Rheological Characterization as a Tool for Evaluating Mineral Suspensions for Paper Coatings

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ABSTRACT

Suspensions, used for paper coating, based on calcium carbonate pigments with different particle size distribution and different co-binders have been characterized, both using a rotational rheometer, and a capillary viscometer. The results indicated that the viscosity at high shear rates depended on hydrodynamics, whereas at low shear rates it depended mainly on interactions between the constituents.

INTRODUCTION

High quality printing papers are pigment coated. The coating is applied to the paper in the form of a water-based suspension, consisting of pigment and binders (divided into latex-binder and co-binder). The coating process is rheological demanding, and a controlled rheology of the suspension is prerequisite as well for the runnability as for the printing properties of the coated sheet.

There are several stages, from the making of the colour to the forming of the coating layer, which have to be accounted for. During mixing and pumping the shear rates are low to moderate, whereas during the forming the shear rates are often well above 10^6 s^{-1}. Thus rheological characterization of the suspensions has to be performed in different shear rate regions. No single rheometer is capable of spanning the entire shear rate range of interest. Therefore, data from different rheometers have to be combined.

Kaolin based suspensions have been extensively studied, but, in spite of the fact that ground calcium carbonate is the most frequently used pigment in Europe, relatively little attention has been paid to that pigment in the coating research.

In this paper, suspensions based on commercially available ground calcium carbonates with broad and narrow particle size distribution have been studied. The focus of the study is on rheological characterization of interactions between pigment and binders at low and high shear rates.

EXPERIMENTAL

Materials

The calcium carbonates were supplied as slurries, from Omya, Switzerland, and some data of the pigments are shown in Table 1. As latex-binder, a commercial latex based on carboxylated styrene-butadiene (SB) co-polymer, DL 950 from DOW Europe S.A., Switzerland, was used. The average particle size diameter of the latex particles was 0.15 µm according to the manufacturer. The water soluble co-binders used were carboxymethyl cellulose (CMC), Finnfix 10 from Noviant Oy, Finland, and soy protein, Pro-Cote 4200 from DuPont Soy Polymers, USA. The CMC grade had an average molecular mass of 66 kg/mol and a degree of substitution was 0.78 according to the

Table 1. Coating pigment data from the supplier.

Pigment	Solids content [%]	Specific surface area [m^2/g]	Particles < 2µm [w/w%]	Particles < 1µm [w/w%]	Median particle size by weight (d_{50}) [µm]
Hydrocarb 90	78 ±1	12.5	90	64	0.70
Covercarb 75	72 ±1	9.0	95	75	0.52

manufacturer. The mineral suspension formulations are presented in Table 2 along with results from the measurements.

Methods

All examined suspensions were prepared using conventional bench scale methods. The co-binder was first added to the pigment slurry and then the latex. The resulted suspensions were then diluted with water to keep the total volume fraction of solid material to 0.40 in all suspensions, whereas the concentrations of the aqueous co-binder solutions were adjusted to the same concentration by weight as in the final coating colour suspensions. Finally the pH was adjusted to 8.

In order to quantify the state of aggregation within the systems, rheological measurements were performed not only on the final coating colour suspensions, but also on the pigment slurries, on the pigment slurries added with co-binder and on the co-binders in aqueous solution, respectively.

To study the adsorption of the co-binders on the pigment, liquid phases from the pigment slurries added with co-binder were also isolated by centrifugation at 6,466 g for 4.5 h.

Rheological measurements

In the study three different rheometers have been used. At low shear rates, up to 1500 s^{-1}, measurements were carried out using a rotational controlled stress rheometer, MCR 300, Physica Messtechnik GmbH, Germany. The measurements were performed at 25°C, using double gap geometry for low viscous and cone-plate or cup-bob geometry for the more viscous suspensions.

At high to ultra high shear rates a capillary viscometer, ACAV A2, from ACA Systems Oy, Finland, was used. The capillary viscometer is specially designed for measuring mineral suspensions used for paper coatings. The samples were tested at shear rates up to one million reciprocal seconds, which corresponds to the highest shear rates the suspensions are exposed to in the coating process. The capillary, made of glass, had a length of 90 mm and a diameter of 0.50 mm. When the length over radius ratio exceeds 200, here 360, Bagley correction for end effects was and could be neglected[1].

The Brookfield viscosity was also measured at 100 rpm (SCAN-P 50:84) by a RVDVI+ Viscometer, from Brookfield Engineering Laboratories Inc., USA.

RESULTS AND DISCUSSION

From the measurements at low shear rates, using the rotational rheometer differences in the rheological properties were observed between the suspensions containing different type of pigment. However these differences were more pronounced upon variation of the co-binders used.

In the shear rate range up to 1500 s^{-1}, suspensions for paper coating can be described with help of the Bingham equation[2], see Eq. 1.

$$t = t_o + ?_p \cdot \dot{g} \qquad (1)$$

Table 2. Formulations# and characteristics of the suspensions used.

Covercarb 75 [pph]	Hydrocarb 90 [pph]	CMC [pph]	Soy protein [pph]	Latex [pph]	Brookfield 100 rpm [mPas]	Yield Stress [Pa]	Plastic Viscosity [mPas]	Liquid Phase Plastic Viscosity [mPas]	High Shear Viscosity' [mPas]
100	-	-	-	-	55 *	0.3	10.8	-	42
100	-	1	-	-	1580 †	45.2	122.6	6.9	62
100	-	1	-	10	1640 †	53.5	58.7	-	33
100	-	-	2	-	710 *	18.8	66.6	2.2	60
100	-	-	2	10	1990 ‡	46.2	58.6	-	32
-	100	-	-	-	45 *	0.2	7.5	-	16
-	100	1	-	-	984 †	28.2	58.5	7.1	35
-	100	1	-	10	906 †	29.9	40.8	-	21
-	100	-	2	-	480 *	13.0	46.7	2.7	32
-	100	-	2	10	890 ‡	28.0	46.0	-	21
-	-	1	-	-	-	0.1	5.9	5.9	-
-	-	-	2	-	-	0.1	3.0	3.0	-

Formulations are based on pph (parts per hundred parts dry pigment)

* Brookfield spindle no 3, † Brookfield spindle no 4, ‡ Brookfield spindle no 5.

' High shear viscosity values are presented at 500,000 s^{-1}

The total volume fraction of solid material in all suspensions was 0.40, whereas the concentrations of the aqueous co-binder solutions were adjusted to the same concentration by weight as in the final coating colour suspensions.

where t denotes the shear stress, t_o the yield stress, $?_p$ the plastic viscosity and $\dot{g}$ the shear rate.

Using the Bingham equation the yield stress and the plastic viscosity, were estimated for the suspensions studied. The yield stress could be taken as measure of aggregation in the systems, and the yield stress is expected to increase with increasing degree of aggregation in the suspension.

At low shear rates, the flow curves for the pure pigment suspensions were Newtonian (yield stress values equal to zero) and the pigment with the narrow particle size distribution exhibited the highest viscosity (see Table 2). Knappich et al.[3] have shown that this type of pigment yields porous coating layers.

Addition of co-binder to the pigment slurries gave yield stress values, which were approximately the same for CMC and soy protein. The yield stress values, and the plastic viscosities were, however, markedly higher for the pigment with the narrow particle size distribution.

When adding latex to the pigment/co-binder suspensions, the plastic viscosity decreased for the suspension with CMC and increased for the one with soy protein. The latter suggests that the soy protein interacted with the latex used.

Another interesting observation from the low shear rate measurements was that the yield stress values for the coating colours and the pigment slurries added with CMC coincided (see Fig. 1 and 2), whereas addition of the latex to the pigment slurry added with soy protein increased the yield stress value.

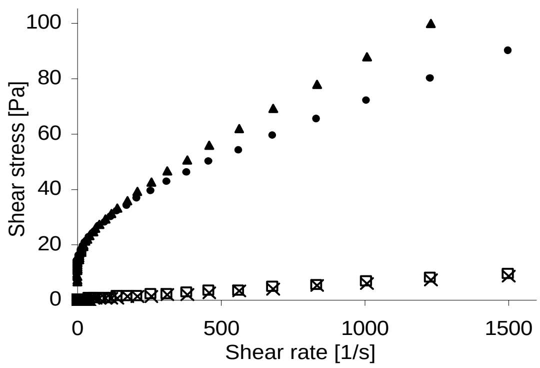

Figure 1. Flow curves for coating colour based on Hydrocarb 90 and CMC: (?) Pigment slurry added with CMC, (?)Coating colour, (?) Pigment slurry, (x) CMC.

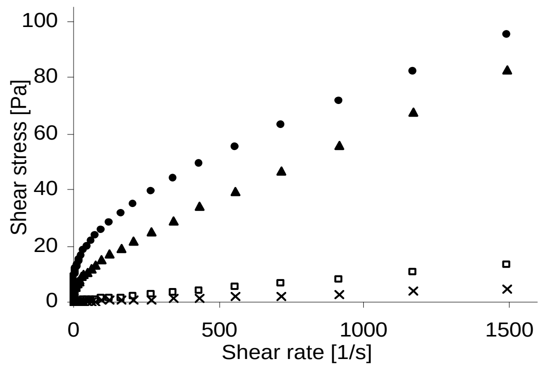

Figure 2. Flow curves for coating colour based on Hydrocarb 90 and soy protein: (?)Coating colour, (?) Pigment slurry added with soy protein, (?) Pigment slurry, (x) Soy protein.

The rheological measurements at low shear rates were, as already mentioned, also performed on the liquid phases of the mineral suspensions. A comparison of the viscosity of the liquid phases isolated by centrifugation to that of the separately prepared aqueous co-binder solutions indicated, that the soy protein, in contrast to the CMC, adsorbed on the pigment. Since both soy protein and CMC aggregated the pigments, this suggests that CMC interacted weakly with the pigment by a depletion mechanism, while the interaction between pigment and protein was achieved through a stronger bridging mechanism[4].

The results obtained from the capillary viscometer indicated that the viscosity at high shear rates was dependent only on the hydrodynamics. This suggests that the interaction was weak between the co-binders and pigments, and that the liquid phase viscosity as well as the volume fraction pigment governed the viscosity of the suspensions. The suspensions based on the pigment with the narrow particle size distribution exhibited the highest viscosities. When latex was added, the degree of polydispersity increased in the coating formulations and this was more pronounced for the pigment with the narrow particle size distribution. Therefore the viscosity was reduced more for this pigment. This is studied and discussed by Knappich et al.[3].

CONCLUSIONS

The results obtained at low shear rates showed that the viscosity of the suspensions was depended both of type of pigment and co-binder used. Moreover the results showed that CMC and soy protein interact according to different mechanisms with the pigment, CMC by a depletion mechanism, and soy protein by a bridging mechanism.

At high shear rates the viscosity was mainly controlled by the pigment used.

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