

Effect of Pluronic F127 triblock copolymer adsorption on the colloidal stability and rheological performance of silica dispersions

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ABSTRACT

The colloidal stability of a model paper coating dispersion consisting of silica particles, Pluronic F127, starch and glycerol was studied with respect to temperature responsiveness of PF127 and its adsorption on the silica surface. The rheological characterization was accomplished in terms of rotational and oscillatory tests.

INTRODUCTION

Concentrated particles suspensions of kaolin, silica, calcium carbonate, talc or similar pigments have a broad variety of industrial applications and are put into practice in products such as paint, ink, paper electronic devices^{1,2}. In the paper coating process, the coating dispersions are subjected to tremendous variation in the applied stresses- from low shear flow conditions during pumping or settling, to extremely high shear rates during blade metering (around 10^6 s^{-1}). Rheological characterization can be used not only for monitoring technological aspects (i.e., “runnability”), but also as a probe of colloidal interactions and dispersion stability, which can be used for governing information on structural organization and re-organization on particle aggregate scale. The wet state of the coating dispersions have impact at both the macroscopic properties of coating dispersion and the

microstructure of the dry coating layer in its final state³.

The PEO-PPO-PEO (PEO:poly(ethylene oxide), PPO:(poly(propylene oxide)) block copolymers adsorption and organization at the solid-liquid interface is of fundamental interest and can provide us with useful information regarding new possibilities for paper coating dispersions, 3D printing, etc⁴.

The present investigation focuses on the adsorption of PEO-PPO-PEO triblock copolymer on silica particles at different temperatures and its impact on the rheological performance of the dispersion. The used PEO-PPO-PEO block copolymer is a temperature responsive polymer, which makes it possible to alter the immobilization solids (ϕ_{max}) of the suspension by changing the temperature. The investigated model coating dispersions were based on silica particles, PEO-PPO-PEO block copolymer, starch and glycerol. The rheological properties of these dispersions, e.g. maximum packaging volume (ϕ_{max}) and storage modulus, were used to investigate the influence of temperature and particle concentration on the particle-particle interactions and the aggregation process. Starch-silica suspensions have been turned into temperature responsive systems by the addition of temperature responsive block copolymer which opens new possibilities for producing starch-based temperature responsive dispersions.

EXPERIMENTAL

Materials

Water-borne suspensions based on spherical silica particles, Levasil 30/50 (here denoted as SP), supplied as an aqueous suspension, and Pluronic F127, hydroxypropylated and oxidized potato starch and glycerol were prepared.

The silica particles showed negative ζ -potential at pH between 2 and 10, which suggested that the net surface charge at this pH region is negative, and had BET surface area of 40 m²/g, average particle diameter of 68 nm and assumed to have density of 2.2 g/cm³.⁵

Pluronic F127 (BASF), a PEO-PPO-PEO triblock copolymer with M_w of 12600, was used without further purification. PF127 becomes insoluble in water upon heating because it possesses a lower critical solution temperature (LCST).

The used hydroxypropylated and oxidized potato starch (Solcoat P55 by Solam (Germany)) has a degree of substitution with respect to hydroxypropyl groups of around 0.1 according to the supplier. In order to have the exact same quality of starch for all experiments, all the necessary amount of starch was jet cooked at approx. 122 °C and pressure of 2 bar followed by freeze-drying. The freeze-dried powder was cold-water soluble. Glycerol (product number G7757;Sigma Aldrich) was used as an external plasticizer for starch⁶ since it assists in increasing the film formation and flexibility of thermoplastic starch.

Methods

Since PF127 is temperature responsive polymer, all suspensions of SP, PF127, starch and glycerol were prepared and stored in a water bath, at controlled temperature 10 °C \pm 3 °C, which is well below the gelation temperature, in order to avoid any uncontrolled gelation. As first step, the "as-received" SP suspension was diluted with 10

mM NaCl aqueous solution to the desired particle concentration, then 6 parts by weight of PF127 per hundred parts of dry SP particles (pph) was added to the SP suspension. The SP-suspension was then equilibrated under gentle stirring during 2 h. After that 3 pph glycerol and subsequently 9 pph freeze-dried starch powder were added to the mixture, followed by gentle stirring during additional 2 h. Finally the pH of the suspension was adjusted to pH=9 before performing the rheological tests.

The rheological behaviour of the suspensions was tested by a controlled stress rheometer (Paar Physica, MCR 300, Graz, Austria) using a coaxial standard measuring system CC17 according to ISO 3219. Flow curves, amplitude sweeps and frequency sweeps experiments were performed for different SP solid contents and at two different temperatures, 20 °C and 30 °C.

PF127 adsorption was measured by an indirect method based on polymer depletion, i.e. measurement of polymer concentration in solution before and after adsorption where the PF127 concentration in the supernatant was determined by potentiometric titration method by converting the non-ionic triblock polymer into a pseudo-cationic compound which could be determined in a precipitation reaction using sodium tetraphenylborate⁷ (Metrohm Application Bulletin No. 230/1e).

RESULTS AND DISCUSSIONS

The PF127 adsorption on SP from aqueous solution at 20 °C and 30 °C and pH=9 was measured and the results indicated typical polymer adsorption that was not influenced considerably of the temperature changes and reached a pseudo-plateau at equilibrium concentration of PF127 in solution ca 0.7 % with adsorbed PF127 amount of $m_2^s \approx 0.4 \text{ mg/m}^2$ at 20 °C and $m_2^s \approx 0.6 \text{ mg/m}^2$ 30 °C, (Figure 1). These results are in a good agreement with the results presented by Malmsten et al.⁸, where they found that the adsorbed amount PF127

on silica surface at 25 °C was around 0.4mg/m².

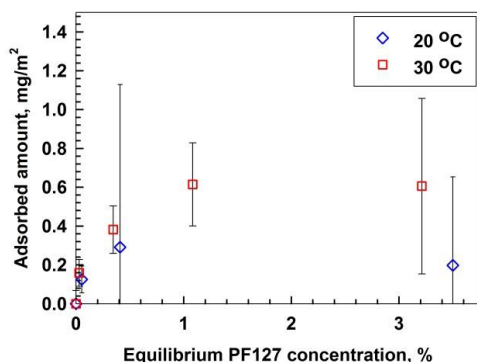


Figure 1. PF127 adsorption on SP from aqueous solution, 0.01 M NaCl, pH 9, 3.0 wt% SP. Error bars indicate standard deviation.

In order to investigate how PF127 affects the flow properties at different temperatures, a series rotational tests for SP suspensions with volume fraction solid phase (ϕ) ranging from 0.05 to 0.32 were performed at 20 °C and 30 °C. The shear rate was ranging from 4000 to 1 s⁻¹. The relative composition of the suspensions was kept constant despite the increase in volume fraction solid. The flow curve data was evaluated and information regarding the structure of the suspension was extracted in terms of the plastic viscosity according the Bingham plastic model, Eq. 1.

$$\tau = \tau_0 + \eta_{PL}\dot{\gamma} \quad (1)$$

where τ is the shear stress, τ_0 is the Bingham yield stress, η_{PL} plastic viscosity and $\dot{\gamma}$ shear rate. This evaluation was performed for all of the silica dispersions- at all ϕ . An estimation of the volume fraction of the flocs (ϕ_f) in the SP suspensions was done by fitting the data to the Krieger-Dougherty equation⁹ given by Eq. 2.

$$\frac{\eta_{PL}}{\eta_0} = \left(1 - \frac{\phi_f}{\phi_{max}}\right)^{-[\eta]\phi_{max}} \quad (2)$$

where $[\eta]$ is the intrinsic viscosity, η_0 is the viscosity of the aqueous phase and ϕ_{max} is the volume fraction at maximum packaging of the particles that was obtained for the suspension with starch and glycerol but without PF127 in order to eliminate the effect of flocculation in the system due to starch and glycerol and to be able to observe more clear the influence of PF127 on the flocculation process. Value for $\phi_{max}=0.52$ at 20 °C was obtained from the Quemada equation¹⁰. This value for the maximum volume fraction solids and Eq. 2 were used to obtain a ratio of floc volume to SP volume, C_{fp} :

$$C_{fp} = \frac{\phi_f}{\phi_p} \quad (3)$$

C_{fp} can be used as a measure of floc density or of the amount of branching of particle chains with in a floc. The more open the structure of a floc is, the larger its C_{fp} value is¹¹(Figure 2).

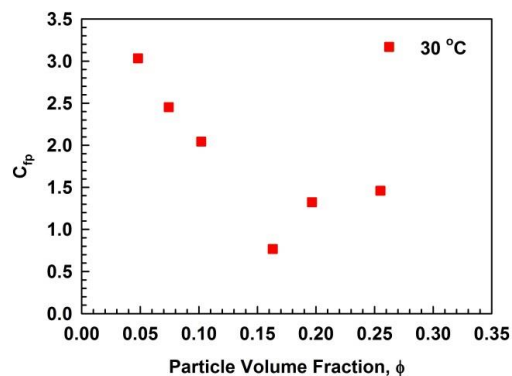


Figure 2. Calculated floc density, C_{fp} , versus SP volume fraction at 30 °C.

At 20 °C and $\phi \leq 0.16$, C_{fp} values less than 1 were observed, indicating a dispersing action by FP127 at low volume fraction particles and at low temperatures.

For 30 °C, floc structures were detected at almost all ϕ , since $C_{fp} > 1$ at all values of ϕ except at $\phi \approx 0.16$. Strong flocculation and open flocs for SP suspensions with $\phi \lesssim 0.1$ were indicated. At higher SP concentrations, i.e. at $\phi \gtrsim 0.2$, a weaker flocculation was observed. There seems to be two different regions depending on particle volume fraction.

The flocs in this region ($\phi \gtrsim 0.2$) were denser than these at $\phi \lesssim 0.2$. The results in *Figure 2* indicate a transition from open floc structure to a dens floc structure. The decrease in C_{fp} -values with increasing volume fraction solid phase in the region of low ϕ suggests that the flocs may be disrupted by the increase in shear stress that occurs at highest particle concentration.

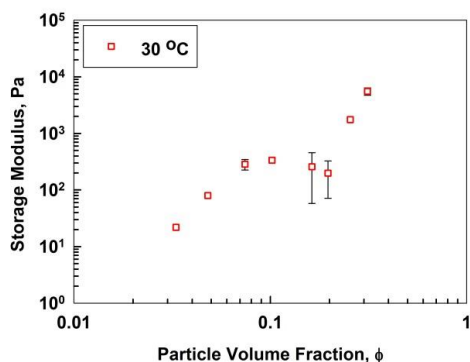


Figure 3. Storage modulus, G' , as a function of SP volume fraction at 30 °C. G' from frequency sweeps at $\omega=8.86$ rad/s and $\gamma=0.025\%$.

The viscoelastic properties of suspensions have been modelled based on the assumption that the particle network consists of close packed fractal flocs^{12,13}. These fractal gel models predict a power law behaviour that is expressed by Eq. 4.

$$G' = G_0 \phi^p \quad (4)$$

where G_0 pre-exponential factor and the power exponent, p , represents the microstructure of the suspension.

The correlation between G' and ϕ for the investigated model coating dispersion systems was found to be strong (*Figure 3*). These results seem to be consistent with the calculated floc density from the rotational tests (*Figure 2*). At 30 °C there were two different well-defined regions depending on particles volume fractions that are separated by a short plateau region. At $\phi \gtrsim 0.2$, the pre-exponential factor increased sharply with increasing ϕ , indicating an increased dispersing action of added PF127 at high volume fractions. When the temperature was lowered to 20 °C, substantially lower values on storage modulus were observed at $\phi \leq 0.2$, compared to the situation at 30 °C. This observation is consistent with similar effects on the C_{fp} values shown in *Figure 2*.

One additional interesting feature is the short plateau in G' values at 30 °C between $0.1 \lesssim \phi \lesssim 0.2$ (*Figure 3*). This plateau behaviour could probably be explained in terms of structural rearrangement initiated by the created particle gel structure and reduced SP mobility.

CONCLUSIONS

The flocculation of the model coating system of SP-starch-PF127-glycerol at solid volume fraction $\phi \lesssim 0.2$ is to a large extent controlled by the temperature. The calculated values for floc density, C_{fp} and the measured Storage modulus, G' , suggest different floc structures- at low temperature PF127 acts as dispersing agent and at the higher temperature strong particle-particle interactions rise which leads to the formation of open-structured flocs. At particle concentration $\phi \gtrsim 0.2$, both C_{fp} - ϕ and G' - ϕ relations suggest decrease in the strength of attraction between the particles and the formation of dense flocs in the suspensions. A short plateau in the

measured G' values in between $0.1 \lesssim \phi \lesssim 0.2$ was observed. This plateau behaviour could probably be explained in terms of structural rearrangement.

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