# The influence of thickeners on the surface structure of coatings, a relationship between surface structure, colloidal stability and viscosity

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## ABSTRACT

The colloidal stability of polystyrene suspensions and the surface microstructure of the corresponding coating layers were investigated. The effects of addition of three water-soluble thickeners were compared. An Atomic Force Microscope was used to investigate the surface structure. The surface structure was interpreted by calculating the pair distribution function and the colloidal stability was investigated by rheological measurements. The suspensions containing the alkali-swellable emulsion had the highest viscosity and the lowest degree of order in the dry surface layer. Quite a good correlation was observed between the surface microstructure and the amount of polymer added, despite the fact that the different thickeners destabilized the suspensions by different mechanisms.

## INTRODUCTION

Coating colors are applied to the surface of paper to improve the optical performance and the print quality[1]. The rheological properties of the coating color depend strongly on the interactions between the different components in the coating color and can control the final surface structure. Therefore, it is important to characterize the rheological behavior of the coating color. It is also important to characterize the surface structure of the coating layer since the particle orientation and the degree of order of the surface determine the gloss and affect the penetration of fluids, e.g. printing inks[2-4].

The aim of this study was to examine correlations between the rheological properties of the wet color and the surface structure of the corresponding dry layers, as measured by pair distribution function, $g(r)$, analysis, where $r$ is the radius of a ring centered at a particle.

## EXPRERIMENTAL

This study compared three of the most commonly used water-soluble thickeners; carboxymethyl cellulose (CMC), poly (vinyl alcohol) (PVA) and an alkali-swellable acrylic polymer emulsion (ASE). The model coating colors were all based on polystyrene (PS) pigment.

The effects of the thickeners on the surface structure and on the colloidal stability were investigated. The colloidal stability of the PS suspensions was investigated by viscosity measurements. The apparent viscosity and the aqueous phase viscosity were measured in order to elucidate the colloidal stability and degree of flocculation.

The apparent viscosity and the aqueous phase viscosity were measured with a rotational rheometer (MCR 300, Physica Messtechnik GmbH, Germany) at concentrations of thickener corresponding to 0.1 parts (by wt.) per hundred parts of dry pigment (pph), 0.2 pph, 0.3 pph and 0.5 pph. The suspension was stored over night prior further experiments.

All viscosity measurements were performed at 23°C. The measuring geometry was concentric cylinders. Both single and double gap systems were used. In order to obtain the aqueous phase of the different suspensions, the suspensions were centrifuged for 4 h and then subsequently filtered under external pressure. Clear aqueous phases were obtained.

The coating colors were drawn down on polyester substrates and the surface microstructure of the dry layers was investigated by Atomic Force Microscopy (AFM, Nanoscope III). The AFM images taken of the were processed by an image analysis program and subjected to pair distribution function, $g(r)$, analysis and the correlation length was calculated[5-6]. Each of the thickeners was investigated at three different concentrations.

## RESULTS

### Viscosity

The apparent viscosities ($\eta$) and the aqueous phase viscosities ($\eta_0$) for the polymer-containing PS suspensions were measured. The relative viscosities ($\eta_r$) of the suspensions were calculated from the apparent viscosity and the aqueous phase viscosity (*Eq. 1*).

$$\eta_r = \frac{\eta}{\eta_0} \qquad [1]$$

The apparent viscosity of the ASE-containing suspensions increased rapidly with increasing concentration of ASE. In the PVA- and the CMC-containing suspensions the concentration of the water-soluble polymer had less effect on the apparent suspension viscosity (*Figure 1*) compared to the ASE-containing suspensions.

The aqueous phases of the CMC- and PVA-containing suspensions were obtained by centrifugation and filtration. The aqueous phases of the ASE-containing suspensions were prepared synthetically with the same ASE concentration as the real aqueous phases would have had without adsorption. This was due to filtration problems that occurred with the ASE-containing suspensions.

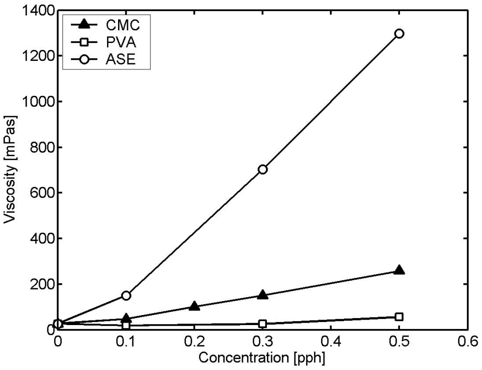

Figure 1. The viscosity of the PS suspension vs. the concentration of water-soluble polymer. Shear rate 30 $s^{-1}$, temperature 23 °C and pH = 8.

The aqueous phase viscosities are presented in *Table 1.* The viscosities were in the range of 1.5–5.5 mPas and 1.1–1.5 mPas for the aqueous phases of the CMC- and PVA-containing suspensions, respectively. The (synthetic) ASE aqueous phase had much higher viscosity than the experimentally obtained values for the CMC- and PVA-containing suspensions. The viscosity of the ASE aqueous phase was strongly affected by the concentration of added polymer.

Table 1. The viscosities of the aqueous phases of CMC, PVA and ASE at 23 °C. The ASE aqueous phases were prepared synthetically.

| **Polymer** | **Content [pph]** | **Viscosity [mPas]** |
|---|---|---|
| CMC | 0.1 | 1.60 |
| | 0.2 | 2.66 |
| | 0.3 | 3.12 |
| | 0.5 | 5.18 |
| PVA | 0.1 | 1.13 |
| | 0.3 | 1.25 |
| | 0.5 | 1.52 |
| ASE | 0.1 | 8.88 |
| | 0.3 | 134.25 |
| | 0.5 | 589.00 |

The relative viscosities of the CMC- and PVA-containing PS suspensions were calculated and taken as a measure of the degree of flocculation (*Figures 2 and 3*). Wallström et. al.[5] reported that flocculation in CMC-containing PS suspensions seems to follow a depletion flocculation mechanism, i.e. particle destabilization induced by the addition of a free polymer. However, the osmotic pressure difference is so small at a low polymer concentration that flocculation may not occur. As the polymer concentration is increased above the overlap concentration, the depletion layer thickness decreases while the osmotic pressure increases[7-9]. Thus the degree of flocculation is not expected to increase at very high concentrations of non-adsorbing soluble polymer (due to reduction of the depleted volume at high concentrations), in good agreement with the behavior shown in Figure 2.

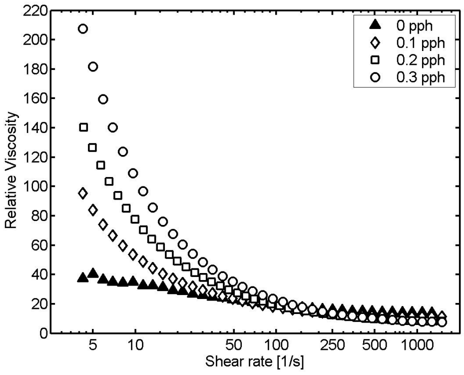

Figure 2. The relative viscosity of CMC-containing suspensions at 23 ° C.

The flocculation mechanism for the PVA suspensions was investigated by viscosity measurements. The relative viscosity of the PVA-containing suspensions indicated that the suspensions were not flocculated at 0.1 and 0.3 pph PVA (Figure 3). The relative viscosities were practically identical at those levels of PVA. Figure 3 shows that a small amount of PVA seems to stabilize the suspension. The low aqueous phase viscosities of the PVA-containing suspensions (Table 1) support the idea of a flocculation/stabilization mechanism in which adsorbed PVA-molecules are involved. Both stabilization and flocculation of suspensions could be governed by polymer adsorption or by some synergetic interaction in which the adsorbed polymers are involved. The well-known pigment shock observed upon addition of PVA is due to bridging flocculation[10]. A homogeneous distribution of the adsorbing polymer prior to adsorption (without local surpluses or deficits) promotes steric stabilization[11-14]

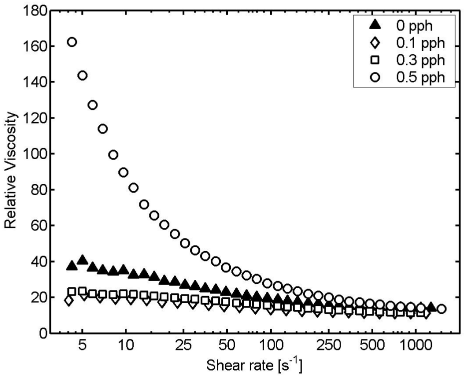

Figure 3. The relative viscosity of PVA-containing suspensions at 23 ° C.

## Surface structure

The structure of the uppermost layer was investigated by means of AFM, operating in the tapping mode. Topographic images of the surfaces were taken and processed by an image analysis program. Pair distribution function analysis was performed based on the particle centre positions in the uppermost layer. From the pair distribution function, $g(r)$, the correlation length $(\zeta)$ was calculated. The correlation length was normalized with respect to the particle diameter, *d*.

It could be seen that the correlation length decreased with increasing amount of added polymer. The normalized correlation length $(\zeta / d)$ shown in table 2 for different contents of polymer confirmed that the pure polystyrene layers possessed the highest degree of order (*Table 2*). It could be seen that the 0.1 pph PVA-containing layers gave a higher degree of order than the 0.1 pph CMC- and ASE-containing layers. It can also clearly be seen that the addition of polymer gave a lower degree of order for the coating layers.

Table 2. The normalized correlation length at different amounts of added thickener.

| **Polymer added** | **Content [pph]** | **Correlation length** ($\zeta / d$) |
|---|---|---|
| CMC | 0.0 | 4.7 |
| | 0.1 | 2.9 |
| | 0.2 | 2.0 |
| | 0.3 | 1.9 |
| PVA | 0.0 | 4.7 |
| | 0.1 | 3.4 |
| | 0.3 | 2.0 |
| | 0.5 | 2.0 |
| ASE | 0.0 | 4.7 |
| | 0.1 | 2.5 |
| | 0.3 | 1.7 |
| | 0.5 | 1.6 |

Correlations between viscosity parameters (i.e. the suspension viscosity, the aqueous phase viscosity and the relative viscosity) and the correlation length were investigated.

No correlation between the relative viscosity and the correlation length ($\zeta / d$) was observed. It could be seen that an increase in the aqueous phase viscosity led to a decrease in the degree of order of the surface structure. It could also be sent that the correlation length at the high concentration limit corresponded well to the viscosity of the suspension.

However neither the suspension viscosity, the aqueous phase viscosity nor the relative viscosity could be used alone to predict the surface structure. Instead, a relative good correlation was observed between the surface microstructure and the amount of polymer added, despite the fact that the different thickeners destabilized the suspensions by different mechanisms. The surface microstructure seemed to be strongly affected by the concentration of water-soluble polymer in the aqueous phase of the wet coating during the course of the consolidation (drying) process.

## CONCLUSIONS

The degree of correlation between viscosity parameters (i.e. the suspension viscosity, the aqueous phase viscosity and the relative viscosity) and the surface structure of the dry coatings (i.e. the correlation length) was investigated. The best correlation seemed to be between the correlation length and the amount of polymer added, despite the fact that the investigated thickeners destabilized the suspensions by different mechanisms. This indicates that the initial viscosity parameters are not the most important parameters with respect to the surface microstructure of the final coating layer. Instead, the surface microstructure seemed to be strongly governed by the increase in concentration of water-soluble polymer during the course of the consolidation (drying), indicating that the final surface microstructure was created quite late in the consolidation process.

## ACKNOWLEDGEMENT

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