THE POTENTIAL USE OF MICRO- AND NANO-FIBRILLATED CELLULOSE AS A REINFORCING ELEMENT IN PAPER

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ABSTRACT

The use of nanofibrillar cellulose as a reinforcement agent in paper has been evaluated on a high-speed pilot paper machine. Using mill pulp and mill process waters, two different grades of nanocellulose were tested at 1% and 2% addition levels together with 1% of cationic starch. The results indicate significant increase in tensile strength, enabling up to 8 g/m^2 grammage reduction. Paper had a slightly lower scattering coefficient and lower air permeability. Wire-section dewatering was reduced a little, with a loss of less than one percentage point of solids content, whereas dry matter after wet pressing even increased upon nanocellulose addition. The reason for this unexpected observation is still unclear. Total retention remained constant after nanocellulose addition was started.

INTRODUCTION

Interest is increasing in micro- and nanofibrillar celluloses, or nanocelluloses, which represent suprastructures of cellulose fibres. Much research effort has been expended to demonstrate their usefulness as a strengthening agent in paper and board [1], a viscosity modifier in water-based systems [2] or as an oxygen-barrier material in packaging [3,4].

A wide variety of nanocellulose families with different properties can be produced depending on the manufacturing method [5]. The main groups, shown in Fig. 1, are nanofibrillar cellulose, nanocrystalline cellulose, and bacterial cellulose. The common factor is that in all of these, the basic building block is the cellulose elemental fibril. In nanofibrillar cellulose, both the crystalline and amorphous regions are preserved, and the resulting material consists of long flexible fibrils. Moreover, varying amounts of hemicelluloses remain in the material depending on the fibre source. In nanocrystalline cellulose, only the crystalline parts remain, and the resulting material consists of stiff nanorods.

A common challenge in manufacturing of nanofibrillar cellulose is high energy consumption. High energy use increases production cost, but more significantly, it is also an indication of low production capacity. Especially with purely mechanical methods, energy levels of up to 20 MWh/t of dry matter have been reported [1,6]. Recent research, using suitable pretreatment methods, has enabled significant reductions in energy consumption [5, 7], making large-scale production more realistic. The most common pre-treatment methods are modifying fibre charge, either by TEMPO-mediated oxidization [8,9,10] or by carboxymethylation to a low DS [7,11,12,13], or weakening the fibres with enzymatic treatment [7,14]. The advantage of charge-modification methods is that the fibrils will also become smaller than with mechanical methods only, thus improving nanocellulose properties. Fibre charge promotes fibrillation because it increases repulsion between the cellulose microfibrils.

As a paper additive, nanocelluloses act principally on internal bonding, leading

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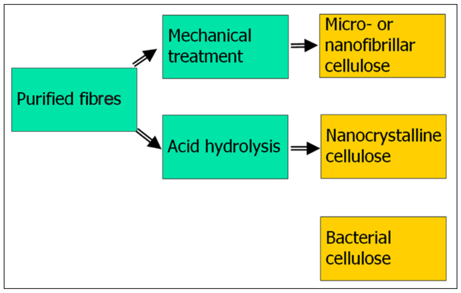

Fig. 1 - Grouping of nanocellulosic materials.

to the following effects:

- moderate increase in dry tensile strength, larger with chemical than with mechanical pulp
- marked drop in air permeability
- lower light scattering and thus lower opacity
- denser paper
- increased hygroexpansivity.

These will be reviewed in more detail in the next section.

The potential as a strengthening agent in paper is based on the fact that nanocellulose has a high surface area and therefore many sites for hydrogen bonding. Nanocellulose has a character similar to chemical pulp fines, except that because of their much smaller size, the particles could be regarded as superfines. It is known from earlier research that cellulose fines improve bond strength and tensile strength, but they can have a detrimental effect on light scattering [15,16,17].

Despite the abundance of research into nanocellulose, all the published research with paper has been on a laboratory scale. To determine the real potential of the material, its properties should be demonstrated in industrial trials. As a step in this direction, the potential of nanocellulose on a high-speed paper machine was evaluated using a mill-type forming section and press configuration.

EARLIER RESEARCH

Several papers have been published on the effect of nanocellulose on paper properties.

Eriksen [1] added 4% of mechanically manufactured nanocellulose into laboratory TMP handsheets. He observed increased air resistance and a modest increase in tensile strength. Moreover, light scattering decreased by -4 m2/kg. In particular, the quantitative changes were the following:

- Tensile strength + 7%–+21% (+3 Nm/g–+ 7 Nm/g)
- Air resistance (Gurley), strong increase, from 40 s to 200 s.

Taipale [18] added 6% of mechanically manufactured nanocellulose to laboratory handsheets. In his study, the pulp was long-fibre bleached chemical pulp. He noticed a strong increase in Scott Bond (+ 55%) and a good increase in tensile index (up to + 15 Nm/g).

Similarly to Taipale, Manninen [19] added 5% of Masuko-refined nanocellulose to chemical pulp handsheets. She noticed similar increases in tensile strength to those seen by Taipale and also determined that nanocellulose increased the hygroexpansion coefficient of freely dried sheets by up to +30%.

Heijnesson-Hulten [10,13] used TEMPO-oxidized nanocellulose in laboratory CTMP handsheets. With addition levels at 5%, there was an increase in Z-strength by almost 200% (from 137 kPa to 387 kPa). In addition, the tensile index increased noticeably, at +20%, although the absolute change was not as dramatic, at 8 Nm/g, as with the chemical pulps in the Taipale and Manninen studies. Besides the increases in strength, bulk decreased by 13%.

Processability issues have also been studied. The main effects of nanocellulose are the poorer drainage of laboratory handsheets and lower solids content after a laboratory wet-pressing procedure. Retention can also be an issue, because it is well known that fines retention is lower than fibre retention.

In her study, Manninen [19] noticed that with a 5% addition of nanocellulose into chemical pulp, the drainage time of laboratory handsheets almost doubled. Moreover, the dry solids after a standard wet-pressing procedure were two to four percentage points below the reference case.

With TEMPO-oxidized nanocellulose, Heijnesson-Hulten reported drainage time increases of 0 s–1.5 s (from a level of 2.5 s) with 100% CTMP pulp [13]. The drainage time increase tends to accelerate with larger amounts of nanocellulose.

Comparing these studies, it seems that drainage can be a bigger issue with chemical pulp, but the strengthening effect of nanocellulose is also greater.

A wet-pressing study simulating realistic wet pressing was reported in [20]. In this study, a dynamic pressing simulator was used with TMP laboratory handsheets. The dry matter after wet pressing was found to have been reduced by less than 0.5 percentage points, but drainage was affected more. NFC reduced solids after forming by approximately 1.5 percentage points and increased drainage time by up to 60%.

Retention of nanocellulose has not been extensively studied. One main reason for this is that nanocellulose is difficult to detect in paper because it is chemically similar to the pulp, and after drying, the fibrils cannot be seen with microscopic methods. However, some concerns exist about how well such fine material is retained in the web. It is known that fines retention is typically smaller than the average retention value.

In the literature cited above, the amount of nanocellulose added has been high, typically approximately 5%. Compared to this, the effects on, e.g., tensile strength seem fairly small. This may be the results of inefficient methods of adding nanocellulose or of a saturation effect at lower amounts than those added. Manninen showed [19] that the effect of mechanically prepared nanocellulose increased steadily until 5% addition, and then the effect leveled off. With grades manufactured using chemical pre-treatment, the saturation point may be at some other level.

EXPERIMENTAL METHODS

Materials

As a paper strength additive, nanofibrillar cellulose is a better choice than nanocrystalline cellulose. The flexibility of the fibrils promotes better conformity to the fibre surfaces and therefore a larger bonded area. The amorphous regions and the hemicelluloses present also provide more groups for hydrogen bonding. Moreover, because of its higher yield compared to nanocrystalline cellulose, nanofibrillar cellulose is a potentially cheaper material to manufacture. Therefore, as in all earlier research on nanocellulose as a paper-strengthening agent, nanofibrillar cellulose was chosen for this research.

In this work, the properties of two types of nanocellulose manufactured at UPM's pilot facilities were tested. Different pre-treatment methods using some combination of the steps shown in Fig. 2 were used to make the two grades. The main characteristics of the materials are shown in Table 1. The measurements were made at a constant consistency which is less than the manufacturing consistency to achieve comparable viscosity and turbidity values. Viscosity was measured with a Brookfield RVDV-III viscometer at 10 rpm using a Vane spindle. Turbidity was measured with a HACH P2100 Turbidometer using a nephelometric principle (90□ angle between light source and detector). Strong mixing was used to dilute the samples to the measurement consistency.

Generally, the lower the turbidity, the more nanoscaled the material is. However, flocculation of the fibrils may also affect turbidity, although the individual fibrils would be nanoscaled. A higher viscosity generally indicates the same thing, but viscosity also reflects the properties of the fibril network. Viscosity is usually higher for longer fibrils.

The pulp used was machine-chest chemical pulp from a paper mill. The pulp is a mixture of Finnish SW/HW with no filler. Because mill pulp was used, it already contained some additives, namely a small amount of wet-end starch from the machine circulation.

For a more realistic study, recirculated water from the paper mill was also used. It was collected from the mill on the day before the trial.

Cationic potato starch, Raisamyl 50021 (DS = 0,035), 1% of the pulp dry weight, was used in all trials. The starch was the same in all trials. Starch was cooked on site and dosed in batches to the stock during trials.

A two-component retention system adapted from that used in the paper mill was used. Dosage of the retention aids was not modified with nanocellulose addition.

To be economical, the amount of nanocellulose should be small, preferably at the addition levels of other strength additives. Therefore, dosages of 1% - 2% were selected.

Nanocellulose was diluted to 0.5% consistency before addition.

Methods

Trials were done on a narrow pilot paper machine capable of high operating speeds. The machine did not have a press section, but it was equipped with the possibility of preparing small reels.

The specifications of the pilot machine were as follows:

- Configurable wire section with the possibility of running the machine in gap former, hybrid former, or Fourdrinier mode
- Maximum web speed 2500 m/min
- One-nip shoe press, shoe length 350 mm
- Maximum line load 2000 kN/m
- No drying section.

The former was run in hybrid former configuration with a one-nip shoe press.

Variables during the trial

The paper composition was as follows:

- Basis weight 50–65 g/m^2
- Nanocellulose type AS or KS
- Nanocellulose dosage 0%, 1%, or 2%

Paper machine

- Press load (1250, 1500, 1750, 2000 kN/m)
  - o 1500 kN/m was used as a reference value
- Paper machine speed (600, 800, 900 m/min)
  - o 600 m/min was used as a reference value.

Solids content samples were collected after the wire section, after the press section, and from the reel. Paper was reeled after the press section, and paper samples were dried before measuring. Paper samples were dried with a Kodak-type drying drum. Sheets were placed between plotting boards, and the surface temperature of the drying cylinder was 100°C.

RESULTS

General

Good overall runnability was achieved during the trial. No paper strength- or dewatering-related web breaks took place, total retention level was constant, and formation remained good without any additional adjustment need. Press- and former-section dewatering

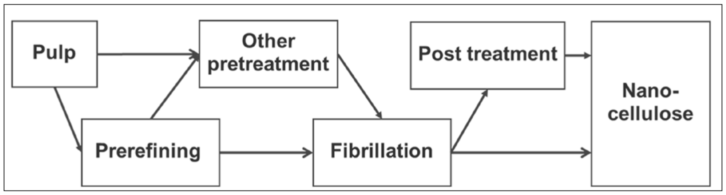

Fig. 2 - **Possible routes of manufacturing nanofibrillar cellulose using pre-treatments.**

TABLE 1 Main characteristics of the nanocelluloses used in this research.

Nanocellulose	Viscosity Consistency = 0,8%	Turbidity Consistency = 0,1%
Type AS	16 600 mPa	64 NTU
Type KS	8 000 mPa	63 NTU

remained at an acceptable level and is discussed in the following section.

Forming-section dewatering

Former-section dewatering was analyzed based on solids-content samples taken at the end of the former section. Based on the results achieved, nanocellulose addition led to 0.5–1 percenetage-point loss of dry matter after the wire section. Initial dewatering slowed down, and a greater share of water was removed at the flat vacuum boxes at the end of the wire section. Figure 3 shows the solids content after the wire section for 65 g/m² paper.

Press-section dewatering

Contrary to expectations, the dry solids content of the paper web increased when nanocellulose was added to the stock. The nanocellulose-containing paper web arrived at a lower solids content to the press section, and therefore press dewatering must have been very effective. Figure 4 shows press solids-content results with 65 g/m² paper.

The mechanism for high press dewatering of a nanocellulose-containing web was studied further to gain more understanding of the reasons for this unexpected result. It is commonly known that increasing web speeds and pressing temperatures speed up dewatering. However, no differences in the temperatures recorded-during the trial were noticed.

Water-retention value (WRV) of the furnish typically increases with nanocellulose addition, and this should lead to lower after-press solids content, which does not support the result obtained here. However, the single-nip shoe-press section is a relatively new technology, and relatively few paper machines are operating with this unit. It is believed that possible reasons for the improved after-press solids content for a nanocellulose-containing web are related to press configuration and to the pressure pulse in the shoe press, resulting in

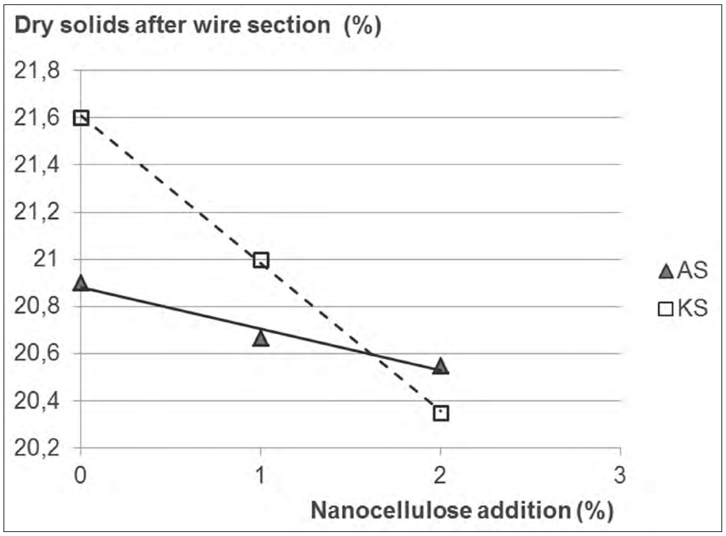

Fig. 3 - Solids content after the wire section. The figure shows the results with 65 g/m² paper.

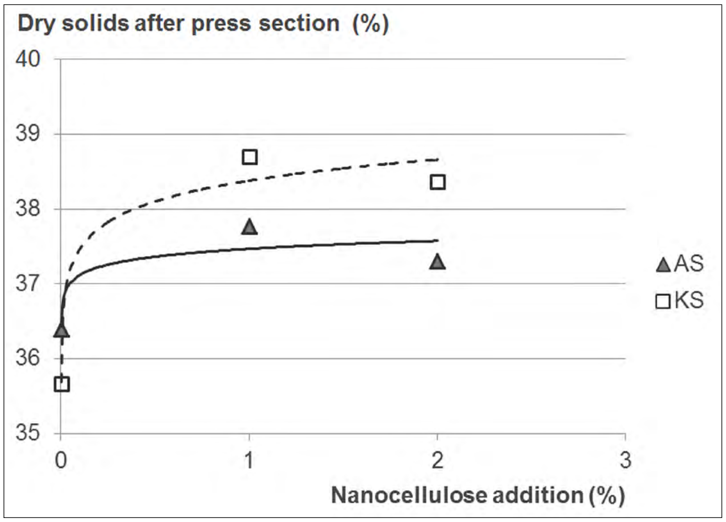

Fig. 4 - Solids content after the press section. The figure shows the results with 65 g/m² paper. The points represent the average of different press loads.

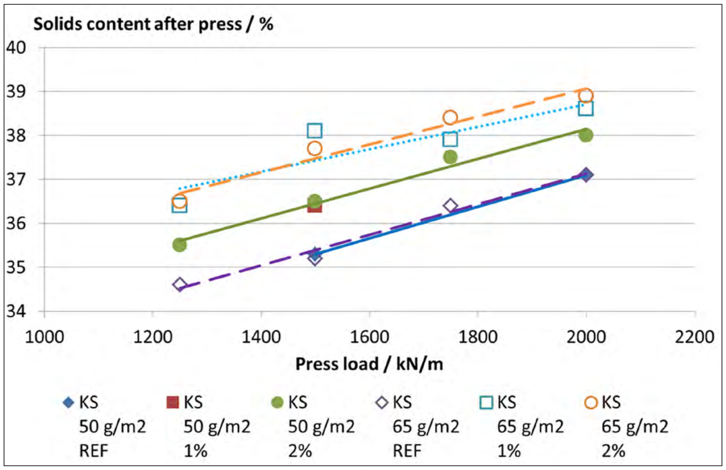

Fig. 5 - Nanocellulose-containing paper produced systematically higher after-press solids than the reference case; the shoe press functioned even better as speed was increased.

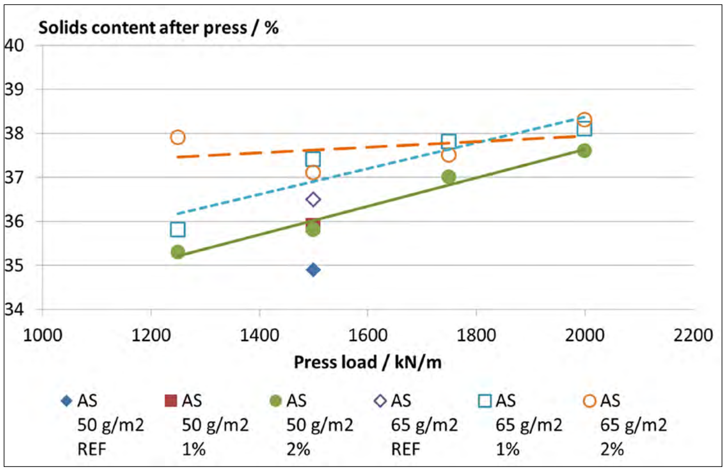

Fig. 6 - Nanocellulose-containing paper produced systematically higher after-press solids than the reference case; higher speed slightly decreased after-press solids.

differences in rewetting. It is also possible that at the reference point (0% nanocellulose), for some reason, the dry matter content became too low.

As a function of press load, the after-press solids behaved as expected (Figs. 5 and 6).

Retention

Total retention remained at a very high level during the trial, greater than 94%. The furnish used had no filler and was based totally on beaten pine and birch Kraft pulps. Nanocellulose addition seemed to have had practically no effect on the achieved retention, as shown in Fig. 7. Neither did nanocellulose type seem to have any major effect on retention.

Paper properties

Paper properties were analyzed based on reeled and sheet-form separately dried samples. The effects of nanocellulose on strength properties and air permeability of the paper were of special interest, and the results will be presented in the following section. The results were also partly compared with a practical application, and the basis-weight reduction potential was evaluated.

Generally, as shown in Fig. 8, nanocellulose-containing trials gave higher density values than the reference case. This is based on the strong network-building and bonding capabilities of nanocellulose.

Tensile strength was calculated as a geometric average of machine-direction and cross-direction strength to form an impression of total tensile-strength potential regardless of possible variations in the tensile ratio of the paper.

As seen in Fig. 9, nanocellulose-containing paper had a higher tensile strength than the reference case. Based on these results, it was estimated that up to 8 g/m^2 basis-weight reduction potential existed without compromising tensile strength. AS-type higher-viscosity nanocellulose seemed to give slightly higher tensile values than KS-type nanocellulose.

In the case of air permeability, as shown in Fig. 10, nanocellulose gave a 20%–30% lower porosity than the reference case. Translated into basis-weight reduction potential, approximately 8 g/m^2

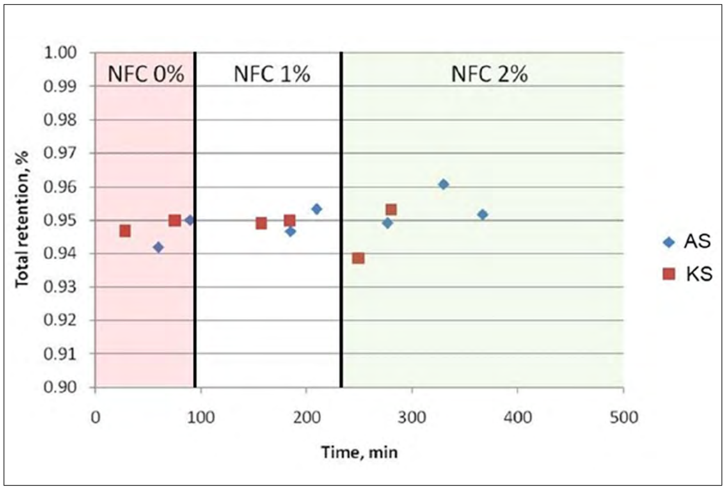

Fig. 7 - Total retention remained constant during the trial despite increased nanocellulose content.

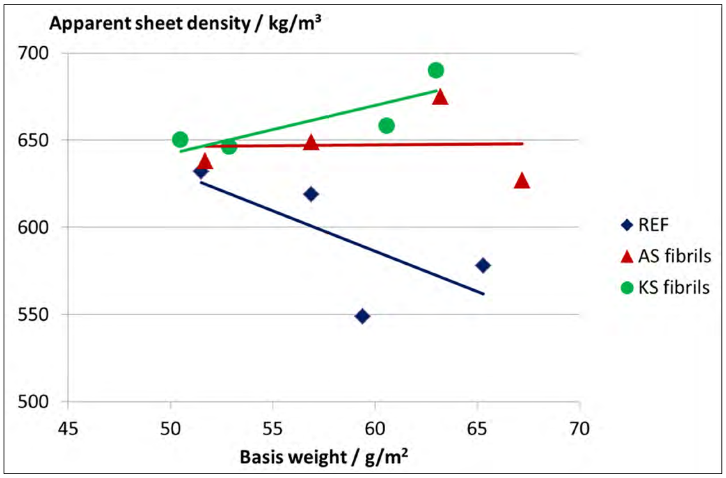

Fig. 8 - Nanocellulose addition led to higher sheet density. Press load was 1500 kN/m for all trials, and nanocellulose addition level was 1%–2%.

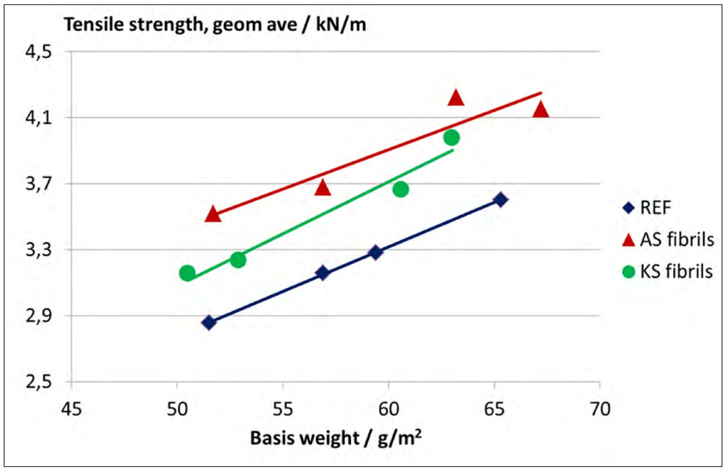

Fig. 9 - Tensile strength, geometric average MD*CD. Press load was 1500 kN/m for all trials, and nanocellulose addition level was 1%–2%.

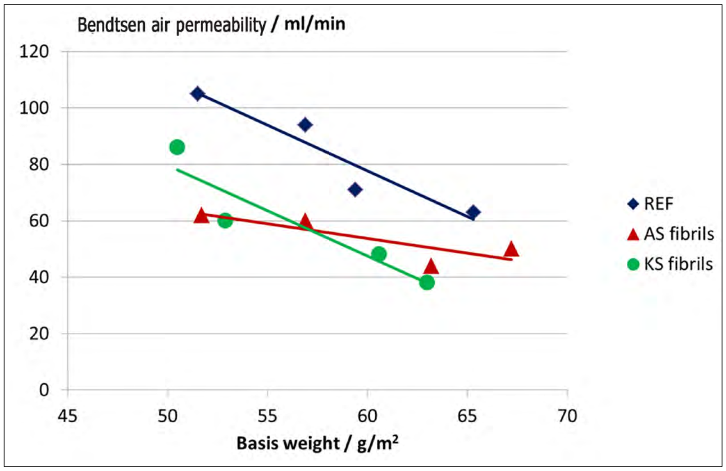

Fig. 10 - Bendtsen air permeability. Press load was 1500 kN/m for all trials, and nanocellulose addition level was 1%–2%.

lower basis weight with nanocellulose-containing paper would have given the same air permeability as the reference case.

Optical properties of paper became worse after nanocellulose addition. At a constant basis weight, approximately two to three percentage points lower opacity was measured. This opacity loss arose mainly from improved bonding, which reduced the light-scattering surface.

This loss of opacity did not support the basis-weight reduction target in the same way as the good tensile and air permeability results. If full advantage had been taken of the improved strength properties to lower the basis weight, the result would have been approximately six percentage points lower opacity.

Opacity and light-scattering results are shown in Figs. 11 and 12.

CONCLUSIONS

Nanocellulose addition to paper resulted in interesting paper properties. First of all, nanocellulose affected paper strength beneficially even at low dosage levels. Both tested nanocelluloses gave practically identical results.

There were no runnability or major production-efficiency issues during the trials. Solids content measurements indicated much better press dewatering than expected, for which the reason is not totally clear. A negative effect on opacity was observed. The relevance of opacity is highly application-dependent and should be taken into account when testing nanocellulose for different end-uses. The strength increase indicates beneficial use in packaging papers and boards, where loss of opacity is not as critical. Printing and writing papers can benefit if the increase in strength is used to increase filler level. The very marked increase in elastic modulus could provide bending stiffness in structural (layered) products and also partly compensate for the effect of possibly lowered basis weight.

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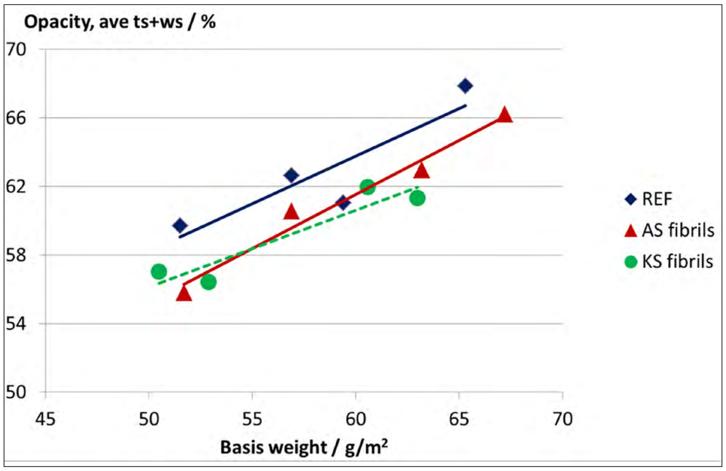

Fig. 11 - **Opacity of the paper samples. Press load 1500 was kN/m for all trials, and the nanocellulose addition level was 1%–2%. Average of top-side and wire-side measurements.**

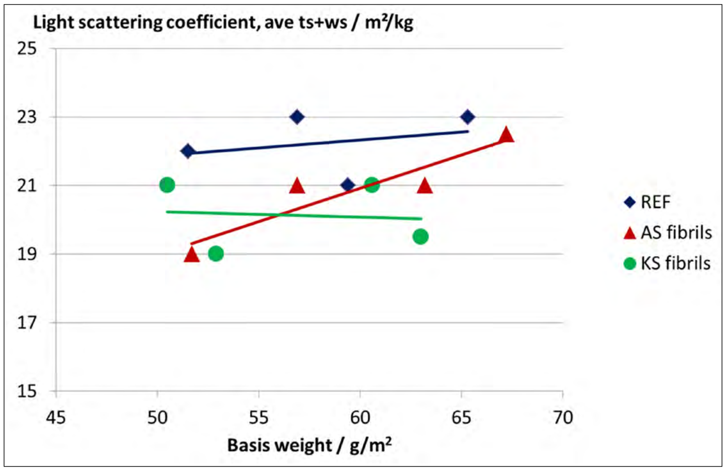

Fig. 12 - **Light-scattering coefficient of the paper samples. Press load was 1500 kN/m for all trials, and the nanocellulose addition level was 1%–2%. Average of top-side and wire-side measurements.**

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