Extensional Viscosity of Paper Coating Suspensions studied by Converging Channel-Flow and Filament Stretching

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ABSTRACT

The extensional viscosity of three coating suspensions having different thickening systems was investigated with different techniques: converging two channel-flow and filament stretching. A polyvinyl alcohol-containing suspension showed the lowest extensional viscosity. The previously reported slower dewatering for this coating colour can thus not be explained in terms of extensional viscosity.

INTRODUCTION

Although the importance of extensional rheology for the paper coating process has been widely accepted for some years, most research has hitherto been focussed on the extensional behaviour in the metering stage and at the nip exit in film coating 1-5.

After metering, dewatering of the coating colour occurs through a increasingly thick immobilised layer of coating colour, which acts as a filter cake. It is likely that both shear and extensional viscosity be important also in this process.

The influence of the extensional viscosity of the filtrate on the rate of filtration has been discussed previously, with another focus than the paper coating process6,7,8.

In previous publications 9,10, we have reported on the dewatering behaviour of three different coating colours. These differed with respect to the thickener (co-

binder) used. The thickeners used have been carboxymethyl cellulose (CMC), a polyacrylate-based alkali-swellable emulsion (ASE) and polyvinyl alcohol (PVA). In the cited studies, PVA has shown a much slower dewatering than the other two coating colours. The explanation suggested⁹ has been the formation of a denser filter cake at the interface between wet coating colour and base paper for the coating colour containing PVA.

The object of this work was to investigate whether the slower dewatering observed for the PVA colour could be explained in terms of a higher extensional viscosity at low strain rates.

In this paper, we show results from measurements on coating colours and on aqueous solutions of the thickeners utilised. These measurements were performed using two different techniques: converging channel-flow and filament stretching.

It should be kept in mind that the criteria formulated by Walters¹¹ for a steady state-value of the extensional viscosity cannot usually be met by any instrument available today. The values obtained should thus be regarded as transient values rather than *the* extensional viscosity.

MATERIALS

The formulations of the coating colours and of the aqueous solutions investigated are summarised in Table 1. The ground calcium carbonate (GCC) was Hydrocarb 90 (Omya

relationship (K and n). Also given are the concentrations of the thickeners in the aqueous					
solutions. (pph = parts per hundred parts of dry pigment)					
Coating colour	CMC	ASE	PVA		
GCC / pph	70	70	70		
Kaolin / pph	30	30	30		

11

0.35

25.5

0.23

11

0.7

9.8

0.28

Table 1. Formulations of the three coating colours and the constants of the power law-

AG, Switzerland), the kaolin Century International (Kaolin B.V., the Netherlands), the styrene–butadiene latex DL 950 (DOW Europe S.A., Switzerland), the CMC Finnfix 30 (Noviant Oy, Finland), the ASE Sterocoll HT (BASF AG, Germany) and the polyvinyl alcohol Mowiol 2098 (Kuraray Specialities GmbH, Germany). The coating colours are denoted with the abbreviated thickener.

METHODS

S–B Latex / pph

CMC / pph ASE / pph

PVA / pph

K

п

Coating colour preparation and characterisation

For the colours used in the converging channel-flow experiments, flow curves were obtained using a Bohlin VOR (Bohlin Instrument Ltd, United Kingdom). The constants of the power law-relationship, which were used in the converging channel-flow calculations, are given in Table 1.

Converging channel-flow measurements

The theory of this technique has thoroughly reviewed previously been 3,11,12

The measuring cell, which is shown in Fig. 1, consists of a sample reservoir connected to a hyperbolic die and a piston. The measuring geometry is

mounted on a tensile tester (Instron 5542, Instron Corporation, United States).

11

1.4

5.0

0.29



Figure 1. Side view of the converging channel-flow measuring cell

During measurement, the piston is allowed to move downwards at a pre-set speed. For a fluid obeying a power lawrelationship, the strain rate ($\dot{\varepsilon}$) is given by:

$$\dot{\varepsilon} = \frac{3n+1}{n+1} (Q/\pi) \frac{(1/r_1^2) - (1/r_0^2)}{H}$$
(1)

In Eq. (1), n is the power law-exponent and Q the volume flow rate. The other parameters are given by Fig. 1.

The transient extensional viscosity $(\overline{\eta_E})$ is given by the ratio of the normal stress difference $(\tau_{zz} - \tau_{rr})$ to the strain rate, i.e.

$$\overline{\eta_E} = \frac{(\tau_{zz} - \tau_r)}{\dot{\varepsilon}} \tag{2}$$

The contribution of shear to the total pressure drop may be evaluated using a relationship from Ref. 12. However, if the shear contribution is negligible, the normal stress difference is calculated using the force (F_t) with which the piston is pressed down:

$$\left(\tau_{zz} - \tau_{rr}\right) = \frac{F_t}{\pi r_0^2} \tag{3}$$

The success of this method thus relies on the shear being confined to an infinitesimally narrow region close to the walls of the measuring geometry. The method is reliable only at low Reynolds numbers and it is therefore not suitable for Newtonian fluids.

Filament Stretching

Filament stretching is the technique for extensional viscosity measurements that has gained the most attention in the recent years 11,13,14. The device used in this work is the Haake CaBER 1 (Thermo Electron GmbH, Germany)

In the filament stretching rheometer, a volume of sample is placed between to rigid plates (cf. Fig. 2). As the upper plate is moved upwards, a liquid filament with a cylindrical geometry is formed. The diameter of this filament is monitored using a laser micrometer.

The calculation of extensional properties from the geometry of the liquid filament has been outlined in detail by McKinley and co-workers (work informatively compiled in Ref. 15), and only a brief summary is given here.

After cessation of the movement of the upper plate, the Hencky strain (ε) is given by the ratio of the filament diameter at zero time (t), i.e. the diameter of the rigid plates D_0 , to the diameter at time $t(D_{mid})$:

$$\varepsilon = 2 \ln \left[\frac{D_0}{D_{mid}(t)} \right] \tag{4}$$





And the transient extensional viscosity by:

$$\overline{\eta_E} = \frac{2\sigma/D_{mid}(t)}{\left(\frac{-2}{D_{mid}}\frac{\mathrm{d}D_{mid}}{\mathrm{d}t}\right)} = \frac{-\sigma}{\frac{\mathrm{d}D_{mid}}{\mathrm{d}t}} \tag{5}$$

In Eq. (5), σ is the surface tension of the fluid investigated.

RESULTS

The results from converging channel-flow measurements on the three coating colours are shown in Fig. 3.

Here, all three coating colours show a strain-thinning behaviour, with the slope of the CMC-curve being less steep than those for ASE and PVA. The values for the extensional viscosity seem to level off and reach a plateau value, a pattern, which is most clear for ASE and PVA. This plateau value is higher for ASE than for CMC and PVA.



Figure 3. Results from the converging channel-flow measurements of the coating colours containing CMC (♦), ASE (▲) and PVA (●), respectively

Transient extensional viscosity results from the filament stretching measurements are shown in Fig. 4.



Figure 4. Results from filament stretching measurements of the coating colours containing CMC (♦), ASE (▲) and PVA (●). Extensional viscosity is given as a function of Hencky strain.

The simplicity of the expression for ε (Eq. (4)), with only two, directly measured parameters, makes it convenient to show the extensional viscosity as a function of Hencky strain in Fig. 4. In Fig. 4, all three coating colours show a decreasing extensional viscosity with increasing strain rate. The slopes are however much steeper for CMC and ASE than for PVA. In the Hencky strain range covered, PVA has the lowest extensional viscosity.

A similar pattern may be seen also in the results from the filament stretching measurements on thickener solutions (Figs 5a-c). For all polymers, the extensional viscosity decreases with decreasing concentration.



Figure 5a,b and c. Filament stretching results on solutions of CMC (top), ASE (centre) and PVA (bottom). Extensional viscosity is also here given as a function of the Hencky strain.

The CMC-solutions show the highest extensional viscosities compared to solutions of ASE and PVA. The CMC- and PVA-solutions have a Newtonian or nearly Newtonian behaviour whereas the ASE-solutions are strain thinning.

The measurements on the thickener solutions using converging channel-flow technique were unsuccessful, probably due to inappropriately chosen size of the hyperbolic die. The results from these measurements are not presented here.

DISCUSSION

Since both techniques yield transient values for the extensional viscosity, the results are not directly comparable. However, the trends may be evaluated and give useful information regarding the extensional behaviour.

Although no calculations have been performed, it is assumed that the low degrees of stretching obtained in the techniques used here correspond reasonably well to the extensional deformation during dewatering.

In neither of the techniques utilised, results were obtained that could confirm the hypothesis of a high extensional viscosity being the reason for the previously reported slow dewatering for PVA. Instead, PVA showed lower or approximately similar extensional viscosities as did CMC and ASE. This is true for the aqueous solutions of the thickeners (Fig. 5) as well as for the coating colours (Figs 3 and 4).

The mass concentrations of the thickeners in the coating colours and in the aqueous solutions studied are given in Table 2.

Table 2. Theoretical thickener

concentration in the continuous phases of the coating colours and concentrations in the thickener solutions (Fig. 5). All values are given as % by weight

Coating colour	CMC	ASE	PVA
Theoretical	0.40	0.20	0.80
thick. conc.			
Thick. Conc.	7.6;	3.2;	10.7;
Fig 5	8.5;	5.9;	12.2;
	9.3	8.0	13.5;
			14.7

It should be kept in mind that the thickeners used here adsorb to the pigments and latex to different extents and that the actual concentrations in the aqueous phases may significantly lower.

The results presented in Fig. 5 illustrate an extreme case, with thickener concentrations significantly higher than those encountered in the continuous phase of the coating colours. They however give an indication of the extensional viscosity contribution from the thickener.

In Fig. 5, there is a slight difference between the solutions of CMC and PVA on the one hand and the ASE-solutions on the other, with ASE showing a strainthinning behaviour and the other two being nearly Newtonian. Nevertheless, the PVAsolutions show by far the lowest extensional viscosities.

CONCLUSIONS

Measurements on three coating colours as well as on aqueous solutions of the thickeners were performed using converging channel-flow and filament stretching. The trend in results was similar in all measurements, with PVA having a lower transient extensional viscosity than CMC and ASE.

Having obtained these results, it seems that the most likely reason for the slow dewatering of PVA is the previously presented formation of a much denser filter cake at the interface between wet coating colour and base paper. Although the effect of extensional viscosity may be important in other stages in the process, its role in determining the dewatering rate seems to be negligible.

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REFERENCES

1. Glass, J.E. (1988), "Associative Thickeners in Paint Technology and Potential Application in Paper Coatings", *Proc. TAPPI 1988 Coating Conference*, 287-297.

2. Lavoie, P.-A., Carreau, P.J. and Ghosh, T. (1997), "Rheology of suspensions: the flow behaviour of coating colours", *J. Pulp Pap. Sci.*, **23**, J543-J547.

3. Isaksson, P., Rigdahl, M., Flink, P. and Forsberg, S. (1998), "Aspects of the elongational flow behaviour of coating colours", *J. Pulp Pap. Sci.*, **24**, 204-209.

4. Kokko, A. (2001), "Evaluation of viscosity, elongational viscosity and dewatering of coating colours at high shear rates", Doctoral Thesis, Åbo Akademi university, Turku, Finland.

5. James, D.F., Yogachandran, N. and Roper, J.A.III (2003), "Fluid elasticity in extension, measured by a new technique, correlates with misting", *Proc. TAPPI* 2003 Adv. Coat. Fund. Symp., sess. 4.

6. Kozicki, W. and Kuang, P.Q. (1994), "Cake Filtration of Suspensions in Viscoelastic Fluids", *Can. J. Chem. Eng.*, **72**, 828-839.

7. Drost, M.A. and Windhab, E.J. (2001), "Nich-newton'sches Fließverhalten con Bier beim Durchströmen von porösen Medien als mögliche Erklärung für einen plötzlichen Anstieg der Druckdifferenz bei der Kieselgurfiltration", *Monatsschr. Brauwiss.*, **54**, 44-47. 8. Hwang, K.-J. and Chen, Y.-S. (2001), "The Role of Elastic Effect in Filtration of Particles Suspended in Viscoelastic Polymeric Solution", *J. Chin. Inst. Chem. Engrs.*, **32**, 529-536.

9. Jäder, J., Järnström, L. and Engström, G. (2003),"The Immobilization Cell Revisited: Prediction of Dewatering Kinetics and Immobilised Layer Properties for Coating Colours, *Nord. Pulp Pap. Res. J.*, **18**, 382-387.

10. Jäder, J., Engström, G. and Järnström, L. (2003), "An Approach to Rheological Evaluation of Dynamic Water Retention Measurements for Paper Coating Suspensions", Ann. Trans. Nord. Rheol. Soc. **11**, 145-148.

11. Walters, K. (1992), "Recent Developments in Rheometry", *Proc. XIth Int. Congr. on Rheology*, 16-23.

12. Wikström, K. and Bohlin, L. (1999), "Extensional flow studies of wheat flour dough. I. Experimental method for measurements in contraction flow geometry and application to flours varying in breadmaking performance", *J. Cereal Sci.*, **29**, 217-226.

13. Petrie, C.J.S. (1995), "Extensional Flow – A Mathematical Perspective", *Rheol. Acta*, **34**, 12-26.

14. Tirtaatmadja, V. and Sridhar, T. (1993),

"A Filament Stretching Device for Measurement of Extensional Viscosity, *J. Rheol.*, **37**, 1081-1102.

15. McKinley, G.H. and Sridhar, T. (2002) "Filament-stretching rheometry of complex fluids", *Annu. Rev. Fluid Mech.*, **34**, 375-415.