

Measurement and control of extensional viscosity in barrier coating dispersions

WATTI LEHTIMÄKI, ANDREAS SCHRÖDER, VESA KUKKAMO,
AND MARTTI TOIVAKKA

ABSTRACT: This study aimed to understand the effect of various rheological additives on the extensional viscosity of barrier coating dispersions, as well as to understand the role extensional viscosity plays in stabilizing a liquid curtain. The apparent extensional viscosity was measured using two devices that create accelerating flows: a capillary viscometer and an orifice rheometer. Additives tested include several polyvinyl alcohols, a high molecular weight polyethylene oxide, and carboxymethylcellulose. Extensional viscosity plays a significant role in stabilizing a liquid curtain, as it slows down hole expansion and prevents impurities and disturbances from causing holes in the first place. Some of the additives could substantially increase the extensional viscosity of the dispersions without increasing the shear viscosity outside the typical range of processability for a curtain coater. Some of the additives exhibited coil-stretch transition, meaning they start increasing extensional viscosity above a certain extension rate. Polymers with low chain lengths exhibited finite extensibility, which indicates the polymer chain has fully extended and cannot provide further extensional viscosity, even though the extending force is increased. Polymeric additives with stiff or branched chains significantly raised shear viscosity without increasing extensional viscosity. Both methods could reliably measure extensional viscosity in curtain coating barrier dispersions.

Application: Extensional viscosity can be used to improve the operating window of a curtain coater and reduce reliance on surfactants. This study compares different viscoelastic additives and discusses two methods of measuring extensional viscosity.

Curtain coating has been found to be a suitable technique to apply barrier coating dispersions on paper and paperboard. Both dynamic surface tension and extensional viscosity of the coating material are important physico-chemical properties that contribute to the operational window and runnability of a curtain coater. Insufficient curtain stability can result in serious product quality problems, such as uncoated areas from holes, and in the worst case, a curtain breakup and production stoppage. The Weber number, given in Eq. 1, is commonly used to predict the stability of a liquid curtain. It compares the momentum flux pushing a hole towards the paper web with the surface tension force expanding the hole:

$$We = \frac{\rho Q_c V_c}{2\sigma} \quad (1)$$

where ρ is fluid density, Q is flow rate per unit width, V is curtain velocity, and σ is surface tension.

A curtain is considered stable if the Weber number is larger than 1, i.e., a hole in the curtain reaches the paper web before it expands to the die, breaking up the curtain. Typically, curtain stability is increased by lowering the dynamic surface tension of the coating material. However, while numerous fast acting surface-active agents are available, their use is often limited by their potential migration in the final coated product, which creates challenges to fulfill the food-contact regulation requirements.

An alternative way to increase the curtain stability is to manipulate the viscosity of the coating material. During a curtain breakup event, extensional viscosity slows down the expansion of a hole that would otherwise eventually break up the curtain, as it resists the two-dimensional flow. Stable curtains at Weber numbers as low as 0.2 have been found using high molecular weight polymer solutions such as polyethylene oxide [1]. Extensional viscosity induces elastic stress into the curtain, hindering perturbations from causing holes in the first place and thereby improving the runnability of the coater and the quality of the final product [2]. The extensional viscosity of the curtain can also help mitigate coating defects, such as microskip, arising from the impingement with the paper web, where the coating color can be stretched up to twentyfold in a few microseconds [3].

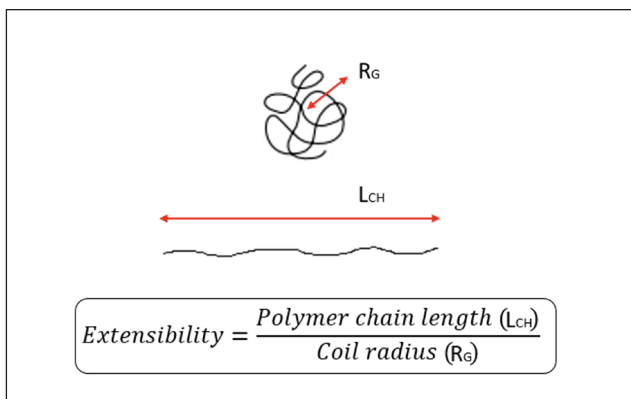
The behaviors of dilute polymer solutions can be described using the finitely extensible nonlinear elastic dumbbell with Peterlin approximation (FENE-P) model. The FENE-P model is derived from the kinetic theory of dilute polymer solution [4]. It simplifies a polymer chain to an elastic dumbbell consisting of two beads linked by one spring. Polymers in dilute solutions form entangled Gaussian coils that can be extended by the liquid flow. The extensibility of a polymer describes how much the polymer can stretch from its relaxed coil state to its maximum length. A flexible polymer can fit into a smaller coil and thus flex more when unraveled than a stiff polymer with a looser coil state [5].

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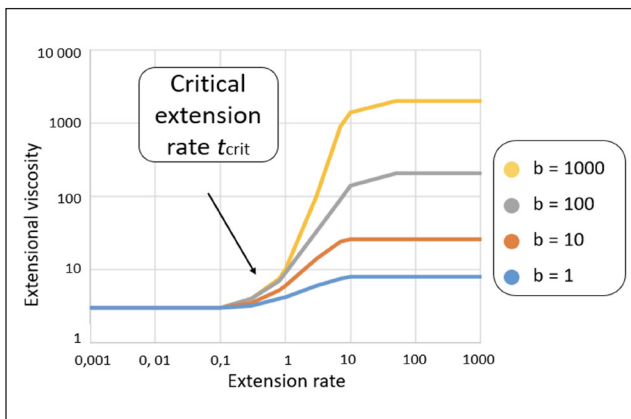
A longer polymer chain also increases extensibility. Previous work [6,7] has revealed that polymers in dilute solutions exhibit a phenomenon called coil-stretch transition. At a specific extension rate, the restoring force of the coil is exceeded, and the polymer starts unraveling. This results in a strong, abrupt increase in the extensional viscosity of the fluid. The transition between the coil and the stretched state is sharp and occurs over a small extensional rate interval. The critical strain rate decreases with increasing molecular weight [6]. Each polymer also has a finite extensibility at its characteristic deformation rate, beyond which no further increase in extensional viscosity is observed.

In general, a maximum increase in extensional viscosity can be expected from high molecular weight linear polymers that form small coils when in their relaxed state. Critical extension rate and finite extensibility are visualized in **Figs. 1–2**. The finite extensibility parameter b has been successfully linked to a FISER-type measurement [8].

The goal of this study was to evaluate and compare the effects of different rheology modifiers on the extensional viscosity of barrier dispersions used in curtain coating. By increasing the stability of the curtain with the help of extensional viscosity, thinner coat weights can be coated, higher machine speeds can be used, and the amount of surfactant used can be lowered.



1. Extending of coiled polymer chains.



2. Critical extension rate and finite extensibility (b is the finite extensibility parameter).

MATERIALS

A styrene-acrylate copolymer-based barrier dispersion provided by CH-Polymers (Espoo, Finland) with a solids content of 50%, mean particle size of 8 μm , and density of 1100 kg/m^3 was used together with polyethylene oxide, carboxymethylcellulose (CMC), and four different grades of polyvinyl alcohol (PVA). The unmodified dispersion had a Brookfield viscosity of 97 mPas. All Brookfield viscosity measurements in this study were measured using spindle no. 3 at 100 rpm. **Table I** lists the properties of the additives used [9].

Additive	Properties
PVA1	Polyvinyl alcohol, 88% hydrolyzed, viscosity in a 4% solution: 95 mPas
PVA2	Polyvinyl alcohol, 98% hydrolyzed, viscosity in a 4% solution: 56 mPas
PVA3	Polyvinyl alcohol, 88% hydrolyzed, viscosity in a 4% solution: 56 mPas
PVA4	Branched polyvinyl alcohol, 88% hydrolyzed, viscosity in a 4% solution: 200 mPas
PEO	Polyethylene oxide, 8 000 000 g/mol
CMC	Carboxymethylcellulose, 450 000 g/mol

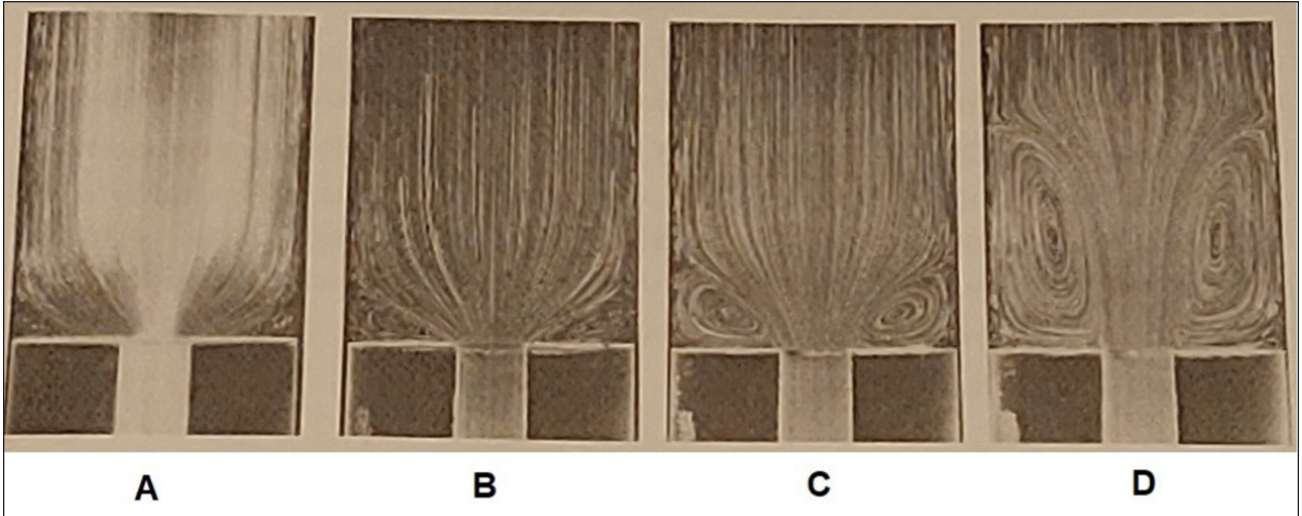
1. Properties of the polymeric additives used and the dispersions made using them.

The PVA pellets were dispersed in reverse osmosis purified water at 25°C to a concentration of 12 wt%, after which the mixture was heated to 90°C–95°C for 40–60 min under constant mixing to create a PVA solution. The polyethylene oxide solution was created using a Silverson L5M-A high-shear mixer (Silverson; Chesham, UK) and adding polyethylene oxide (PEO) powder to reverse osmosis purified water in small amounts every 20 min under high-shear mixing (around 2800 rpm) until a 4 wt% gel-like solution was formed. The CMC was added into reverse osmosis purified water under constant high shear mixing to create a 4 wt% viscous solution. When used, each additive was added to the dispersions under low shear mixing and then mixed at around 200 rpm for 15 min.

METHODS

Eklund capillary viscometer

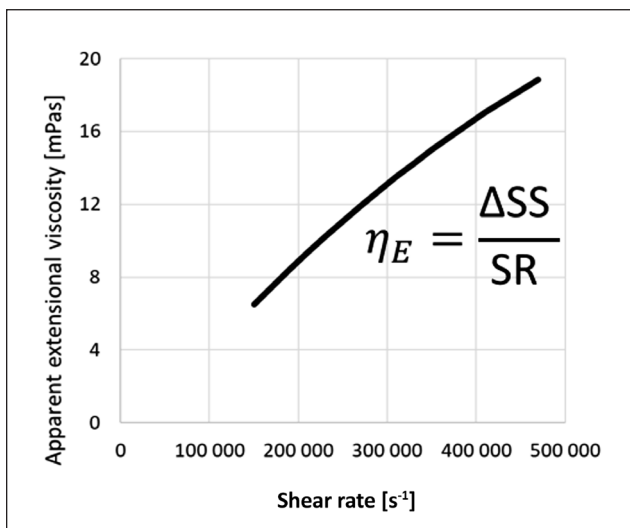
The first method used to measure extensional viscosity in this study was the Eklund capillary viscometer and the method proposed by Kokko [10]. As the fluid enters a capillary, it is both sheared and extended. The stretching of the fluid induces vortices at the capillary entrance, resulting in an excess pressure loss, which is ascribed here to the apparent extensional viscosity of the sample. Although the dispersions used in this study are shear thinning and therefore not Boger fluids, **Fig. 3** created using Boger fluids can be used to describe how the vortices are formed at



3. Vortex enlargement for an elastic Boger fluid at increased flow rates (from A to D) [11].

the capillary entrance. From here on, the term extensional viscosity is used when discussing the measured apparent extensional viscosity. Apparent extensional viscosity is the extensional viscosity that exceeds the Trouton ratio of a Newtonian fluid. The Trouton ratio is the extensional viscosity divided by the shear viscosity. The kinetic energy correction was used to account for the additional pressure drop caused by the acceleration of the fluid when entering a capillary.

The extensional viscosity measurement was performed with capillaries of two different lengths (50 and 100 mm) having the same nominal diameter of 0.51 mm. The extensional viscosity vs. shear rate curves, **Fig. 4**, are plotted based on the shear stress difference between the measurements obtained with the two different capillaries, as shown in **Fig. 5**.



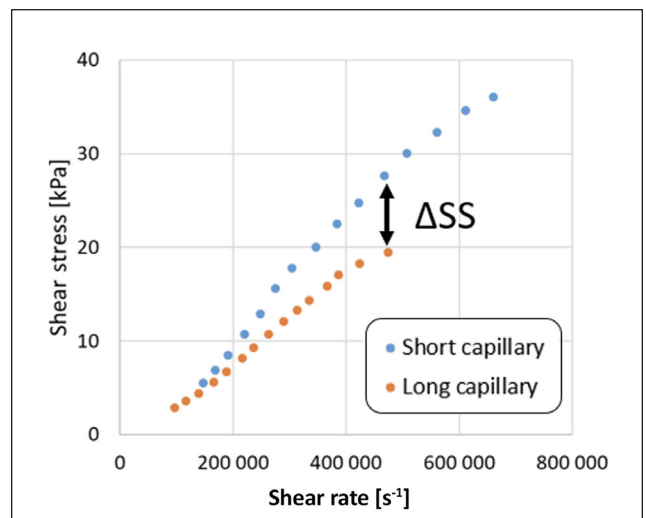
4. The resulting apparent extensional viscosity curve, η_E .

ACA AX-100 orifice rheometer

The second method used to measure extensional viscosity was the ACA AX-100 orifice rheometer (ACA Systems; Sotkuma, Finland) [12]. The orifice rheometer is a special case of a capillary viscometer where a capillary with “zero” length is used. The accelerating flow is created at the entrance of the orifice. The pressure loss is measured and compared to the kinetic energy of the liquid pushed through the capillary. The result of this is the Euler number, which indicates the amount of extensional viscosity exhibited by the liquid [12]. The Euler number is calculated using Eq. 2:

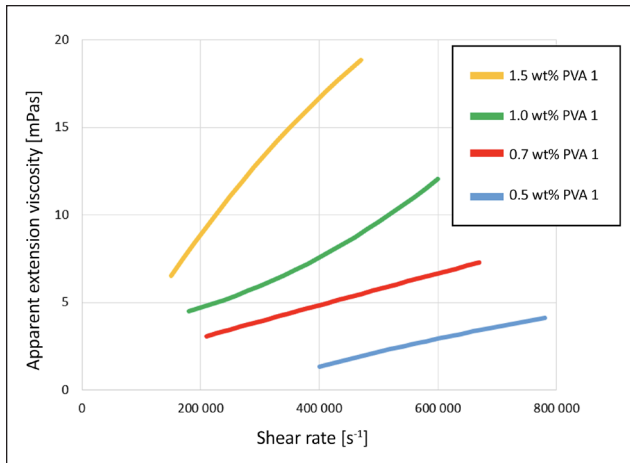
$$Eu = \frac{p}{p_k} = \frac{p}{\frac{1}{2}\rho v^2} = \frac{p}{\frac{1}{2}\rho\left(\frac{Q}{\pi R^2}\right)^2} \quad (2)$$

where p is pressure, v is velocity, Q is flow rate, and R is radius.

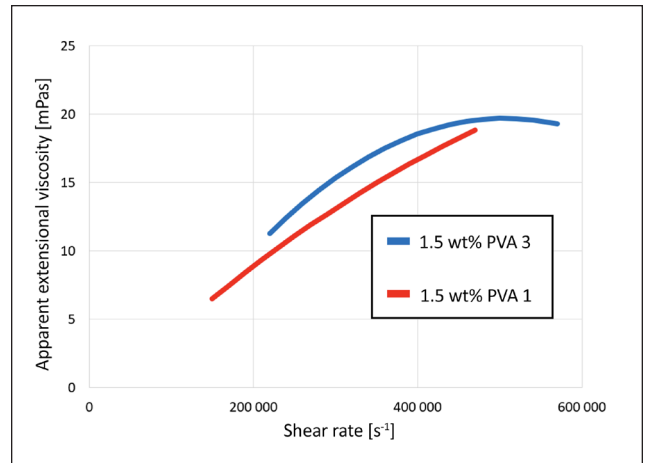


5. Viscosity measurements for two same diameter capillaries with different lengths.

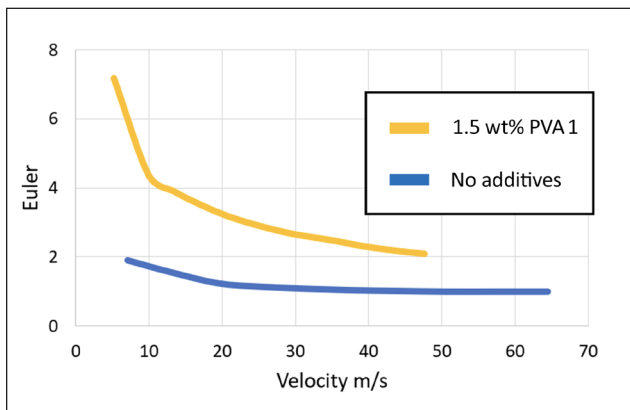
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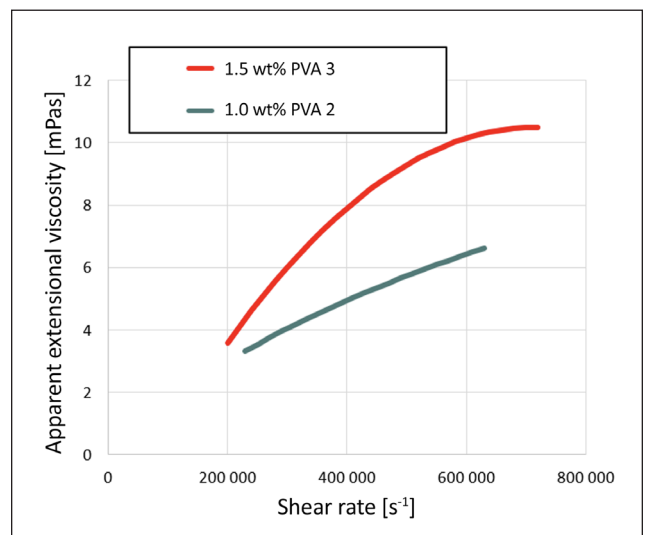
6. Influence of addition level of high molecular weight polyvinyl alcohol (PVA) on the apparent extensional viscosity measured using the Eklund capillary viscometer.



8. Influence of molecular weight of PVA on the apparent extensional viscosity measured using the Eklund capillary viscometer.



7. Influence of addition level of high molecular weight PVA on the apparent extensional viscosity measured using the orifice rheometer.



9. Influence of degree of hydrolysis of PVA on the apparent extensional viscosity measured using the Eklund capillary viscometer.

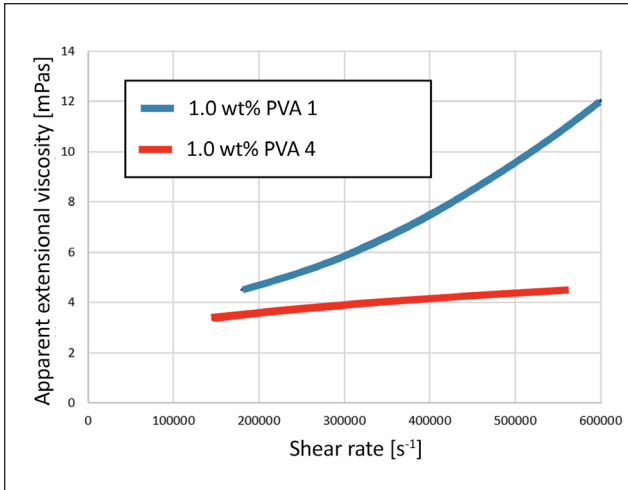
RESULTS AND DISCUSSION

The influence of PVA, PEO, and CMC addition on the extensional viscosity of the barrier dispersion was measured. As shown in **Fig. 6**, the high molecular weight PVA1 increased the extensional viscosity, with a clear addition level dependence. The steepness of the extensional viscosity curves increases with the addition amount, and if extrapolated, the curves seem to converge at around 100 000 s⁻¹, suggesting a start of the coil-stretch transition. None of the samples seem to have reached an extensional viscosity plateau caused by finite extensibility. The maximum amount of PVA that can be used is limited by the maximum shear viscosity tolerated by the coating process being used. In this example, the Brookfield viscosity increased from 300 mPas to 830 mPas when PVA addition level was increased from 0.5 wt% to 1.5 wt%. **Figure 7** shows a clear increase in extensional viscosity with the addition of high molecular weight PVA.

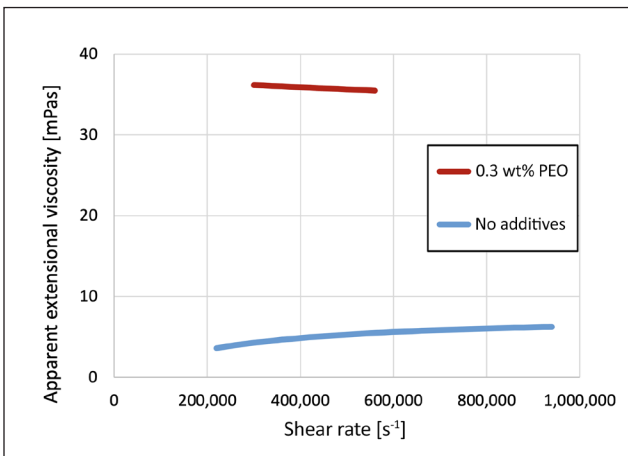
Figure 8 compares two different molecular weight PVA additives. While the influence on the extensional viscosity

is on a similar level for both, the lower molecular weight PVA3 appears reach a plateau at a shear rate beyond 400 000 s⁻¹, indicating finite extensibility of the shorter polymer at that point.

The results of the experiments conducted with differing degree of hydrolysis of the added PVA indicate that the degree of hydrolysis plays a role in creating extensional viscosity in PVA-containing dispersions. As **Fig. 9** shows, a lower degree of hydrolysis has a higher positive effect on the extensional viscosity of the dispersion. Li et al. claim that the hydroxyl groups in PVA form hydrogen bonds with each other while stiffening the chain and preventing it from acting like an ideal coil. He also argues that the esterified hydroxyl groups found in partly hydrolyzed PVA have no significant interactions with hydroxyl groups [13]. As the 88% hydrolyzed PVA3 has fewer hydroxyl groups, it can



10. Influence of PVA with branched chains on the apparent extensional viscosity compared to a linear chain PVA.

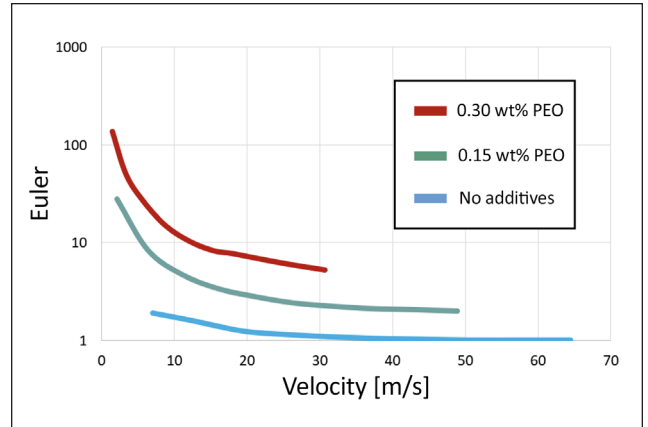


11. Influence of polyethylene oxide (PEO) addition on the apparent extensional viscosity measured using the Eklund capillary viscometer.

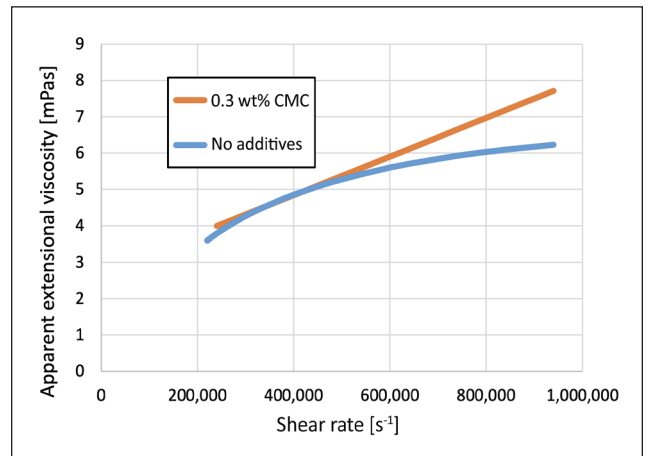
coil into a smaller coil, thus increasing its extensibility and increasing the extensional viscosity of the dispersion.

A branched chain PVA was also tested for extensional viscosity (Fig. 10). The effect on extensional viscosity was minimal compared to the linear PVA1, as the branched nature of the polymer chain does not allow it to form a coil. The branched chains did form entanglements, raising the Brookfield viscosity to 700 mPas, which is significantly higher than the 555 mPas for the same addition amount of linear PVA1.

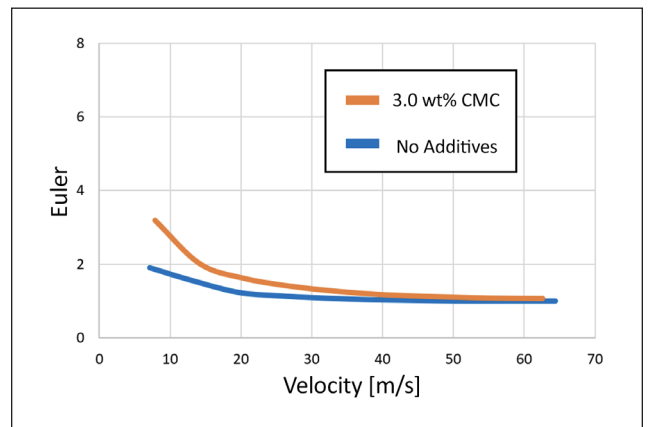
Polyethylene oxide is well known to increase the extensional viscosity of fluids. Trouton ratios of the order 10^5 have been found for high molecular weight PEO solutions [2]. Figure 11 and Fig. 12 show the influence of PEO on the extensional viscosity when added to the barrier dispersion. As expected, even a small addition amount considerably increases the extensional viscosity. The fact that the Fig. 11 viscosity curve is flat suggests a low critical strain rate for coil opening. The orifice rheometer measurement



12. Influence of two different PEO addition levels on the extensional viscosity measured using the Orifice rheometer.



13. Influence of carboxymethylcellulose (CMC) addition on apparent extensional viscosity measured using the Eklund capillary viscometer.



14. Influence of CMC addition on extensional viscosity measured using the orifice rheometer.

further confirmed the huge increase in extensional viscosity (Fig. 12). Extensional flow resistance already at very low shear rates is a benefit, as extensional viscosity is preferable in curtain coating at both high and low shear rates. Also

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noteworthy is that the Brookfield viscosity remained at a reasonably low level of 346 mPas.

Carboxymethylcellulose is a common thickener used in paper coating formulations. The effect of CMC on the apparent extensional viscosity of coating colors has previously been studied by [9]. No significant impact was found, which was explained by the lack of such network structures that could increase the extensional viscosity. The results of the current work agree with those of Kokko; only a marginal effect on the extensional viscosity can be seen in **Figs. 13–14**. Unlike PEO and PVA, CMC does not behave like an ideal chain when dissolved in water. As CMC is a polyelectrolyte, the repulsion between charged segments will stiffen the polymer, making the CMC behave more like a semiflexible worm-like chain [14]. As worm-like chains are significantly less coiled than ideal chains, the chain unraveling causing extensional viscosity is missing.

CONCLUSIONS

Extensional viscosity plays a significant role in the stability of a liquid curtain and thus has the potential to improve runnability and enlarge the operational window of a curtain coater. As the expansion of a hole in a liquid curtain is a two-dimensional flow, extensional viscosity resists it, slowing down the rim speed and allowing the hole to be pushed down into the paper web by inertial forces instead of breaking up the curtain. Extensional viscosity also induces elastic stresses into the curtain, making it more resistant to perturbations forming holes.

Extensional viscosity can be built into latex barrier dispersions by adding high molecular weight linear polymers that behave like or close to ideal Gaussian chains when

dissolved in water. A small addition of PEO increased the extensional viscosity over a wide shear rate range, without excessively increasing the Brookfield viscosity. The only discovered downside of PEO as a viscoelastic additive was its poor solubility in water, which significantly lowers the solids content of the dispersion if one aims for high addition levels via first dissolving it in water. The PVA increased the extensional viscosity as well, but to a lower degree. It also exhibited behaviors such as critical extension rate for coil unraveling and finite extensibility, which are predicted by the FENE-P polymer model. A high hydrolysis degree and branched molecular structure of PVA reduced the extensional viscosity increasing effect. The CMC addition did not increase the extensional viscosity, which is hypothesized to be due to its less flexible backbone when compared to the other polymers used.

Both types of capillary viscometers could be used to reliably measure the extensional viscosity of latex barrier dispersions. **TJ**

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ABOUT THE AUTHORS

We undertook this study to try and solve a current problem of an emerging technology, curtain barrier dispersion coating. The study tries to apply findings from other curtain coating processes to the production of fiber-based packaging materials.

The most difficult aspect of this study was adding the viscoelastic additives in a way that would minimize the effect on the solids content of the dispersion. This was addressed by performing dilution tests.

We found that viscoelasticity, which is easy to see, can be very tricky to reliably measure. It was interesting to find how well the coil-stretch transition and finite extensibility could be seen in the results.

With this information, mills may be able to reduce reliance on surfactants to run their curtain coaters.



Lehtimäki



Schröder



Toivakka



Kukkamo

The next step is to try and implement the finding into curtain coating processes.

Lehtimäki is product development engineer for MM Kotkamills Board Oy in Kotka, Finland. Schröder was a Master's student, and Toivakka is professor at Åbo Akademi University in Turku, Finland. Kukkamo is CEO of ACA Systems Oy in Sotkuma, Finland. Email Lehtimäki at watti.lehtimaki@gmail.com.

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