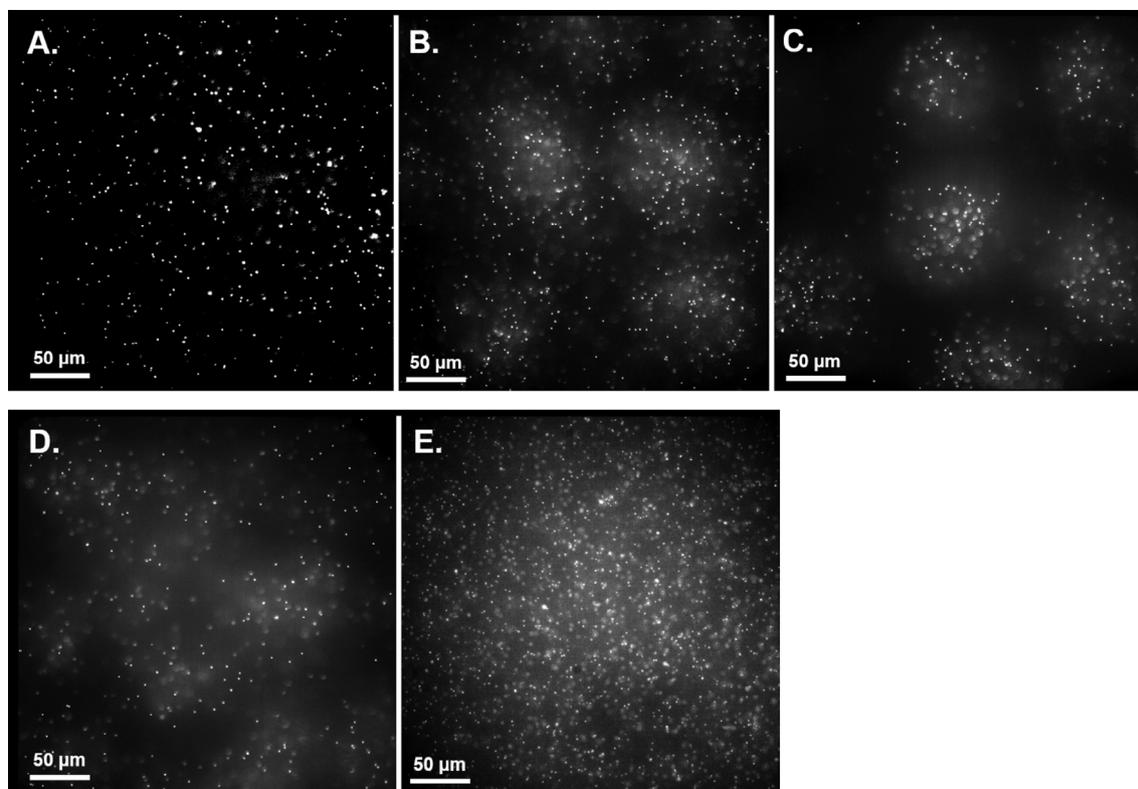
**Fig. 8.** Light microscope images of 30% Silica-1% PF127-**0**% starch after 10 min (A) in the gel state at T = 35 °C, as well as after 30 min (B) and 60 min (C) in the gel state. Also images for 1% starch (D) and **2.5**% starch (E) after 60 min in the gel state at T = 35 °C.

adsorbed on the silica particle surface. In summary, for the sample without starch, MPT results obtained in the gel state demonstrate the formation of a porous network with thick lamellae of agglomerated silica particles with Pluronic molecules adsorbed onto the surfaces. Once this network is formed, the overall structure no longer changes, therefore the MSD behavior of tracer particles within viscous region is almost constant even one hour after the gel formation.

The agglomeration mechanism presumably results from depletion flocculation of the silica particles. Initially PF127 adsorbs on the SP, and then the excess of unadsorbed PF127 in the solution causes the particles to flocculate via a depletion mechanism. A Similar mechanism has been proposed by Sun and Raghavan [14] explaining the sol-gel transition in synthetic nano clay and PF127 mixtures. As a consequence a much lower pluronic concentration (~1 wt%) is needed allowing the sol-gel transition as compared to a pure pluronic solution where a minimum of ~15 wt% is required [11,13]. Nevertheless, the question why particles agglomerate in a porous structure remains. However, other flocculation mechanisms, such as bridging flocculation, are in principle also possible. In latter case, the layer of PF127 covering SP would become "sticky" at high temperatures. Such stickiness could lead to attractive interactions between adjacent particles and cause thermogelation. Additional experiments are needed to judge the dominating aggregation mechanism; however, it is beyond the scope of the present paper.

Increasing the starch concentration to 1 wt% (Fig. 8D) and/or 2.5 wt% (Fig. 8E) leads to homogenization of the tracer particle repartition one hour after the sol-gel transition unlike the starch free system (Fig. 8C). A partial breakdown of the large silica agglomerates and formation of much thinner lamella were still visible at 1 wt% starch, while these agglomerates completely disappeared at 2.5 wt% starch. For the sample with 1 wt% starch, black

areas decrease strongly to achieve a matrix thickness of ~15–20 μm which correspond to an agglomeration of 20–30Si particles. The fact that MSDs, for both samples containing starch, become time-independent after 40–50 min was due to a time-dependent permanent reorganization such as shrinkage and hardening of the small-scale silica-Pluronic network. For samples with and without starch, the DWS results showed that the silica network was formed after 2 min. However, due to the presence of starch, the large-scale porous silica agglomerates partly or completely disappeared in the starch-containing suspensions. Without these agglomerates, the viscous regions contained a weak and mobile network of silica and pluronics that resulted in hardening and shrinkage of the network mesh size until the tracer particle are completely trapped. Thus, starch polymers seemed to hinder the agglomeration of silica particles in large porous clusters. This was probably due to additional polymer-polymer interactions introduced by the starch. Formation of inclusion complexes between starch and PF127 may compete with micelle formation, thereby decreasing the number of PF127 micelles in the bulk solution. The presence of these complexes may lead to a different depletion flocculation aggregation mechanism than without starch and lead to the formation of a much more homogeneous network.

## 4. Conclusions

In this study, we have investigated the sol-gel transition of a three-component silica-Pluronic-starch thermosensitive system using classical rotational rheology and for the first time microrheology methods namely diffusive wave spectroscopy (DWS) and multiple particle tracking (MPT). They particularly provide insight into microstructure, interactions and local dynamics of the sample. In general, studies concern binary systems composed of Pluronic

and nanoparticles investigated by means of rheology [15] and/or small angle neutron scattering (SANS) [14,16]. Main advantages of microrheological techniques are the small sample volume used (<1 ml), the rapidity of the measurement (~5 min) and the suitability measuring fragile structures without destruction as it is the case for samples investigated here during the gelation process. We have also shown that MPT and DWS are powerful techniques that can be used to investigate turbid solutions of highly concentrated silica suspension, up to 50 wt%, which is not possible using SANS.

We found that the sol-gel transition requires a relatively low Pluronic concentration (~1 wt%) and a good agreement in the determination of the transition temperature between rheological and DWS measurements; latter temperature being independent of the sample composition with a constant value equal to ~25 °C. Additionally, we innovatively demonstrated that the kinetic of gelation can be characterized using DWS. The transition was fast for all investigated samples, less than 2 min. Besides this fast process, a second slow process was observed in the gel state indicating a permanent motion and rearrangement of the structure at longer times. MPT experiments performed in the liquid state show that tracer particles, independently of their diameter, have a purely diffusive behavior 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 within an elastic matrix built of assembled silica particles and that the size of these areas decreases slowly with time with a characteristic length scale or mesh size less than 1 μm.

Finally, we have originally shown by performing MPT measurements that the presence of starch in the system, a non-thermosensitive polymer, affects significantly micro-rheological properties. Systems without and with various starch concentrations exhibit similar bulk viscoelastic properties in the gel state, but notably different microrheological behavior. This discrepancy is explained in terms of microstructural differences supported by light microscope images. The system without starch is probably formed of a thick elastic matrix built of agglomerated adsorbed Pluronic-Si particles and large interconnected pores of diameter ~50 μm. Increasing starch concentration leads to the formation of a much thinner network. Starch molecules prevented agglomeration of silica particles into large cluster. In both cases, the agglomeration mechanism is presumably due to depletion flocculation of the silica particles. Our findings are both conceptual and generic and further investigations are needed in order to understand the effects of replacing starch by another non-thermosensitive polymer that does not form complexes with pluronic.

## Acknowledgement

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2017.12.051.

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