

The Influence of Extensional Properties on the Dewatering of Coating Colours

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The influence of the extensional viscosity on the dewatering rate was investigated on three coating colours, containing various water-soluble thickeners (carboxymethyl cellulose (CMC), an alkali-swellable thickener (ASE) and polyvinyl alcohol (PVA)), that had earlier shown significant differences in dewatering. Measurements were performed on aqueous solutions of the thickeners and on the complete coating colour systems. Even at the elevated concentrations investigated, the PVA solutions did behave almost Newtonian in shear as well as in extension, with extensional viscosities well below those of the CMC and ASE solutions. None of the three thickeners studied showed any strain-hardening effects. There was no indication of any contribution of extensional flow resistance during dewatering. It is concluded that the substantially slower dewatering of the PVA-based coating colour, compared to those containing CMC or ASE, is not due to an increased extensional viscosity of the aqueous phase but is due to other factors.

L'influence de la viscosité élongationnelle sur le taux de déshydratation a fait l'objet de recherches axées sur trois sauces de couchage contenant divers épaississants solubles dans l'eau (du carboxyméthylcellulose (CMC), un épaississant dilatable aux alcalis (ASE) et de l'alcool polyvinylique (PVA)) et qui s'étaient révélées très différentes sur le plan de la déshydratation. Des mesures ont été prises à partir de solutions aqueuses des épaississants et de systèmes complets de sauces de couchage. Même aux concentrations élevées étudiées, les solutions de PVA se sont comportées de façon presque newtonienne en cisaillement comme en extension, et leurs viscosités élongationnelles ont atteint des niveaux bien inférieurs à ceux des solutions de CMC et de ASE. Aucun des trois épaississants étudiés n'a présenté d'effets de rhéo-durcissement. Aucun apport de résistance à l'écoulement élongationnel n'a été relevé pendant la déshydratation. En conclusion, la déshydratation substantiellement plus lente de la sauce de couchage au PVA, comparativement à celle qui contient du CMC ou de l'ASE, ne résulte pas d'une viscosité élongationnelle accrue de la phase aqueuse, mais bien d'autres facteurs.

INTRODUCTION

The importance of extensional viscosity for the coating process has long been suspected [1–3]. Indeed, there are several stages in the process where an extensional flow could occur

and be important, and even dominate over the shearing flow: film splitting in a metered size press; passage of the coating colour under the metering blade or rod; and the application of coating colour using jet flow, curtain coating or spray techniques [4,5].

Results presented by Carreau and Lavoie [4] showed no significant extensional contribution to the rheological behaviour of kaolin-based coating colours. This is in contrast to the reasoning of Schurz [1], which was presented before the launch of the first extensional rheometer suitable for dispersions. Schurz argued that the extensional viscosity of a dispersion is three times the shear viscosity only at deformation rates very close to zero. Increase of the deformation rate leads to an increase in the extensional viscosity up to a maximum, followed by a strain-thinning region. The shear viscosity, on the other hand, is monotonously decreasing. James et al. [6] performed measurements on coating colours using a filament stretching device, and they found a correlation between the extensional properties (fluid elasticity) and the degree of misting in a film coater.

No such correlation was found for the rheological properties under shear. Increasing elasticity of a fluid led to an increasing degree of misting for the coating formulations investigated.

The possible role of extensional viscosity in the dewatering of coating colours after application is clear when the immobilized layer formed at the interface between the base paper and the freely flowing coating colour is considered. This layer acts as a filter cake slowing down the rate of dewatering and, in this dewatering process, the flow properties, due to both shear and extension, of the aqueous phase of the coating colour are important.

Approaches where the extensional effects are included in the discussion of the filtration of particles suspended in viscoelastic polymeric solutions have been presented by Kozicki and Kuang [7] and by Hwang and Chen [8]. In the former, the contribution to the pressure drop over a filter cake from elongational flow is evaluated. Their analysis is based on an extensive mathematical model. The latter takes its theoretical starting point from [4] and uses a similar constant pressure-filtration system for

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the filtration experiments. In [5], it is concluded that a higher extensional viscosity of the filtrate would lead to a denser filter cake with a higher filtration resistance. However, neither of these methods has been applied to coating colour dewatering.

In previous publications [9,10], we have reported on the dewatering behaviour of three coating colours, which differed with respect to the thickener (co-binder) used. The thickeners were carboxymethyl cellulose (CMC), a polyacrylate-based alkali-swelling emulsion (ASE) and polyvinyl alcohol (PVA). In the studies cited, PVA has shown a much slower dewatering than the other two coating colours. The explanation suggested has been that a denser filter cake is formed at the interface between the wet coating colour and the base paper when the coating colour contains PVA. However, the question has also been raised whether a higher extensional viscosity of the PVA-containing coating colour may contribute to the slow dewatering of this system. Experiments carried out by Kurath [11] have indicated that PVA solutions do have a significant extensional viscosity. However, the results cited for PVA were not compared to results for other coating colour thickeners. If a higher extensional viscosity does exist for the aqueous phase of the PVA coating colour, this would promote the formation of a denser filter cake, according to Hwang and Chen [8].

The object of the present work was to confirm or reject the hypothesis that a higher extensional viscosity may be the reason for the slower dewatering observed with the PVA-containing colour. In this paper, we present the results of measurements on coating colours and on aqueous solutions of the thickeners utilized. These measurements were performed using two techniques: converging-channel flow and filament stretching.

However, it should be kept in mind that the criteria formulated by James and Walters [12] for a steady-state value of the extensional viscosity cannot usually be met by any instrument available today. Thus, the values obtained should be regarded as transient values rather than steady-state extensional viscosity data. Figure 2.1 in [12] illustrates the enormous differences in the results obtained with different measurement techniques, even with such well-defined fluids as the M1. Thus, an agreement in the values obtained using different measurement techniques is not to be expected for complex fluids such as coating colours or even shear-thinning viscoelastic thickener solutions. Nevertheless, we will try to correlate the information extracted about extensional flow resistance of coating colours and thickener solutions with the dewatering properties of these formulations. The thickener solutions are treated here as model systems for the aqueous phase of the corresponding coating formulations. To get measurable effects in extensional flow experiments, thickener solutions have been investigated at polymer concentrations about an order of magnitude above those present in typical coating formulations.

TABLE I
FORMULATIONS OF THE THREE COATING COLOURS

Coating colour	CMC	ASE	PVA
GCC, pph	70	70	70
Kaolin, pph	30	30	30
S-B latex, pph	11	11	11
CMC, pph	0.7		
ASE, pph		0.35	
PVA, pph			1.4
Thickener conc. in aqueous solutions, % by wt	7.6; 8.5; <u>9.3</u>	3.2; <u>5.9</u> ; 8.0	10.7; <u>12.2</u> ; 13.5; 14.7
σ , mN m ⁻¹	70.7 ± 0.9	35.4 ± 1.4	61.7 ± 0.6
R , 10 ¹³ m ⁻²	8.27 ± 0.43	18.7 ± 1.1	60.9 ± 9.9

pph = parts per hundred.

S-B = styrene-butadiene.

The theoretical thickener concentrations, the thickener concentrations in the aqueous solutions investigated and the specific resistance to filtration for the filter cakes are also given.

The concentration of the measured solution is underlined.

TABLE II
CALCULATED AND MEASURED CONCENTRATIONS OF THE SYNTHETIC AQUEOUS PHASES

Thickening polymer	CMC	ASE	PVA
Theoretical thicken. conc., % by wt	1.1	0.57	2.3
Concentration, % by wt	1.2	0.24; 0.77	2.3

MATERIALS

The formulations of the coating colours and of the aqueous solutions investigated are summarized in Table I.

The ground calcium carbonate (GCC) was Hydrocarb 90 (Omya AG, Oftringen, Switzerland), the kaolin Century (Kaolin International B.V., Woerden, The Netherlands), the styrene-butadiene latex DL 950 (Dow Europe S.A., Freienbach, Switzerland), the CMC Finnfix 30 (Noviant Oy, Äänekoski, Finland), the ASE Sterocoll HT (BASF AG, Ludwigshafen, Germany) and the PVA Mowiol 20-98 (Kuraray Specialties GmbH, Düsseldorf, Germany). For all the coating colours, the solids content was adjusted to 64.5 ± 0.1% and the pH to 8.5 by the addition of NaOH.

The coating colours are denoted with the abbreviation for the thickener used. All coating colours and thickener solutions were measured without extra addition of salt.

As outlined previously [10], the amounts of thickener in the coating colours were chosen to give approximately the same Brookfield viscosities and to have coating colours with an acceptable runnability at the chosen solids content. For PVA, however, a lower Brookfield viscosity was needed to have sufficient control of the coat weight

when performing pilot coater trials.

For each thickener, one of the aqueous solutions was measured with respect to surface tension (σ) using the pendant drop method. This value was assumed to be constant for all concentrations of the thickener. The concentration of the measured solution is underlined in Table I, where the surface tension values are also given. The values for the specific resistance to filtration of the filter cakes (R) are given for the three coating colours, from [10].

METHODS Shear Rheology

To account for the possibility of an elevated shear viscosity being the reason for the slow dewatering of PVA, theoretical concentrations of the thickening polymer in the aqueous phases were calculated. These calculations were performed assuming no adsorption of the thickener onto the pigment or latex surfaces, and the values are given in Table II. From these

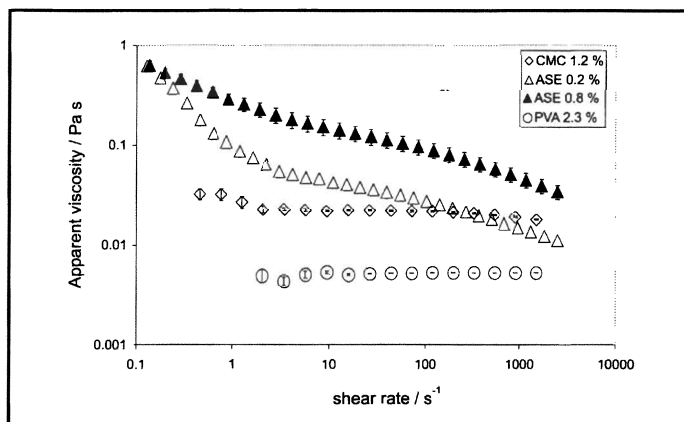


Fig. 1. Shear viscosity of the synthetic aqueous phases.

results, synthetic aqueous phases were prepared, the target concentrations of which were the theoretical concentrations. The actual concentration values obtained are given in Table II.

The shear viscosities of these phases were measured using a stress-control MCR 300 (Physica Messtechnik GmbH, Ostfildern, Germany). The shear viscosity curves are given in Fig. 1. However improbable the assumption of no adsorption may be, the viscosities of these solutions serve as upper limits. Due to difficulties in reaching the exact concentration (0.57% by wt) in the case of ASE, two concentrations were examined. For both of these, the shear viscosity was higher than for PVA in the shear rate range investigated.

For the coating colours used in the converging-channel flow experiments, shear flow curves were obtained using a strain-control Bohlin VOR (Bohlin Instrument Ltd., Malvern, UK). These curves were fitted to a power law relationship (Eq. 1):

$$\tau = K\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, $\dot{\gamma}$ the shear rate and K and n the constants of the power law relationship (see Table III).

The coating colours and the aqueous thickener solutions investigated in the extensional flow experiments were rheologically characterized in shear flow using an MCR 300. The shear rheology data showed satisfactory correlation between the two instruments. The viscosity curves are presented as log-log diagrams in Fig. 2.

Figure 2 shows clearly that the solutions of CMC or ASE (Figs. 2A,B) have significantly higher low-shear viscosities and that they are significantly more shear-thinning than solutions of PVA (Fig. 2C). The polymer concentrations are chosen such that the high-shear viscosity for the three types of thickener is ~ 1000 mPa·s at $\dot{\gamma} = 1000$ s⁻¹. It is commonly accepted that, at these higher shear rates, the apparent viscosity does not reflect any of the chemical interactions within the coating colour. Instead, it reflects merely the continuous-phase viscosity. All three coating colours are shear-thinning in the shear-rate region investigated (Fig. 2D). At lower shear rates, CMC and ASE

have considerably higher apparent viscosities than PVA.

In Table IV, results are presented from the oscillatory shear measurements. These results include the storage and loss moduli at an angular frequency (ω) of 10 s⁻¹ in the linear viscoelastic region ($G'_{LVR}(10)$ and $G''_{LVR}(10)$,

respectively); the critical strain, i.e. the upper limit of the linear viscoelastic region (γ_C); as well as the storage ($G'_{LVR}(\omega)$) and loss ($G''_{LVR}(\omega)$) moduli at angular frequencies of 0.0185 (low) and 36.1 s⁻¹ (high), respectively for the polymer solutions. For the coating colours, $G'_{LVR}(\omega)$ and $G''_{LVR}(\omega)$ are given at

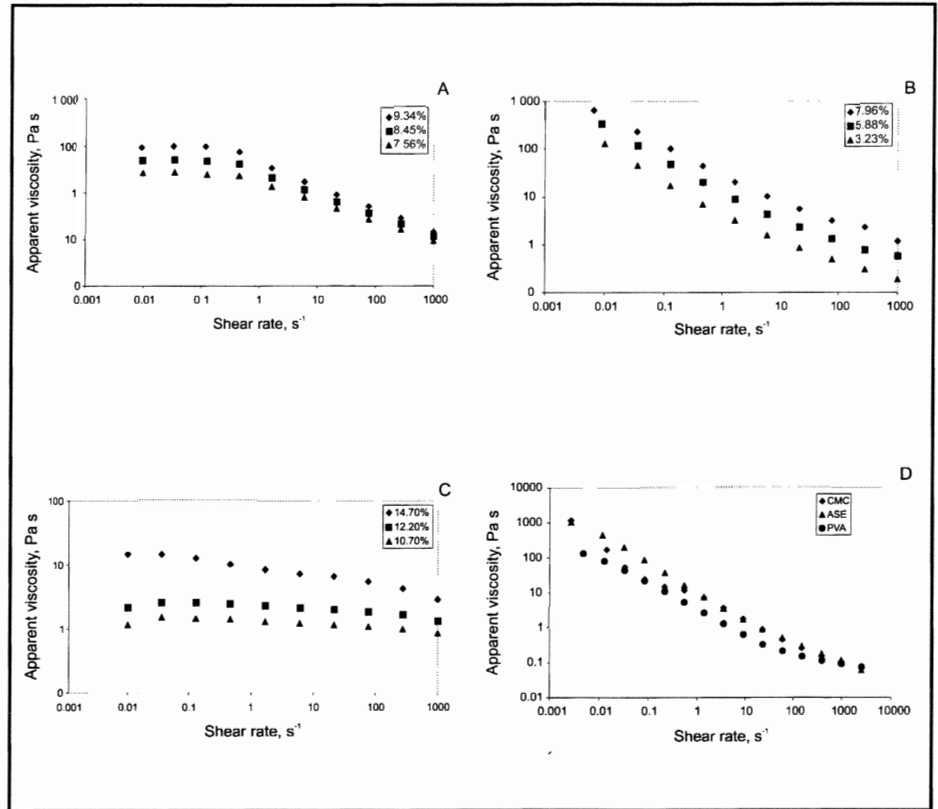


Fig. 2. Viscosity curves of aqueous solutions of (A) CMC, (B) ASE, (C) PVA and (D) of the coating colours used in the filament-stretching measurements. The measurements were performed at 23°C.

TABLE III
CONSTANTS OF THE POWER LAW RELATIONSHIP
(K AND n IN EQ. 1)

Coating colour	CMC	ASE	PVA
$K, \text{Pa}^{1-n}\text{s}^{-n}$	9.8	25.5	5.0
n	0.28	0.23	0.29

TABLE IV
OSCILLATORY SHEAR CHARACTERIZATION

	$G'_{LVR}(10),$ Pa	$G''_{LVR}(10),$ Pa	$\gamma_C,$ Pa	$G'(low),$ Pa	$G'(high),$ Pa	$G''(low),$ Pa	$G''(high),$ Pa
CMC colour	520	91.8	0.267	424	725	68.9	211
CMC 9.34%	42.7	78.0	16.4	1.47	107	2.26	187
CMC 8.45%	21.6	45.8	16.4	0.306	57.3	1.05	117
CMC 7.56%	14.4	33.1	16.4	8.86×10^{-2}	39.4	0.680	86.5
ASE colour	255	30.5	0.267	226	304	30.5	101
ASE 7.96%	108	52.7	3.16	35.3	150	12.0	103
ASE 5.88%	60.9	25.0	3.16	2.86	74.9	6.99	50.1
ASE 3.23%	25.4	10.8	3.16	12.5	35.3	3.76	21.2
PVA colour	30.9	6.54	1.39	33.9	50.3	4.53	44.5
PVA 14.7%	20.4	78.8	37.3	9.60×10^{-3}	57.7	0.966	233
PVA 12.2%	2.62	23.9	37.3	1.51×10^{-7}	9.60	0.162	79
PVA 10.7%	1.03	13.3	37.3	7.58×10^{-8}	3.46	8.17×10^{-2}	44.8

0.213 (low) and 289 s⁻¹ (high), respectively. In brief, all coating colours are predominantly elastic, whereas the aqueous suspensions are predominantly viscous.

Extensional Flow Experiments Converging Channel Flow

The measuring cell of the converging-channel flow technique, which is shown in Fig. 3, 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, Norwood, MA, USA). The theory of this technique has been thoroughly reviewed previously [5,13,14].

During measurement, the piston is allowed to move downwards at a preset speed. For a fluid obeying a power law relationship, the strain rate ($\dot{\epsilon}$) is given by:

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

where Q is the volume flow rate. The geometrical parameters r_1 , r_0 and H are defined in Fig. 3 and n is an integer.

The normal stress difference is calculated from the force (F_t) with which the piston is pressed down:

$$\tau_{zz} - \tau_{rr} = \frac{F_t}{\pi r_0^2} = \tau_E \quad (3)$$

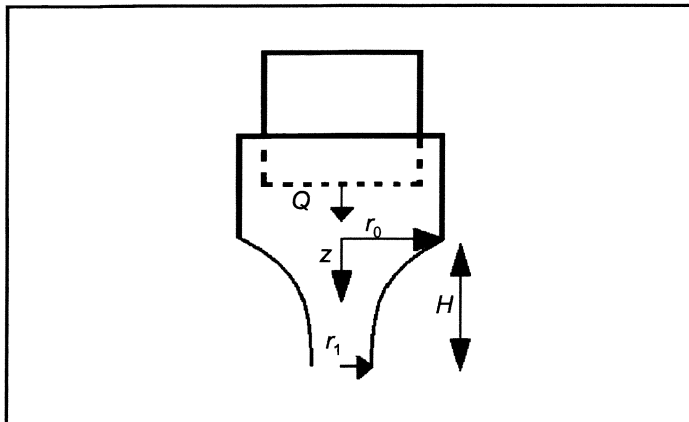


Fig. 3. Side view of the converging-channel flow measurement cell.

Finally, 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.

$$\overline{\eta_E} = \frac{(\tau_{zz} - \tau_{rr})}{\dot{\epsilon}} \quad (4)$$

assuming that the shear contribution is negligible.

The contribution of the shear (P_{shear}) to the total pressure drop (P_{TOT}) over the die, and thereby also the magnitude of the error introduced by neglecting the shear forces, may be calculated as:

$$P_{shear} = \frac{4H(3+1/n)^n (K/\pi)^n Q^n (1/r_0^{3n+1})}{3n+3} \times \frac{(r_0^2/r_1^2)^{(3n+3)/2} - 1}{(r_0^2/r_1^2) - 1} \quad (5)$$

The value of P_{shear} is affected strongly by the value of the power law exponent (n). A low value of n , i.e. a highly shear-thinning fluid, gives a low value of P_{shear} . Thus, the converging-channel flow method is not suitable for Newtonian fluids for which $n = 1$ or for nearly

Newtonian fluids. For the coating colours investigated in this work, the values of n were sufficiently low to assure shear contributions to the total pressure drop of the order of 5%.

Capillary Break-Up Extensional Rheometry (CaBER)

Filament stretching is the technique for extensional viscosity measurements that has gained the most attention in recent years [13,15,16]. The device used in this work is the Haake CaBER 1 (Thermo Electron GmbH, Karlsruhe, Germany)

In the filament-stretching rheometer, a volume of sample is placed between two rigid plates (Fig. 4). When 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 Sridhar [17]. 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 (D_0) to the diameter at time t (D_t):

$$\epsilon = 2 \ln \left[\frac{D_0}{D_t} \right] \quad (6)$$

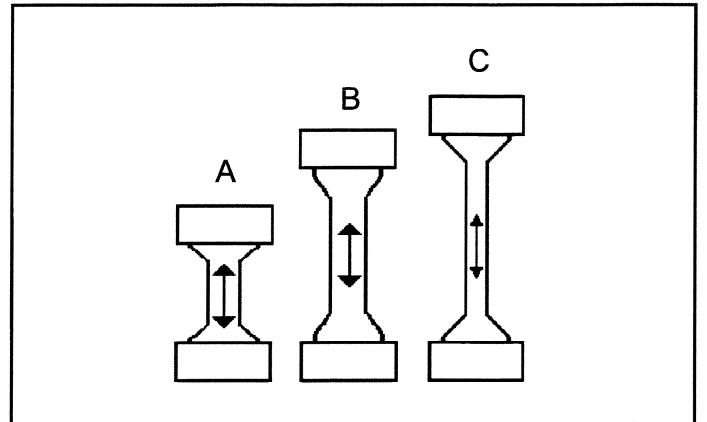


Fig. 4. Idealized view of stretching of a fluid filament (A)–(C). The length of the filament is held constant with time after (C), but the diameter continues to decrease until the filament ruptures.

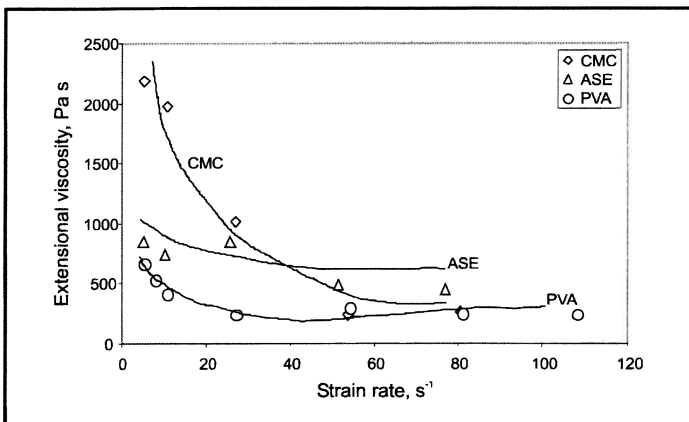


Fig. 5. Results from the converging-channel flow measurements of the coating colours containing CMC (◆), ASE (▲) and PVA (●).

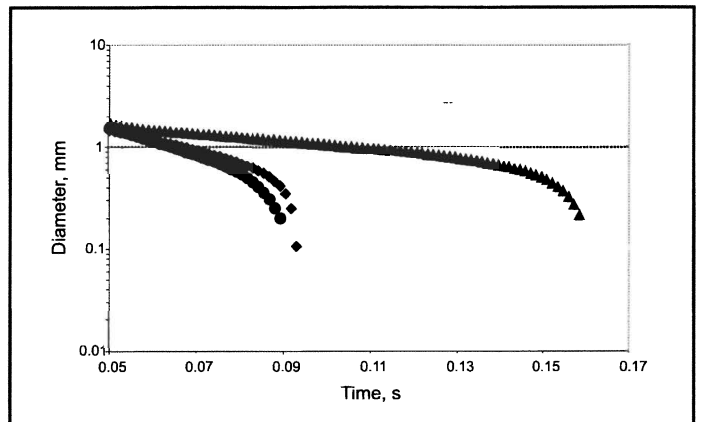


Fig. 6. Filament diameter as a function of time for coating colours containing CMC (◆), ASE (▲) and PVA (●).

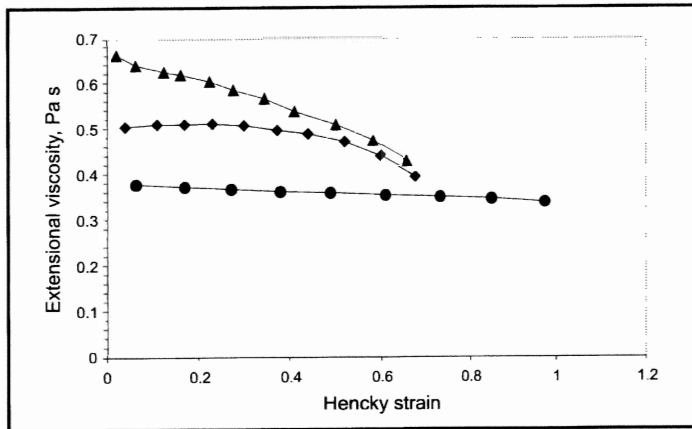


Fig. 7. Results from filament-stretching measurements of the coating colours containing CMC (◆), ASE (▲) and PVA (●). Extensional viscosity is plotted as a function of Hencky strain.

In the present work, D_0 has been set to 1 mm. At diameters equal to or below 1 mm, surface tension dominates the necking process of the filament and gravitational effects may be neglected.

The transient extensional viscosity is given by:

$$\eta_E = \frac{2\sigma / D_t}{\left(\frac{-2 dD_t}{D_t dt}\right)} = \frac{-\sigma}{dt} \quad (7)$$

where σ is the surface tension of the fluid.

RESULTS

In both techniques applied, the strain and strain rate ranges that are investigated are limited by the geometry and performance of the instruments utilized. Extending the strain ranges led to significant reductions in the reproducibility of the results.

The results from converging-channel flow measurements on the three coating colours are shown in Fig. 5. Here, all three coating colours show a strain-thinning behaviour, with the slope of the CMC curve being steeper than those for ASE and PVA. The values for the transient extensional viscosity seem to level off with increasing strain rate and to reach a plateau value, particularly for ASE and PVA. The plateau value is higher for ASE than for CMC and PVA.

The decrease in filament radius with time in the filament-stretching experiments on the coating colours is shown in Fig. 6.

Only diameter values below 1 mm are used in the calculation of extensional viscosity shown in Fig. 7. This exclusion is introduced to fulfil the requirement of Kolte and Szabo [18], who state that the effects of gravity on the filament diameter are negligible only at Bond numbers well below 1, the Bond number (B_o) being given by:

$$B_o = \frac{\rho g R^2}{\sigma} \quad (8)$$

where ρ is the density of the fluid investigated and R the radius of the filament. A broken line in Fig. 6 indicates the 1 mm diameter limit.

The simplicity of the expression for the Hencky strain, ϵ (Eq. 6), with only two directly

measured parameters, makes it convenient to show the extensional viscosity as a function of ϵ in Fig. 7. In this figure, all three coating colours show a decreasing extensional viscosity with increasing strain. However, the slopes are much steeper for CMC and ASE than for PVA. In the Hencky strain range covered, PVA has the lowest extensional viscosity. However, it should be kept in mind that the strain rate is not constant throughout the filament-stretching experiment. The variations in strain rate for the results shown in Fig. 7 are 50–90 s^{-1} (CMC); 40–80 s^{-1} (ASE) and 70–120 s^{-1} (PVA).

In the results from the filament-stretching measurements on thickener solutions (Fig. 8), PVA was shown again to have the lowest extensional viscosity. For all the polymers, the extensional viscosity decreased with decreasing concentration.

The CMC solutions show the highest extensional viscosities. In addition, it is evident that the CMC and PVA solutions have an almost Newtonian behaviour whereas the ASE solutions exhibit an apparent strain-thinning behaviour, which is due to the increasing strain rate. For the PVA solutions, Trouton ratios (T_r), i.e. the ratio of the extensional viscosity to the shear viscosity, of ~ 3 were achieved. This is the behaviour expected of Newtonian fluids.

DISCUSSION

In the pilot coatings, the same coat weight was applied for all coating colours. The

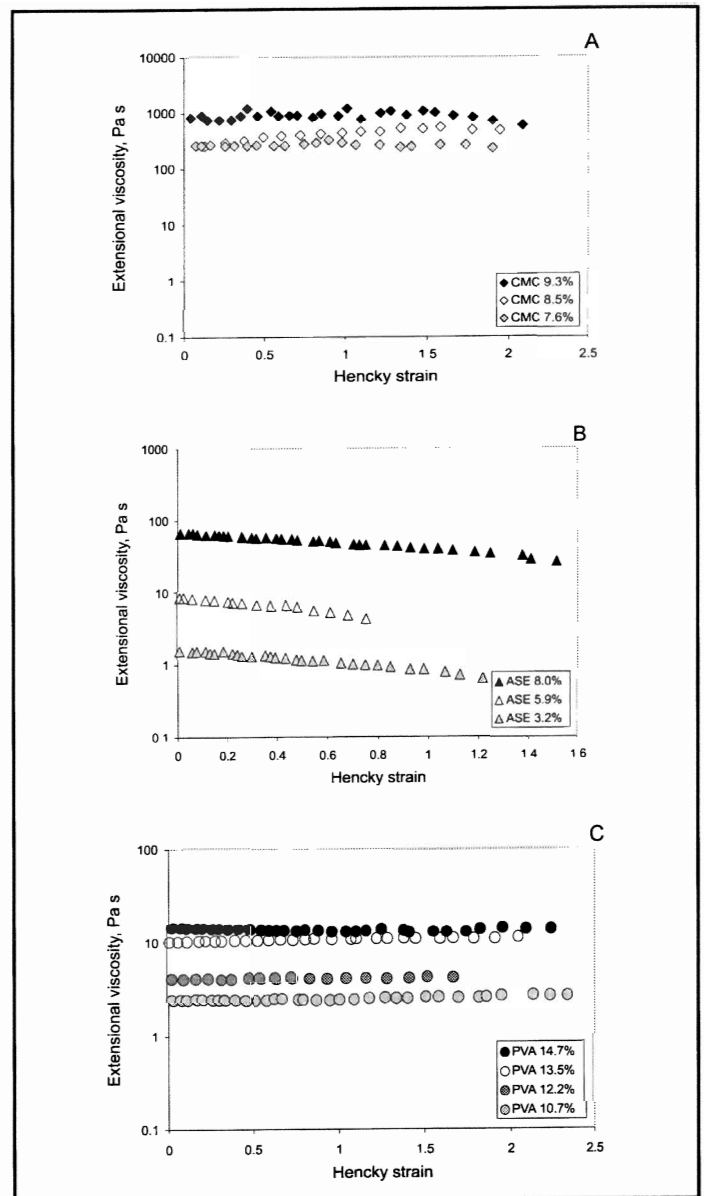


Fig. 8. Filament-stretching results on solutions of (A) CMC, (B) ASE and (C) PVA. The extensional viscosity is plotted as a function of the Hencky strain.

PVA coating colour showed a tendency to cause web breaks at elevated machine speeds. Therefore, the amount of PVA in the coating colour had to be kept at a level yielding Brookfield viscosities lower than those of the CMC and ASE coating colours.

Although the results from the two techniques are not directly comparable, the trends may be evaluated and they give useful information regarding the extensional flow behaviour of paper coating colours.

The results presented in Figs. 5 and 7, with the transient apparent extensional viscosities of coating colours, would be of particular interest when considering the film split in a metered size press [6] or during the application of the coating colour using spray [19] or curtain [20] coating. Similarly, during the dewatering of the coating colour on paper, the flow properties of the aqueous phase of the coating colour are expected to determine the kinetics. The dewatering rate of coating colours similar to

those used here was studied under pilot coater and laboratory conditions by Jäder et al. [9,10]. All the measurements showed a significantly slower dewatering for PVA than for CMC and ASE. In Table IV, the results of the laboratory measurements are summarized in terms of the $dV/d\sqrt{t}$ ratio, where a higher value corresponds to a more rapid dewatering.

Since the aqueous phase consists mainly of the dissolved thickener, it is of interest to compare and discuss the results obtained with the thickener solutions. These solutions were investigated at considerably higher concentrations of thickener than the actual aqueous phases of the coating colours (Table V). This is necessary to get measurable effects with the extensional rheometry techniques used here.

It should be kept in mind that, due to adsorption onto the other constituents of the coating colour, the actual thickener concentrations of the aqueous phases may be significantly lower than those given in Table II. Nevertheless, general trends may be discussed and compared qualitatively to the dewatering results.

The filament-stretching results imply that the slow dewatering of PVA is not due to an elevated extensional viscosity. Instead, PVA showed an extensional viscosity lower than or similar to that of CMC and ASE. For all of the solutions investigated, no signs of increasing extensional viscosity with increasing Hencky strain were observed. This lack of strain hardening is unexpected for polymeric systems, but may be explained by the limited strain range investigated. It is likely that an increase of extensional viscosity would have been detected if higher Hencky strains had been possible to reach.

There is a slight difference in the extensional flow behaviour between the solutions of CMC and PVA, on the one hand, and the ASE solutions on the other, with ASE showing a strain-thinning behaviour and significantly lower maximum Hencky strain than the other two, which are almost Newtonian. Nevertheless, the PVA solutions show by far the lowest extensional viscosity. According to the suppliers, the CMC, the ASE and the PVA have average molecular weights of ~85 000, 10^6 and 125 000 g mol^{-1} , respectively. Thus, the lower extensional viscosity of the PVA solutions may not be explained in terms of the molecular weight. However, the CMC molecule is significantly stiffer than the PVA, due to its constituents. This may explain the differences between CMC and PVA.

Another possible explanation for the differences in extensional viscosity is the existence of differences in the configuration of the polymers in solution. Repulsive interactions originating from electrostatic forces between charged groups lead to expansion of flexible polyelectrolyte molecules. Uniaxial extension of an entangled chain in solution involves the stretching out of entanglements followed by the stretching of polymer chains, the latter of which gives a higher extensional viscosity value [18]. Thus, a more compact polymer configuration may lead to a lower extensional viscosity. To investigate this further, the specific charges of the

TABLE V
PROPERTIES OF THICKENERS

Coating colour	CMC	ASE	PVA
$dV/d\sqrt{t} \cdot 10^9, \text{m}^3 \cdot \text{s}^{-0.5}$	48.5 ± 0.3	55.4 ± 4.4	40.2 ± 0.7
Theoretical thick. conc.	0.22	0.11	0.38
Thick. conc.	7.6; 8.5; 9.3	3.2; 5.9; 8.0	10.7; 12.2; 13.5; 14.7

Dewatering rate ($dV/d\sqrt{t}$ ratio); theoretical thickener concentration in the aqueous phases of the coating colours assuming no adsorption; and concentrations in the pure thickener solutions (Fig. 8). The concentrations are given as % by weight.

TABLE VI
SPECIFIC CHARGE DATA OF THE POLYMER SOLUTIONS

Polymer	CMC	ASE	PVA
Specific charge, eq g^{-1}	$(3.93 \pm 0.154)10^{-3}$	$(5.912 \pm 0.0484)10^{-3}$	$(8.46 \pm 0.281)10^{-6}$

three polymer systems were measured using neutralization titration (Mütek Titrator PCD-Two, Mütek Analytic GmbH, Herrsching, Germany). The results of these measurements are summarized in Table VI.

It is clear from Table VI that PVA has by far the lowest charge density when no extra salt has been added. Thus, a more compact polymer configuration can explain the lower transient extensional viscosity for PVA in the aqueous solutions. However, in a real coating colour containing CaCO_3 and dispersants, ions of various valences lead to a high ionic strength and, also, the CMC and ASE attain more compact configurations. Thus, the results in Table VI should be considered merely as indications of the degree of extension of the polymers in the coating colours. To summarize, the higher stiffness of the CMC molecule and the higher molecular weight of ASE explain, together with Table VI, their higher viscosity compared to PVA.

Thus, the hypothesis that the slower dewatering of the PVA system is due to a denser filter cake caused by a higher extensional viscosity is not supported by our results. An indication of the porosities of the filter cakes is given by the values of R (Table I).

CONCLUSIONS

Measurements on three coating colours as well as on aqueous solutions of their thickeners were performed using converging-channel flow and filament stretching. The trend was similar in all the measurements, with PVA having a lower transient extensional viscosity than CMC and ASE. Solutions of ASE showed a strain-thinning behaviour, whereas the solutions of CMC and PVA were Newtonian or nearly Newtonian.

A possible reason for the lower extensional viscosity of the PVA solutions is a more compact configuration of the polymer in solution. This is due to both a lower degree of electrostatic repulsion between charged polymer segments for PVA compared to CMC and to a lower molecular weight of PVA compared to ASE.

The low dewatering rate of the PVA-containing coating colour cannot be explained in terms of either shear or extensional viscosity.

Instead, a denser filter cake being formed with PVA at the interface between the base paper and the wet coating colour is a more probable cause. 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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