

## The relation between viscoelastic properties of suspensions based on paper coating minerals and structures of the corresponding coating layers

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### ABSTRACT

The viscoelastic properties of polymer containing calcium carbonate based suspensions were studied. Coating films made from the suspensions were drawn down on polyester films. The main focus has been addressed to the relation between the viscoelastic properties of the suspension and the structure of the dry layers. Correlations between the storage modulus and the porosity of the coated layers could be seen.

### INTRODUCTION

Paper coating colours are viscoelastic materials and several studies have been performed in order to measure the viscoelastic properties as such, but also to find its implications on the processability and the final properties of the dry coated layer<sup>1-3</sup>. Most investigations have been focused on kaolin-based coating colours. In the present study aqueous suspensions based on calcium carbonate were investigated. More information is required in order to understand the rheological properties of calcium carbonate based suspensions and coating colours. Especially coating colours containing an alkali-swelling acrylate emulsion have been poorly investigated.

The present investigation presents a comparison between three different water soluble thickeners: carboxymethyl cellulose (CMC), poly (vinyl alcohol) (PVA) and an alkali-swelling acrylate emulsion (ASE).

One grade of calcium carbonate was investigated; ground calcium carbonate (GCC).

It has been shown elsewhere that PVA may either stabilize or destabilize a colloidal suspension<sup>4</sup>. Flocculation induced by PVA follows a bridging mechanism<sup>5</sup>, contradictory to the CMC-containing suspensions which are susceptible to depletion flocculation<sup>5, 6</sup>. The thickening effect of ASE is due to a hydrodynamic volume exclusion mechanism, as described for entangled polymers<sup>7</sup>.

### EXPERIMENTAL

#### Materials

Aqueous suspensions based on ground calcium carbonate (GCC, HC90, Omya, Switzerland) and three different thickeners were prepared. The thickeners used were Poly (vinyl alcohol) (PVA, Mowiol 10:98, Clariant Oy, Finland), Carboxymethyl cellulose (CMC, Finnfix 10, Noviant Oy, Finland) and an alkali-swelling acrylate emulsion (ASE, Sterocoll HT, BASF AG, Germany).

#### Methods

The suspensions were prepared according to the recipes shown in table 1. The dry content was 70 % (by wt) and the pH of the prepared suspensions was adjusted to about 8.5.

|                          | no 1              | no 2              | no 3              |
|--------------------------|-------------------|-------------------|-------------------|
|                          | Parts<br>(by wt.) | Parts<br>(by wt.) | Parts<br>(by wt.) |
| HC 90                    | 100.0             | 100.0             | 100.0             |
| PVA<br>(Mowiol<br>10-98) | 1.0               | 0                 | 0                 |
| CMC<br>(Finnfix10)       | 0                 | 1.0               | 0                 |
| ASE<br>(Sterocoll<br>HT) | 0                 | 0                 | 0.3               |

Table 1. The recipes of the aqueous suspensions.

The rheological behaviour of the suspensions were measured by a rotational rheometer (MCR 300, Physica Messtechnik GmbH, Germany). Flow curves, strain sweeps and frequency sweeps were measured for all three suspensions.

Coating films were drawn down by a bench coater (K Control Coater K101, RK Print-Coat Instruments Ltd., U.K.) on polyester films, and dried in room temperature (23°C). The thickness of the dry coatings was about 51  $\mu\text{m}$ . The optical properties were measured with a spectrophotometer (Minolta Co., Ltd, Japan) and the Kubelka-Munk light scattering coefficient ( $s$ ) was calculated.

The porosity of the coatings was calculated from the densities, knowing the density of each component in the coating formulation. The densities of the coatings were calculated from measurements of grammage and thickness. The thickness was measured between spherical platens<sup>8</sup>.

## RESULTS AND DISCUSSION

Strain sweep at small-amplitude oscillatory shear (SAOS) deformation revealed that the PVA-containing suspensions possessed the highest critical strain (*Figure 1*). The CMC-containing suspensions had the lowest critical strain. However, when the corresponding critical

stress in SAOS deformation measurement was calculated it was shown that the PVA containing suspensions possessed about a magnitude lower critical shear stress than did the suspensions containing any of the two the other thickening polymers. This was in good agreement with differences in yield stress calculated from flow curves (*Figure 2*).

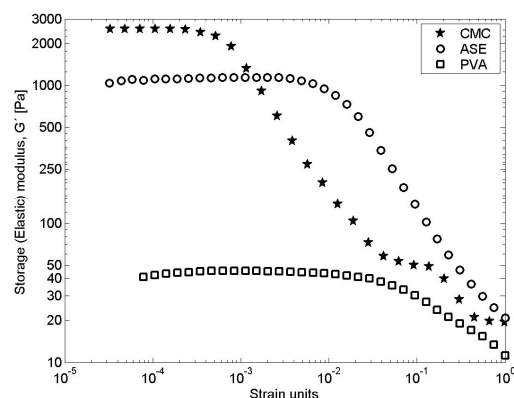


Figure 1. Strain sweeps of the different suspensions. The frequency was 1Hz.

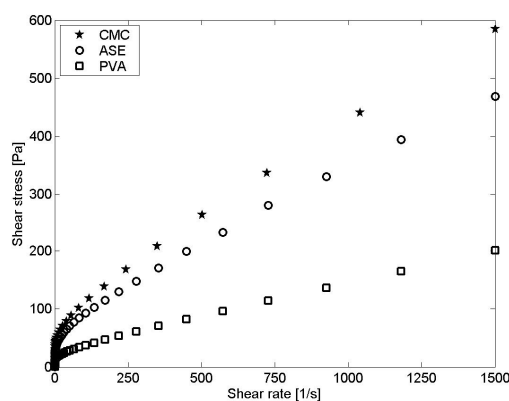


Figure 2. Flow curves for the three different suspensions.

The viscosity of the suspensions was measured (*Figure 3*) and the PVA-containing suspensions had a lower viscosity than the ASE- and CMC-containing suspensions. The ASE- and CMC-suspensions showed about the same viscosity at shear rates of  $1 \text{ s}^{-1}$  or above.

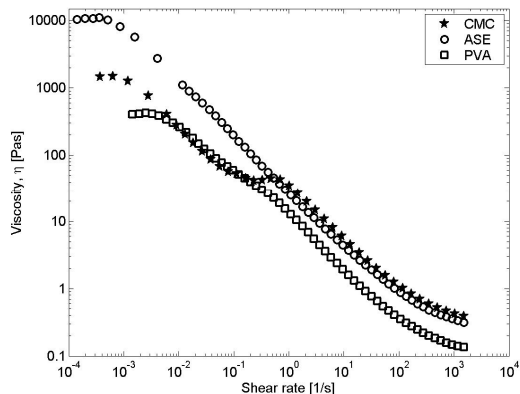


Figure 3. Viscosity vs. shear rate for the different suspensions.

Differences in the viscoelastic behaviour of the three different suspensions were observed when frequency sweeps in SAOS was studied (Figure 4). Even if no single relaxation time was observed, the results from the frequency sweep indicated a profound influence of the polymer-pigment interaction, as well as of molecular weight, on the PVA-containing suspensions storage modulus decreased more rapidly at decreasing frequency than the ASE- and CMC-containing suspensions (Figure 4). This could be explained in terms of PVA absorption on GCC, leaving almost no free PVA left in the aqueous phase of the suspension.

The storage modulus was always higher than the loss modulus (see figure 5), indicating that all suspension had more elastic than viscous response on the applied strain.

It was a clear relation between the storage modulus and the porosity of the coated layers. A high value of the storage modulus correlated to a high porosity of the coated layer. The lowest value of storage modulus and the lowest density of the corresponding dry layer were observed for the PVA-containing suspensions. The CMC- and ASE-containing suspensions gave dry layers of higher porosity than the PVA-containing suspension.

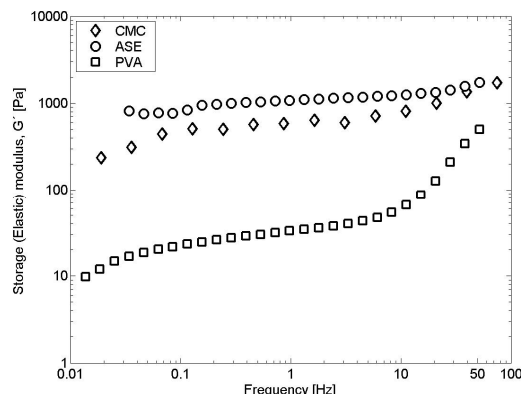


Figure 4. Variations of storage modulus with frequency for the different suspensions.

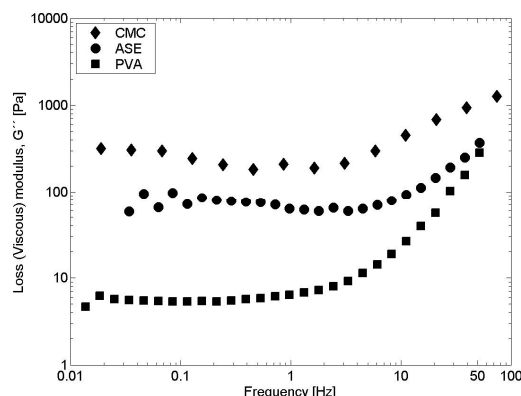


Figure 5. Variations of loss modulus with frequency for the different suspensions.

The Kubleka-Munk light scattering coefficient ( $s$ ) was calculated for the coatings (Figure 6). It was observed that the PVA-containing suspension gave the lowest  $s$ -value of the corresponding dry layer. This observation was in good agreement with the obtained values of porosity and storage modulus.

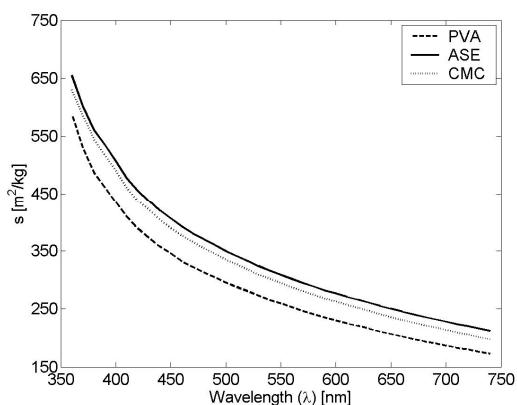


Figure 6. The light scattering coefficient of the coating vs. the wavelength of light.

The ASE containing coatings possessed the highest light scattering coefficient. Even if the CMC-containing layer gave quite similar optical behaviour as the ASE-containing layers, no direct correlation to storage modulus could be observed for these two suspensions.

## CONCLUSIONS

Correlations between the viscoelastic properties and the coated layer structure could be seen. PVA containing suspensions showed a higher critical strain and the low storage modulus due to that the stabilizing effect of adsorbed PVA. At the same time, the porosity of the coatings and the optical properties indicated a correlation between low storage modulus and low porosity and poor light scattering behaviour. However, this relation could not be used for predicting the differences between CMC- and ASE-containing suspensions.

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