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

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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 microstructural 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 Tsol-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 ζ-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/cm3 [25], the BET surface area is 40 m²/g and particle diameter is 75 nm according to dynamic light scattering measurements. The same batch of aqueous suspension of silica particles was used for all the experiments performed in this study.

Pluronic F127 (PF127), a PEO₉₈-PPO₆₇-PEO₉₈ 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 MΩ·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 a 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 dcp = 50 mm, cone angle αcone = 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 Fluor 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 tracer 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 images of these fluorescent beads were recorded onto a computer 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) \( g_2(t) = 1 - \frac{I(t)I(0)}{\langle I^2 \rangle} \) 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 Oelschlager 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, \( T_{gel-t} \) 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. \( T_{gel-t} \) was determined as the point where \( G' \) and \( G'' \) cross each other and a value of \( T_{gel-t} = 25 ± 0.6 °C \) 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 \( G'' \sim \omega \) and \( G' \sim \omega^2 \). In the gel state at \( T = 35 °C \), the system shows a typical gel like behavior with \( G' > G'' \) and constant modulus \( G' = 3000 \text{ Pa} \) 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 \( \omega = 10 \text{ rad s}^{-1} \).

Secondly, Diffusing Wave Spectroscopy (DWS) was used to determine \( T_{gel-t} \). 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 (\( \tau \)) 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 \( T_{gel-t} \) value, we have plotted the variation of the average scattered intensity as function of temperature (Fig. 2B). In latter case, \( T_{gel-t} \) has been determined as the temperature obtained at
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 $T_{\text{sol-gel}}$ values determined from rheological and DWS measurements. In all cases, good agreement has been found between both techniques within the experimental errors. In addition, we observe that all values of $T_{\text{sol-gel}}$ 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 $T_{\text{sol-gel}}$ 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 at $t = 20$ s indicates that the sample is still
DWS measurements. Tsol
rheological measurements. Fig. 4 shows variations of G
\( g \) leading in a strengthening of the network.
contrary continued to evolve slowly over time, at least up to 12
the composition. In addition to this fast process, we also observed
\( G \) of a gel was similar for all samples investigated independently of
curves ended after 120 s. This fast kinetic transition from a liquid
sponding to a slowdown of the diffusion indicates that the gelation
in the liquid state, but the deviation observed at \( t = 70 \) s corre-
spending 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 \( \sim 100 \) s up to 1
h, \( G' \) increases of about 85% from 400 to 740 Pa while \( G'' \) stays con-
stant 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 presen-
tence 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 stor-
age modulus increases by approximately 50% from 1.7 to 2.5 kPa.

<table>
<thead>
<tr>
<th>Si/wt%</th>
<th>PF127/wt%</th>
<th>Starch/wt%</th>
<th>( T_{\text{sol-gel}}/°C ) Rotational rheology</th>
<th>( T_{\text{sol-gel}}/°C ) DWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>1</td>
<td>25.5 ± 0.6</td>
<td>25.0 ± 0.6</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>0</td>
<td>25.5 ± 0.6</td>
<td>24.8 ± 0.6</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>1</td>
<td>25.0 ± 0.6</td>
<td>25.3 ± 0.6</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>2.5</td>
<td>24.3 ± 0.6</td>
<td>24.9 ± 0.6</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>1</td>
<td>26.0 ± 0.7</td>
<td>25.5 ± 0.6</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>1</td>
<td>25.1 ± 0.6</td>
<td>26.5 ± 0.7</td>
</tr>
</tbody>
</table>

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. Micro rheological 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 liq-
uid 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 \( \beta \) close to 1
throughout the probed time scales, where \( \beta \) is given by the relation
\( \langle \Delta r^2 (t) \rangle \sim t^\beta \). 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
\( \eta_{\text{app}} \) has been determined from MSD traces using the relation
\( \langle \Delta r^2 (t) \rangle = 4D t \) 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 trac-
er particle radius. We found \( \eta_{\text{app}} \) = 4.10 and 4.00 mPa s for mea-
surements 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., \( \eta_{\text{bulk}} = 3.7 \) 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 vis-
cous environment. However, at the same time, the MSD absolute
value decreased by almost a factor three, which corresponds to a
\( \eta_{\text{app}} \) increase from 5 to 11 mPa s, respectively. This result con-
ffirms the presence of a slow kinetic process occurring at a micro-
scale level directly after the gel formation. It was only after 80
min that the MSD exhibited a much weaker time dependence
(slope \( \sim 0.5 \)) 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

Table 1

<table>
<thead>
<tr>
<th>Si/wt%</th>
<th>PF127/wt%</th>
<th>Starch/wt%</th>
<th>( T_{\text{sol-gel}}/°C ) Rotational rheology</th>
<th>( T_{\text{sol-gel}}/°C ) DWS</th>
</tr>
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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 show 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 becomes stronger and stiffer which is responsible for the increase in the elastic modulus 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 G₀ = 2.8 ± 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 Konishi [30] also reported the ability of starch to form inclusion complexes with hydrophobic moieties of cellulose ether, latter being responsible of a viscosity enhancement.
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 $T = 20^\circ C$ (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 $\mu m$ separated from each other by black areas of thickness 30–50 $\mu m$, 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 $\mu m$. White areas represents viscous regions that might contain Pluronic residues, which have not been

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**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 $^\circ C$. $G'$ (closed) and $G''$ (open) symbols. 10% error bars for all symbols.

**Fig. 7.** MSDs of individual polystyrene microspheres of diameter 1 $\mu m$ dispersed in suspensions of 30% Silica-1% PF127-0% starch, after 30 min (A) and 50 min (D) in the gel state at 35 $^\circ C$; 1% starch, after 30 min (B) and 50 min (E) in the gel state at 35 $^\circ C$, and 2.5% starch, after 30 min (C) and 40 min (F) in the gel state at 35 $^\circ C$. The red curve is the ensemble-average MSD.
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 pluronic 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 micro rheological 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 micro rheological 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.

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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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