

A Viscometric Study of Temperature-Induced Attractive Forces between Polystyrene Particles in Aqueous Solutions of Cellulose Ethers

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ABSTRACT

The effects of temperature and concentration of soluble polymer on colloidal stability in concentrated aqueous polystyrene (PS) suspensions containing ethyl(hydroxyethyl) cellulose (EHEC) and carboxymethyl cellulose (CMC) were investigated. Both polysaccharides caused destabilisation of the PS suspensions. An investigation of the relative viscosity as a function of the concentration of polysaccharide indicated different destabilisation mechanisms depending on the nature of the solvent-polysaccharide interaction and on the concentration of polysaccharide. An increase in concentration of polysaccharide within the investigated concentration range resulted in substantially higher degree of flocculation of the EHEC-containing suspension at 55°C, which is a temperature 10°C below the cloud point of the used EHEC grade. This behaviour showed that the flocculation mechanisms close to the cloud point of EHEC involved a considerable amount of added polysaccharide, which is typical for colloid destabilisation by surface induced phase separation. The CMC-containing suspensions showed flocculation behaviour typical for destabilisation by depleted polymers. The suspensions were drawn-down on polyester substrate and the resulting surface structures were interpreted by calculating the pair distribution functions. The viscosity of the aqueous phase of the

suspensions seemed to be the predominant factor governing the surface structure. However, the disordering effect of surface induced phase separation seemed to have similar effects as high suspension viscosity.

INTRODUCTION

Colloid stabilisation and destabilisation by dissolved polymers has been subjected to a numbers of studies. Stabilisation of colloid dispersions is one of the most common technical applications for soluble polymers and requires polymer adsorption. However, polymer adsorption may also cause colloid destabilisation. Whether the adsorbed polymer cause stabilization or destabilization depends predominantly on the solution properties of the polymer and on the density profiles of the adsorbed layers^{1,2}. Colloid destabilisation by adsorbed polymers is commonly referred to as bridging flocculation. Another possible destabilisation mechanism in suspensions containing dissolved polymers is depletion flocculation³.

For polymer mixtures, the existence of long-range attractive forces between colloidal particles due to polymer incompatibility has recently been reported⁴. These long-range forces were found to give attractions of a longer range than observed for bridging and depletion. In colloidal systems, these long-range forces resulted in destabilisation by capillary-induced phase

separations (CIPS). Such long-range attractive forces have also been reported for solutions of EHEC, and have been explained in terms of the multi-component nature of EHEC solutions and “chemical polydispersity” of most EHEC samples leading to different solution properties of the different polymer fractions⁵. In addition to all above mentioned destabilisation mechanisms, addition of charged polymers to an aqueous suspension of oppositely charged particles may cause colloid destabilisation by charge neutralisation.

A CIPS mechanism is in general possible if the polymer solution is close to phase separation in mixed polymer solutions (or when the polymer possesses “chemical polydispersity”). In the present work, we have compared the destabilising character of EHEC at room temperature and at temperatures 10°C below the cloud point. As a reference CMC was investigated as a non-adsorbing polymer for which water is a good solvent. The destabilizing power of the different suspensions at different temperatures was evaluated in terms of the relative viscosity.

In addition to the suspension behaviour, the effects of temperature-induced aggregation on the surface structure of dry films were investigated by means of Atomic Force Microscopy (AFM) and by calculating the two-dimensional pair distribution function.

EXPERIMENTAL

Materials

Aqueous suspensions based on negatively charged polystyrene particles with a radius (a) of 0.125 μm . (PS, DPP 711 from Dow Deutschland Inc., Germany) and water-soluble cellulose ethers were prepared. Two different cellulose ethers were used: ethyl(hydroxyethyl) cellulose (EHEC, Bermocoll CL 616 from Akzo Nobel Surface Chemistry, Sweden) with a MW of 70,000 g/mol. and the sodium salt of carboxymethyl cellulose (CMC, FF 10 from

Noviant Oy, Finland) with a MW of 66,000 g/mol. The cloud point for the grade of EHEC used here was about 65°C. The water-soluble polymers were purified by centrifugation and ultra-filtration with 10,000 MWCO filter (Sartorius AG, Germany).

Methods

The solids content of the suspensions were about 20 % (by wt.). The concentrations of cellulose ether were in the range from 0.2 parts (by wt.) per hundred parts of dry pigment (pph) to 5.0 pph. The final PS suspensions were adjusted to pH = 8.0 and stored for approx. 18 h at constant temperature (23°C or 55°C) prior to further experiments. The temperature of each individual suspension was kept constant throughout the remaining steps of this study.

The viscosity of the suspensions and the corresponding aqueous phases (separated by centrifugation) were measured by a rotational rheometer (MCR 300, Physica Messtechnik GmbH, Germany). The relative viscosity (η_r) was taken as a measure of the degree of aggregation and was calculated as

$$\eta_r = \eta/\eta_o \quad (5)$$

where η is the viscosity of the suspension and η_o the viscosity of the aqueous phase.

Coating films were drawn by a bench coater (K Control Coater K101, RK Print-Coat Instruments Ltd., U.K.) and dried at the same temperature as the suspension were prepared at. The thickness of the dry coatings was about 15 μm , i.e. multiple layers consisting of several layers of PS particles were formed.

The structure of the uppermost layer was investigated by means of Atomic Force Microscope (AFM, Explorer 2990, Topometrix, USA) operating in contact mode. Topographic images of the surfaces were taken and processed by an image analysis program. The particle centre

positions in the uppermost layer were acquired in a binary projection. The pair distribution function analysis was adapted to a flat surface, i.e. a two-dimensional system. The surface structure was interpreted by calculating the pair distribution function $g(r)$ given by Hansen et al.⁶

$$g(r) = \frac{1}{N} \sum_{i=1}^N \frac{A_o n_i(r)}{\pi(\delta r^2 + 2r\delta r)} \quad (2)$$

where r is the radius of a ring centred at a particle i , N is the number of particles, A_o is the average area per particle (i.e. $1/\rho$ where ρ is the average number density of particles) and $n_i(r)$ is the number of particle centres contained in a ring of radius r and thickness δr centred at particle i .

RESULTS AND DISCUSSION

The viscosities of the pure aqueous solution at 23°C were measured at different concentrations in order to compare the thickening effect of the two polysaccharides (Fig.1). It was clearly shown that the thickening capacity of EHEC was higher than that of CMC.

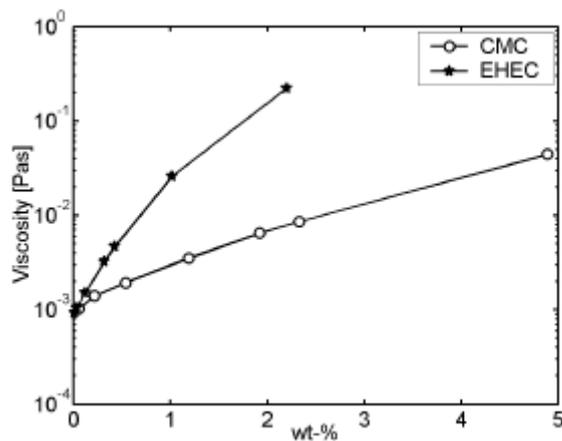


Figure 1. The viscosity vs. the concentration of cellulose ether. Aqueous solutions at 23°C and pH=8.

The viscosities of the continuous (aqueous) phase of the PS suspensions were measured after separation at both 23°C and 55°C. The results obtained at 23°C are shown in Fig. 2. The low value of the continuous phase viscosity at 0.2 pph EHEC, in spite of the high thickening effect shown in Fig. 1, indicated that almost all added EHEC was adsorbed. On the other hand, the continuous phase viscosities of CMC-containing suspensions did not deviate from the expected behaviour for a non-adsorbing polymer. CMC is not expected to adsorb on the PS particles, due to the electrostatic repulsion between the particles and the dissolved polymer. It has been reported elsewhere that EHEC adsorbs on latex surfaces to which CMC does not adsorb⁷.

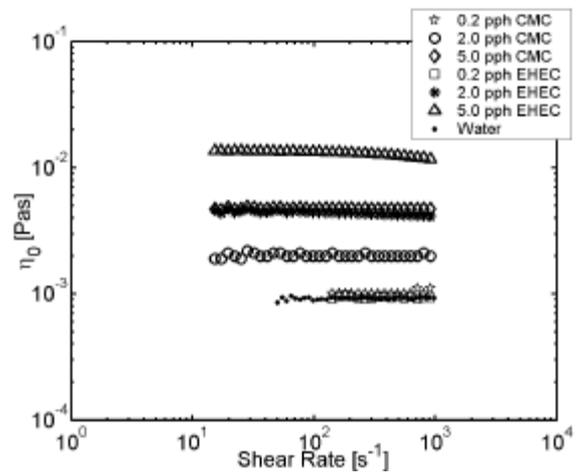


Figure 2. Aqueous phase viscosities of the PS-suspensions. Pure water is included as a reference. Temperature 23°C.

The relative viscosity of the polysaccharide-containing suspensions was calculated and taken as a measure of the degree of flocculation (Fig. 3 and Fig. 4). The relative viscosity of the CMC-containing suspensions indicated that the suspensions were flocculated at high concentrations of CMC. No flocculation was indicated at 0.2 pph CMC. Depletion flocculation is related to the relative

chemical potential of the solvent. Thus depletion flocculation is generally found in dispersions of relatively high concentrations of dissolved polymer. However, at very high concentrations the depletion volume surrounding each particle is reduced, resulting in a maximum in the depletion attractive forces at some intermediate concentration³. Due to Brownian motion and electrostatic stabilization, depletion flocculation needs a certain concentration to overcome the repulsive forces and the thermal motion of particles. The observed behaviour for the CMC-containing suspension indicates depletion flocculation at 2.0 pph and 5.0 pph CMC. The CMC-containing suspension showed in principle the same behaviour at 55°C as at 23°C (cf. Fig. 3 and Fig. 4).

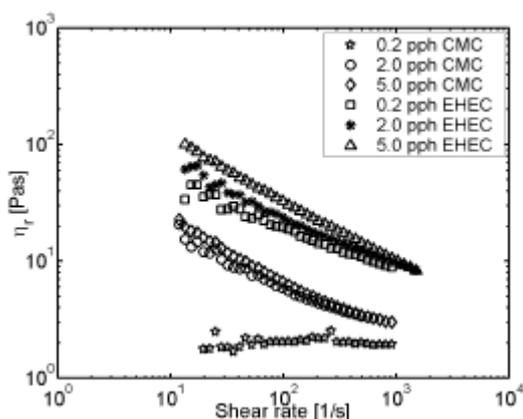


Figure 3. The relative viscosity of the CMC/EHEC-containing suspensions vs. shear rate. Temperature 23°C.

For the EHEC-containing PS suspensions at 23°C, the flocculation started already at a very low addition level and a further increase in concentration level did not substantially affect the value of the relative viscosity (Figure 11). Thus a bridging flocculation mechanism is very likely. Bridging flocculation is expected to occur already at low concentrations, in good agreement with Fig. 3.

Measurements of relative viscosity at 55°C (Fig. 4) revealed a different behaviour of the EHEC-containing suspensions compared to what observed at 23°C. At 55°C, the relative viscosity was dramatically affected by the concentration of EHEC, and the relative viscosity increased with increasing concentration of EHEC. Such increase in the relative viscosity was not expected if bridging flocculation should have been the dominating mechanism.

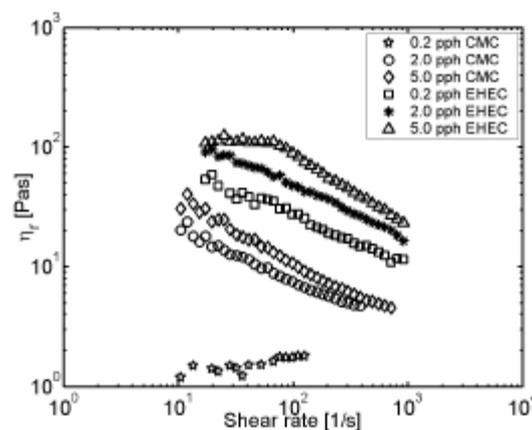


Figure 4. The relative viscosity of the CMC/EHEC-containing suspensions vs. shear rate. Temperature 55°C.

The picture will be even more evident if the relative viscosity of all the suspensions is compared at a constant shear rate of 100 s⁻¹ (Fig. 5). An increase in temperature from 23°C to 55°C had a very small effect on the relative viscosity of the CMC-containing suspensions, while a dramatic effect was observed for the EHEC-containing suspensions. The influence of temperature on colloidal stability is in general difficult to predict for dispersions containing non-adsorbing polymers, but no dramatic effects are expected. The influence of temperature on dispersions containing adsorbing polymers is to large extent governed by the interaction between the solvent and the dissolved polymer. In the case of EHEC-containing dispersions, changes in solvent conditions with increase

temperature make the CIPS mechanism more likely at elevated temperatures. The rapid increase in relative viscosity for the EHEC-containing suspension at 55°C indicates that large amounts of dissolved polymers are taking active part in the destabilization process. This is an evident for the CIPS mechanism. At 23°C, the flocculation behaviour of the EHEC-containing suspension probably reflects both bridging and CIPS.

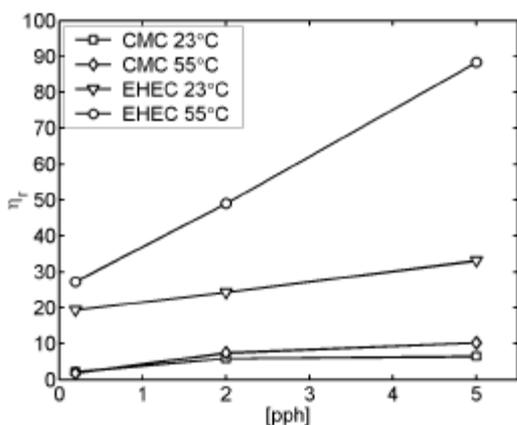


Figure 5. The relative viscosity of the PS suspensions vs. the amount of water-soluble polymer added, at a shear rate of 100 s^{-1} .

The aggregated structure of the PS particles in suspension was not in general visible when the surface structure of dried draw down coatings was examined by AFM. Calculation of the pair distribution function revealed that the surface structure of the EHEC- and CMC-containing layers draw down and dried at 55°C were quite similar to each other at 2.0 pph and 5.0 pph soluble polysaccharide (Fig. 6 and Fig. 7).

The pair distribution functions for both cellulose ethers obtained at 23°C very much resembled the pair distribution curves for the CMC-containing suspension at 55°C shown in Fig. 6. I.e., a high degree of order at 23°C was observed at 0.2 pph cellulose ether, while disorder was observed for the higher levels of cellulose ether.

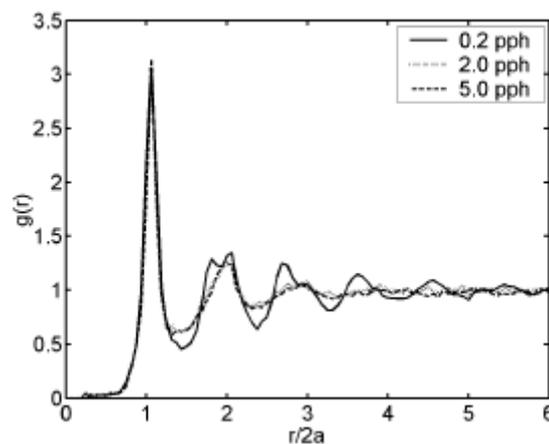


Figure 6. The $g(r)$ -curves for the dry CMC-containing PS layers at 55°C. The radial distance is normalized with respect to the particle diameter ($2a$).

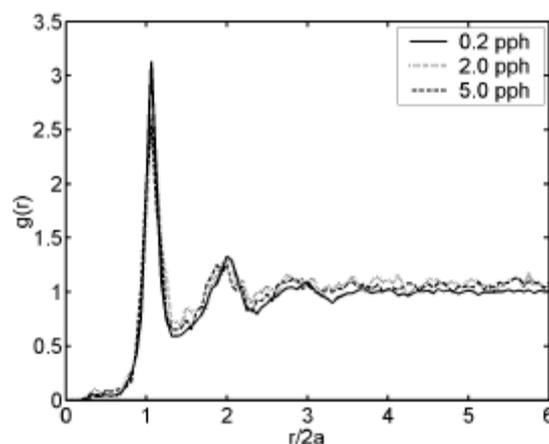


Figure 7. The $g(r)$ -curves for the dry EHEC-containing PS layers at 55°C. The radial distance is normalized with respect to the particle diameter ($2a$).

However, at 55°C and 0.2 pph cellulose ether, a substantial difference between the two cellulose ethers was observed (cf. Fig. 6 and Fig. 7). The $g(r)$ -curve for 0.2 pph EHEC at 55°C showed significantly less surface order than the corresponding CMC-containing layer.

This indicated that the aqueous phase viscosity had a main role for the dry surface structure. The wet structure that existed in

the suspensions did not resist the capillary forces during drying (consolidation), with the exception of the EHEC-containing suspension at 55°C. A possible explanation to this exception is the extended mass transport that has to take place in a CIPS mechanism.

CONCLUSION

The relative viscosity of the systems indicated that different flocculation mechanisms occurred for the EHEC- and the CMC-containing PS suspensions. In the CMC-containing PS systems the flocculation was induced by depletion flocculation and in the EHEC-containing systems the flocculation seemed to be induced by bridging mechanism and by capillary induced phase separation. (CIPS).

AFM supported by pair distribution analysis is a powerful tool in the description of surface structures and order-disorder phenomena that occur during drying (consolidation) of coating layers. The aqueous phase viscosity of the suspensions seemed to be the predominate factor governing the degree of order in the dry layers. Only when the cellulose ether (EHEC) was relatively close to its phase separation temperature, a clear correlation between poor colloidal stability and low degree of order was observed.

ACKNOWLEDGMENTS

The authors thank Dr. Peter Hansen at STFI; Stockholm, Sweden for assistance with the image analysis and Dr. Jouko Peltonen, Åbo Akademi University, Finland for assistance and guidance during the AFM work. The financial support from the Swedish Pulp and Paper Research Foundation, the Knowledge Foundation and the Swedish Agency for Innovation Systems (VINNOVA) is gratefully acknowledged.

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