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:

$$W_e = \frac{\rho Q_e V_c}{2\sigma}$$

where $\rho$ is fluid density, $Q$ is flow rate per unit width, $V$ is curtain velocity, and $\sigma$ 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 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.

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].
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.

### 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/m³ 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].

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

I. 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
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.

**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:

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

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

LITERATURE CITED

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.

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