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Relations between colloidal structures in aqueous suspensions based on silica, starch and PEO-PPO-PEO block copolymer and structures of the corresponding composites

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ABSTRACT

Structures in aqueous suspensions based on dispersed colloidal silica and dissolved starch, glycerol and tri-block copolymer of PEO-PPO-PEO type were studied by scaling relations of rheological parameters vs. volume fraction of particles. Structures of the corresponding dry composites were studied by optical microscopy, scanning electron microscopy and confocal Raman microscopy.

INTRODUCTION

Water-borne suspensions are widely used in several technical applications such as coating, printing, casting, gluing, etc. Such suspensions may consist of mineral particles dispersed in an aqueous polymer solution, where the role of the polymer is to bind the mineral particles together and also to form the continuous phase of the solid composite after drying. It is in general of uppermost importance to control the flow properties and the inter-particle interactions in the suspension in order to achieve the desired properties and structure of the solid composite. The rheology of colloidal systems at high concentrations of the dispersed phase has been extensively studied. For charged particles, the liquid-glass transition has been reported to occur at much lower volume fraction of solid phase than for suspensions of hard sphere particles[1,2].

Temperature responsive polymers possess the unusual behaviour of decreased solubility in water upon heating, followed by phase separation at a certain temperature. This has been reported for cellulose ethers such as ethyl hydroxyethyl cellulose[3] and for hydrophobically modified starches[4,5], just to mention two bio-based thermoreversible polymers. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (PEO-PPO-PEO), known as Pluronics or poloxamers, belong to the most widely studied thermoreversible polymers. The thermoreversible gelation of Pluronics and the influence of temperature on micellization have been reported in a number of studies, see e.g. Bohorquez et al.[6].

The use of polymers with switching properties in solution where the transition can be trigged by changes in pH, temperature, etc. have been proposed in order to control the shape and structure in coating layers and in different 3D-shapes[7]. Temperature responsive polymers enable a unique possibility to control the structure of suspensions by temperature changes.

The effects of temperature on colloidal stability and structure in aqueous suspensions based on dispersed colloidal silica and dissolved starch and a PEO-PPO-PEO type tri-block copolymer were studied in the current paper by scaling relations of rheological parameters (viscosity and storage modulus) vs. volume fraction solid phase.

MATERIALS AND METHODS

Aqueous suspensions of colloidal spherical silica particles, Levasil 30/50 were kindly provided by AkzoNobel, Bohus, Sweden. Triblock copolymer of PEO-PPO-PEO, Pluronic F127 (here denoted as PF127) was kindly supplied by BASF, Ludwigshafen, Germany. Potato starch which was both hydroxypropylated and oxidized (Solcoat P 55) was kindly supplied by Solam, Germany. This starch grade had a degree of substitution (DS) with respect to hydroxypropyl groups of around 0.1. Glycerol with a purity of ≥90% from Sigma Aldrich was used. Aqueous suspensions of silica, starch and glycerol were prepared at pH 9, ionic strength 0.01 and different volume concentration of silica particles (φ), but at a constant ratio between the components: 6 parts by weight of PF127 per hundred parts of dry SP particles (pph), 3 pph glycerol and 9 pph starch. Details of preparation are described elsewhere[8].

Rheology

The rheological measurements were performed on a controlled stress rheometer (Paar Physica, MCR 300, Graz, Austria) and a coaxial standard measuring system CC17. Rheological measurements were performed at a temperature (T) of 20°C, 25°C or 30°C. Flow curves recorded at steady state above a critical shear rate was used to determine the floc volume ratio C_{fp} given by

$$C_{fp} = \varphi_f / \varphi \qquad (1)$$

where φ is the volume fraction solid particles and φ_f the volume fraction of flocs calculated from slightly modified Krieger-Dougherty equation[9]. Small-amplitude oscillatory shear (SAOS) was performed in order to measure the transition from the linear to the non-linear regime, the storage modulus (G') and the loss modulus (G'').

Dry composites

The suspensions were draw-down on polyester films and subsequently dried at 20°C or 30°C for 60 min at 10% RH as described by Petkova-Olsson et al.[10]. The structures of the corresponding dry composites were analysed from top view by optical microscopy (Olympus BX51), scanning electron microscopy (FE-SEM, Leo 1530, Carl Zeiss GmBH; Vienna, Austria) and confocal Raman microscopy (WiTec alpha300 system, Ulm, Germany). Scanning electron microscopy was also used in order to analyse cross sections. Detailed descriptions about the sample preparation and the microscopy analysis are described elsewhere[10].

RESULTS AND DISCUSSION

Steady shear

By fitting the flow curves to the Bingham model, the plastic viscosity (η_{PL}) of the suspensions were obtained, which in turn was used in the slightly modified version of the Krieger-Dougherty equation given by

$$\frac{\eta_{PL}}{\eta_o} = \left(1 - \frac{\varphi_{eff}}{\varphi_m}\right)^{-[\eta]\varphi_m} \qquad (2)$$

where φ_m is the maximum volume fraction solid phase (obtained from suspensions without PF127), φ_{eff} the effective volume of the flowing units (flocs)[11], $[\eta]$ the intrinsic viscosity and $\eta_o$the viscosity of the aqueous phase. Assuming that $\varphi_{eff} = \varphi_f$, the floc density C_{fp}, was calculated from Eqs. 1-2 as

$$C_{\,fp} = \varphi_{eff} / \varphi \qquad (3)$$

Fig. 1 shows the existence of two regimes, one at φ≤0.10 and the other at φ≥0.20. In the low φ regime at 20°C, C_{fp}<1 was observed, indicating the dispersing effect of PF127 at 20°C.

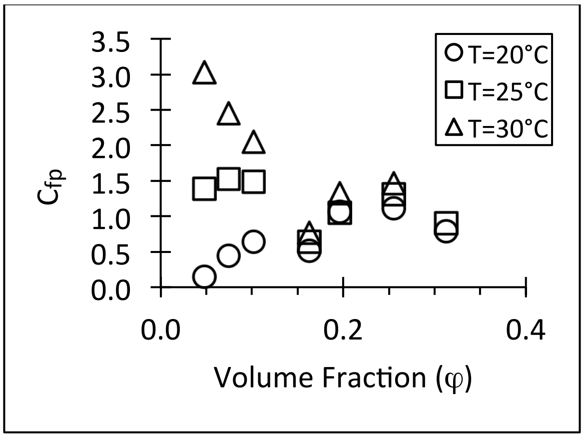

Figure 1. Floc density, C_{fp}, vs. silica particle volume fraction, φ, at 20°C, 25°C and 30°C. Partly based on data from Petkova-Olsson et al.[8].

At the two highest temperatures, a minimum in C_{fp} was observed at $\varphi \approx 0.16$. At $\varphi < 0.16$ and 30°C, the floc volume ratio decreased strongly with increasing φ, while the opposite was observed in the range $0.16 \leq \varphi \leq 0.26$ at all temperatures.

Small-amplitude oscillatory shear

The scaling relation G' vs. φ was obtained from oscillatory shear and is shown in Fig. 2. The results revealed the existence two different regions and a transition between the regions at $\varphi \approx 0.16$. Information about the strength of interactions can be obtained by fitting to the fractal gel model:

$$G' = G_0 \varphi^p \tag{4}$$

where G_0 is a pre-exponential factor and p represents the microstructure of the suspension[12]. In each of the two regions the data points were fitted to Eq. 4 (see Table 1). Low values of the exponent was observed at the highest temperature and $\varphi < 0.16$. The values of p decreased almost three times when going from the region $\varphi \geq 0.20$ to the region $\varphi \leq 0.10$ at 30°C. This indicates a strong inter-particle attraction at 30°C and $\varphi \leq 0.10$. At 20°C the values of p did not differ very much between the two regimes and was rather similar to what observed at 30°C and high φ.

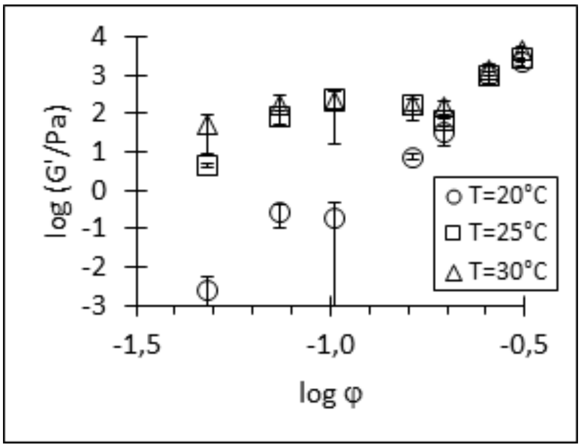

Figure 2. Storage modulus, G' of silica dispersions vs. silica particle volume fraction, φ, at 20°C, 25°C and 30°C. Curve fit to Eq. 2 is not included. Error bars indicate standard deviation from at least triplicates. Adapted from Petkova-Olsson et al.[10].

Table 1. Values the exponent p from Eq.4. Adapted from Petkova-Olsson et al.[10].

Region	p		
	T=20°C	T=25°C	T=30°C
$\varphi \leq 0.10$	6.1	5.4	2.6
$\varphi \geq 0.20$	9.4	8.2	7.4

The scaling relations as well as other rheological parameters indicated a possible transition from a colloidal gel (or a liquid-like state at low temperatures) to a colloidal glass at rather low particle concentrations, which is likely for systems with long-range electrostatic interactions[1,2]. The dispersing effects of PF127 at 20°C are clearly shown by $C_{fp} \leq 1$ in Fig. 1 and by the high value of p in Fig 2 at all φ. In general, steady shear and SAOS gave rather similar information about changes in suspension structures with increasing temperature and particle concentration.

Structures in dispersion after drying

At $0.10<\varphi<0.20$, the minimum in C_{fp} and G' indicated coexistence of two phases at both temperatures, which was confirmed by optical microscopy (Fig. 3). Confocal Raman micrographs revelled that both phases were built of Si and polymers. Cross-sections at high magnification of dry layers made from suspensions at φ=0.07 captured by scanning electron microscopy indicated a rather homogenous micro structure at T=30°C compared to 20°C, which probably can be explained in terms of increased storage modulus of the suspension network with increasing temperature. High G' is expected to prevent substantial shrinkage during drying. Shrinkage may result in a high number of micro-pores in the dry structure. This difference in micro structure between coatings prepared at the two temperatures almost disappeared at φ=0.26.

CONCLUSION

Two different regimes were observed depending on the volume fraction of particles in suspension. At $\varphi\leq0.10$ the results from steady shear revealed the existence of an open floc structure at T=30°C, while well-dispersed particles were observed at T=20°C. At $\varphi\geq0.20$, the structure of the flowing units was dense or well dispersed and rather independent of the temperature. Oscillatory experiments at T=25°C and T=30°C revealed a gel-like disordered state at $\varphi\leq0.10$ with increasing attractive forces between the particles with increasing temperature. A transition to a colloidal glass or a solid-like microcrystalline state was observed at T=25°C and T=30°C when the concentration increased to $\varphi\geq0.20$. At intermediate volume fraction solid phase, both states were coexisting.

Both steady shear and oscillatory shear revealed that PF127 may act as dispersing agent at 20°C. In several aspects, results obtained by steady shear were consistent with results from oscillatory shear.

The observed behaviour was a consequence of the temperature-responsive properties of tri-block copolymers of PEO-PPO-PEO type. The structures of the dry composites prepared at different particle concentrations and temperatures were explained in terms of results from the rheological study, which indicated the possibility to use rheology as a tool to predict structures in the final composites.

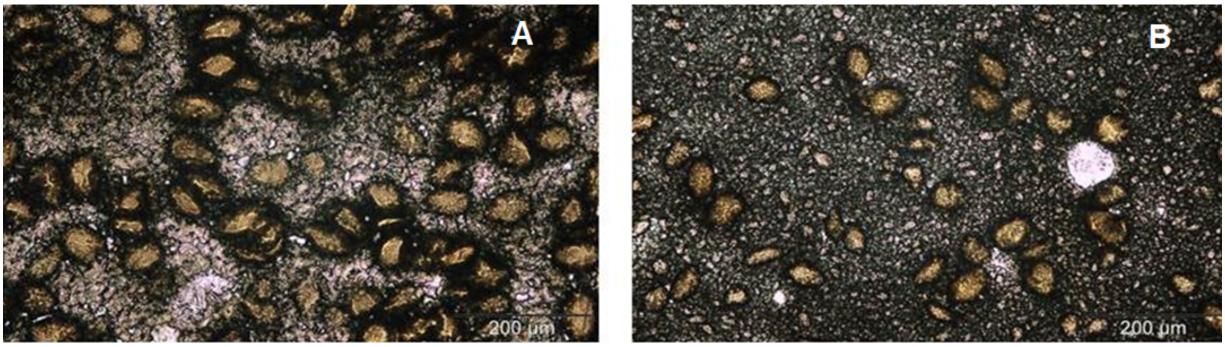

Figure 3. Microscope images of dried coatings in transmitted light at φ=0.16. Adapted from Petkova-Olsson et al.[10]. A: Temperature 20°C during preparation and drying.
B: Temperature 30°C during preparation and drying.

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