Paper technology

Tove Joelsson*, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund and Per Engstrand

High strength paper from high yield pulps by means of hot-pressing

https://doi.org/10.1515/npprj-2019-0087
Received October 11, 2019; accepted January 8, 2020; previously published online February 19, 2020

Abstract: The hypothesis is that it should be possible to modify papermaking conditions in line with the softening properties of high yield pulp fibres and achieve similar strength properties to conventional chemical pulp based paper. We therefore investigated the rheological and physical properties of high yield pulp based papers during hot-pressing. Our results confirm that increased temperature combined with sufficient pressure enables permanent densification by softening of lignin, producing very high tensile strength. This treatment also significantly improved the wet tensile strength in comparison to bleached kraft pulp without using wet strength agents. The high yield pulps used here were spruce based thermomechanical pulp, chemi-thermomechanical pulp, and high temperature chemi-thermomechanical pulp, and birch-aspen based neutral sulphite semi chemical pulp, with spruce-pine based bleached kraft pulp as reference. Rapid Köhten sheets of 150 g/m^2 and 50 % dryness were hot-pressed in a cylinder-press at 20–200 °C, 7 MPa, and 1 m/min. The mechanical properties showed great improvements in these high yield pulp papers, with tensile index increased to 75 kNm/kg and compression strength index to 45 kNm/kg; levels close to and better than bleached kraft. Wet strength increased to 16 Nm/g compared to 5 Nm/g for bleached kraft.

Keywords: high yield pulp; hot-pressing; lignin; paper properties; wet strength.

***Corresponding author: Tove Joelsson,** Mid Sweden University, SE-85170 Sundsvall, Sweden; and MoRe Research Örnsköldsvik AB, Box 70, SE-89133 Örnsköldsvik, Sweden, e-mail: tove.joelsson@more.se, ORCID: https://orcid.org/0000-0002-5813-0188
Gunilla Pettersson, Sven Norgren, Hans Höglund, Per Engstrand, Mid Sweden University, SE-85170 Sundsvall, Sweden, e-mails: gunilla.pettersson@miun.se, sven.norgren@miun.se, hans.hoglund@miun.se, per.engstrand@miun.se
Anna Svedberg, MoRe Research Örnsköldsvik AB, Box 70, SE-89133 Örnsköldsvik, Sweden, e-mail: anna.svedberg@more.se

Introduction

The movement away from environmentally destructive plastics brings paper products into the forefront, as they decay more quickly, are biologically degradable, and are produced from wood fibre, which is a renewable resource. It is also clear that the market for printing papers is declining due to digitalization, while the demand for bio-based packaging solutions is increasing.

Under conventional papermaking conditions, the high yield pulps (HYPs) traditionally used in printing paper products provide too low tensile strength to compete with kraft pulps in products with high strength demands, such as liner and sack paper products. Improved methodologies to produce strong paper materials from HYPs are therefore of great interest.

In mechanical pulp, defibration is an energy demanding process, and so much effort has been made to develop and investigate the properties of the wood fibre material. Many researchers (Atack 1972, Goring 1963, Irvine 1984, Salmén 1982, 1984) emphasize that the thermal transitions of the wood components have a major influence on the mechanical pulping process, mainly due to the softening of lignin and hemicellulose by heating and the plasticising effect of water. The refining energy is significantly reduced when defibration occurs at a temperature of 170 °C (well above the softening point of lignin), due to the viscoelastic properties of the wood fibres. Since the lignin is enriched between the fibres, in the middle lamella, the defibration will take place there, leaving the fibres intact and richly coated with lignin. This was shown experimentally by Atack in 1972; pulp fibres produced in a pressurized refiner at a temperature of 115 °C gave coarse fibre surfaces, while those produced at 170 °C gave smooth fibre surfaces (Atack 1972). Due to the kinetic transition of the lignin, the glass transition temperature (Tg) can shift depending on the shear rate in the refinery or the frequency used in the laboratory methods. This means that a shorter time interval increases the softening temperature of lignin, which is the case in a high-frequency dynamic load refinery where high shear rates apply. This is true for polymers in general that

viscoelastic behaviour depends on the time scale of measurement procedures as well as the temperature (Irvine 1984, 1985). Below Tg, the lignin coated fibres are rigid and glassy, have low flexibility, require more energy when defibrated, and have poorer fibre-fibre bonding ability. In the early 1960s, Gupta et al. (1962) investigated the bonding and adhesion properties of isolated lignin of different origins, applied to paper samples. Their general conclusions were that strength and adhesion increase with lower softening temperature, higher ionization, higher pressure, and longer press time, and that moisture content is important as softener. Hypothetically, to utilize lignin as a strength enhancer, it would be desirable to reduce Tg, to use lignin covered fibre surfaces, to have a sufficiently long hot-pressing time at a temperature well above Tg, and to ensure a high enough initial moisture content. The fact that HYPs may contain extractives that can reduce bonding between fibre surfaces should also be taken into consideration (Rundlöf et al. 2000). Mill scale studies have shown that even small amounts of extractives can have a negative influence on sheet strength.

The tensile strength of paper depends both on the fibre strength and on the bonding strength between individual fibres (Page 1969, Stone and Clayton 1960). Zero span measurements have shown that removing lignin by treating with sodium chlorite at pH 4.5 decrease the strength of individual fibres but increase the strength per unit paper weight. This could be interpreted to mean that lignin in fibre possesses some tensile strength of its own.

In the paper forming section, the strength of HYP based paper can be increased by means of press drying, due to the viscoelastic properties of lignin and hemicellulose (Byrd 1979). During press drying at high temperature, the moist HYP fibres become compressible, which enables densification of the sheets and increases bonded areas, resulting in improved strength properties (Back 1984).

Press drying technology dates back to Mason's innovation in 1925 involving single-stage press drying for hardboard production of very coarse steam exploded fibre material, resulting in three patents (Mason 1931, 1937, 1938). In the late 1970s, Wahren invented the impulse drying technique, where the paper web is passed between a heated press roll and felt covered cold roll; the dwell time in the press nip was a few seconds (Wahren 1982). This technique was further developed in 1990s with an extended nip (shoe press), dwell time up to 50 msec, and temperatures up to 450 °C. The main obstacle to impulse drying was delamination, and so the process never became commercialized. The Condebelt technique was developed in the early 1970s for preserving bulk and increasing strength, and was implemented in industry in 1996 in a Finnish board machine in Pankakoski, Finland. Low temperature and very low pressure were applied, while the time that the paper web was exposed to heat was extended to several seconds (Lehtinen 1998). Throughout the history of papermaking, the improved strength properties achieved by pressing at elevated temperature have been confirmed, but further development of this knowledge has been sparse in recent years (Lucisano 2002, Klinga et al. 2007, Pettersson et al. 2017, Norgren et al. 2018).

The most recent work using a press drying technique was performed by researchers at FSCN, Mid Sweden University, on a laboratory cylinder press available at MoRe Research in Örnsköldsvik (Pettersson et al. 2017, Norgren et al. 2018). The results indicated a possibility of reaching the same level of tensile strength with HYP as with bleached kraft pulp, as well as somewhat better compression strength. Another very important result is that sheets based on lignin-rich pulp show much higher wet strength than sheets from bleached kraft pulps when pressed at a high temperature well above the softening point of lignin.

The main objective of the research presented here is to contribute to the development of new very strong and biodegradable HYP based packaging materials, by achieving increased understanding of how a novel type of hot-pressing technology can be optimised. We studied the rheological and physical properties in paper sheets based on various HYPs when hot-pressed at increasing temperature. Our primary interest was in investigating the development of dry and wet strength properties without adding strengthening agents, which is important from an environmental point of view. We used pressing temperatures ranging from 20 °C to 200 °C, a constant nip pressure of about 7 MPa, and paper sheets with a dry content (d. c.) of 45–50 %. The analysis included fibre and pulp characterization, physical paper properties, scanning electron microscopy (SEM) of paper surfaces, and light microscopy of sheet cross section.

Materials and methods

Paper sheets were prepared from five different pulps: chemi-thermomechanical pulp (CTMP) from Norway spruce (*Picea abies*) with Canadian standard freeness (CSF) of 420 ml, for paperboard; high temperature CTMP (HT-CTMP) from Norway spruce with CSF of 630 ml, for tissue; thermomechanical pulp (TMP) from Norway spruce with CSF of 55 ml, for light weight coated paper; neutral sulphite semi chemical pulp (NSSC) from 90/10 European birch/aspen (*Betula pendula*/*Populus tremuloides*) with

Table 1: Pulp characterisation.

Pulp	CTMP	HT-CTMP	TMP	NSSC	B Kraft
Cellulose (%) (KA 10.314)	46.9	48.2	46.3	52.0	82.1
Hemicellulose (%) (KA 10.314)	25.7	24.4	23.7	24.5	17.5
Lignin (Klason) (%) (T222)	26.6	26.2	28.0	16.8	0.01
Acid soluble lignin (%) (T-UM 250)	0.7	0.7	0.7	6.1	0.4
Acetone extract (%) (ISO 14453)	0.15	0.19	1.27	0.55	0.042
CSF Freeness (ml) (ISO 5267-1)	420	630	55		
°SR (ISO 5267-1, -2)				25	27
Fibre length (mm) (PulpEye)	1.46	1.66	0.83	1.11	1.99
Fibre width (μm) (PulpEye)	31	32	30	27	25
Shive content (sum/g) (PulpEye)	572	112	4907	2556	28
Fines (%) (PulpEye)	34.5	29.0	62.4	13.6	11.2
State of pulp	Dry	Dry	Wet	Wet	Wet

Schopper-Riegler freeness (SR°) of 25, for fluting grades; and a bleached kraft pulp from a mixture of Scots pine (*Pinus sylvestris*) and Norway spruce. The pulps were collected directly from the paper mills. All laboratory work, sheet preparation, hot-pressing, and analysis were performed at the laboratory of MoRe Research Örnsköldsvik AB. Table 1 shows the characterization of the different pulps used in this research. The carbohydrates were analysed with ion chromatography according to SCAN-CM 71:09. Cellulose and hemicellulose were calculated according to an internal MoRe research standard (KA 10.314) as follows:

For hardwood:

$$\textit{Cellulose}\ (\%) = \textit{Glucose}\ (\%)\ \textit{of Carbohydrates} - \frac{\textit{Mannose}\ (\%)\ \textit{of Carbohydrates}}{2}$$

For softwood:

$$\textit{Cellulose}\ (\%) = \textit{Glucose}\ (\%)\ \textit{of Carbohydrates} - \frac{\textit{Mannose}\ (\%)\ \textit{of Carbohydrates}}{3}$$

$$\textit{Hemicellulose}\ (\%) = 100\ (\%) - \textit{Cellulose}\ (\%)$$

Cellulose, hemicellulose, lignin, acetone extract, and acid soluble lignin content in each pulp sample were calculated as percentages of the total weight. The fibre data (Table 1) were analysed with the PulpEye instrument, and calculated as follows:

Fibre length: $l = \sum(l \times l)/\sum(l), \quad l > 0.2\,\text{mm}$

Fibre width: $b = \sum(b \times l)/\sum(l), \quad l > 0.5\,\text{mm}$

$$\textit{Fines} = \sum a/\sum A \times 100\ (\%), \quad l < 0.2\,\text{mm}$$

$\sum a$ is the total area for fibre objects defined as fines, and $\sum A$ is the total area for all analysed objects. The shive content was calculated as the sum of width, b = area/length, when $b > 75$ μm, $l > 0.3$ mm per 1 gram of pulp.

Pulp preparation

CTMP (CSF 420 ml, yield 95 %) and a low energy HT-CTMP (CSF 630 ml, yield 95 %) were produced by the SCA Östrand mill in Sweden, then bleached with peroxide and flash dried to 92.1 % and 91.8 % d. c. respectively. The CTMP used as the reference pulp in this study has been studied thoroughly in earlier research (Pettersson et al. 2017). A low freeness unbleached TMP pulp (CSF 55 ml, yield 98 %) from SCA Ortviken, Sweden was used wet at 29.5 % d. c.. We also used a wet NSSC (yield 83 %, 18.8 % d. c.) and a bleached kraft pulp (yield 45 %, 23.9 % d. c.) which were beaten in a laboratory refiner to 25 and 27°SR respectively. The pulps studied here covered a broad range of properties, differing in terms of freeness, lignin content, cellulose and hemicellulose content, fibre length distribution, fibre width distribution, fines content, and shive content (Table 1). Before making sheets, all pulps were hot-disintegrated according to ISO 5263-3:2004. No chemicals were added to the pulp furnishes.

Sheet preparation

Handsheets were prepared in a Rapid Köthen (RK) sheet former (Paper Testing Instruments, Pettenbach, Austria) according to ISO 5269-2:2004. The fibre suspension was 6.0 g/l. Sheets with a grammage of 150 g/m were formed after vigorous aeration of the fibre suspension just before sheet preparation. The sheets were then press-dried at 100 kPa pressure under restrained conditions at 90 °C until they reached 45–50 % dryness content. The handmade laboratory paper sheets made in the RK equipment had no fibre orientation. The paper sheets were stored in well-sealed plastic bags for approximately 24 h at room temperature before being hot-pressed in a rotating cylinder press.

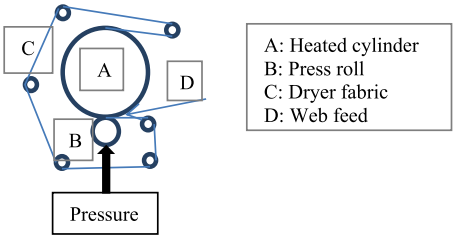

Figure 1: Hot cylinder press machine with oil heated cylinder and one press nip. Reproduced with permission of Pettersson et al., FSCN/Mid Sweden University.

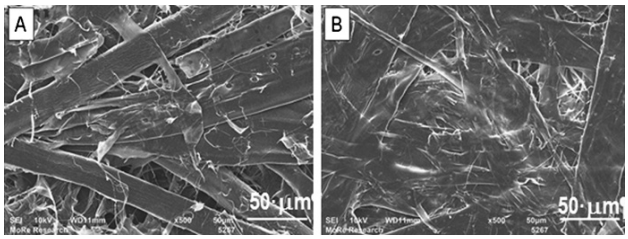

Figure 2: SEM pictures of surface of paper sheets of CTMP pressed at 20 °C (A) and 200 °C (B). Resolution is 500× (50 µm).

Press drying equipment

The hot cylinder press machine used in these experiments was located at MoRe Research Örnsköldsvik AB (Figure 1). The diameters of the cylinder and the press roll were 0.8 m and 0.2 m respectively. The larger cylinder was oil heated, and the fabric was a two-ply felt. The feeding rate was 1 m/min and the press nip was 7 MPa throughout all the trial points. The press time of the felt was about 70 sec and the press nip time was about 1.5 sec calculated on a nip length of about 25 mm measured with sensor films from Fuji (Prescale LW 2.5–10 MPa). The trials were all performed at four different nip temperatures: 20 °C, 100 °C, 150 °C, and 200 °C. The TMP sheets started to delaminate at 200 °C, and so in this case the hot-pressing was done only up to 180 °C. The reason for this delamination was probably the substantially higher fines fraction in TMP with CSF 55, which gives a more closed surface. Moist sheets (45–50 % d. c.) were inserted on the felted fabric between the press roll and the heated cylinder of the rotating drying machine. The paper sheets emerging from the cylinder press were bone dry, above 93 °C. In order to achieve bone dryness in the trial points pressed at 20 °C, they were passed through the cylinder press twice without nip pressure in strain at a temperature of 40 °C.

Sheet testing

Sheet testing was carried out after conditioning according to ISO 187. Grammage was determined according to ISO 536, and density according to ISO 534. Tensile testing was conducted according to ISO 1924-3, which also includes the method for tensile stiffness and elongation to failure. Short span compression test (SCT) index was measured according to ISO 9895. Wet tensile strength was measured according to ISO 3781. The standard deviation (SD) was calculated on 10 measurements for each test point, and is given in the diagrams as 2SD.

Contact angle measurement was carried out according to an automatic drop method with DAT 1100-Fibro System AB and standard T558. SEM analysis of the sheet surface was evaluated on the resolution at 500×. Sheet cross sections were stained with $KMnO_4$ for 6 minutes on cross cuts and then evaluated with light microscope and transmitted light camera lenses 20× (50 µm) and a resolution of 300×. Cross sections were also evaluated with a fluorescent microscope using 20× (20 µm) camera lenses and a resolution of 600×.

Results

Microscopical analysis

The SEM analysis of the CTMP sheet surface clearly showed how the fibres collapsed when pressed at high nip temperature (Figure 2). The fibre structure was much denser and the fibre lines almost vanished at 200 °C.

Fluorescence microscopy analyses of cross sections of CTMP and TMP samples hot-pressed at 20 °C and 200 °C (180 °C for TMP) revealed the presence of lignin as bright yellowish areas, and how the rheology change the form of fibres under these conditions (Figure 3). The arrows in Figure 3 show the bright areas where lignin was enriched, mostly surrounding the fibres. The location of lignin seemed to remain after hot-pressing at 200 °C and 180 °C (Figure 3: B and D).

Cross sections of paper samples of CTMP and bleached kraft pulps were analysed by light microscopy after staining with $KMnO_4$ for 6 minutes (Figure 4). The lignin reacts with $KMnO_4$ and the more intense the colour, the higher the lignin content. This can be clearly seen in Figure 4 when comparing CTMP (26.6 % lignin) to bleached kraft (0.01 %); the stiff fibre structure of CTMP collapsed when pressed at high temperature, whereas the fibres in the bleached kraft were already collapsed at room temperature due to the flexibility of the material.

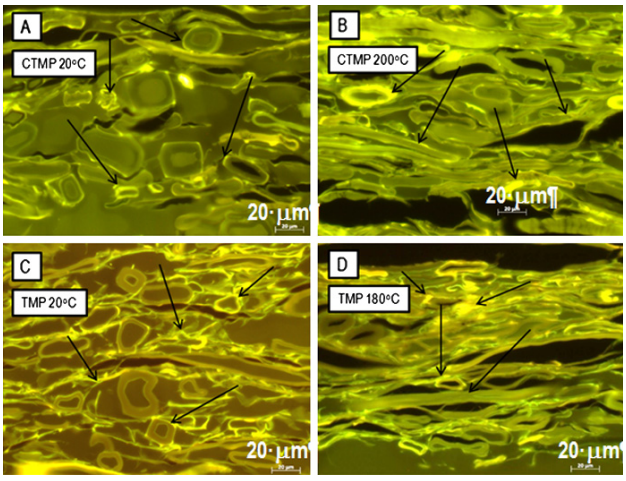

Figure 3: Fluorescent microscopy of cross sections of paper sheets exposed to fluorescence light at a resolution of 600× (20 μm). (A) CTMP hot-pressed at 20 °C, (B) CTMP hot-pressed at 200 °C, (C) TMP hot-pressed at 20 °C, and (D) TMP hot-pressed at 180 °C (D). The arrows point to bright areas that indicate lignin.

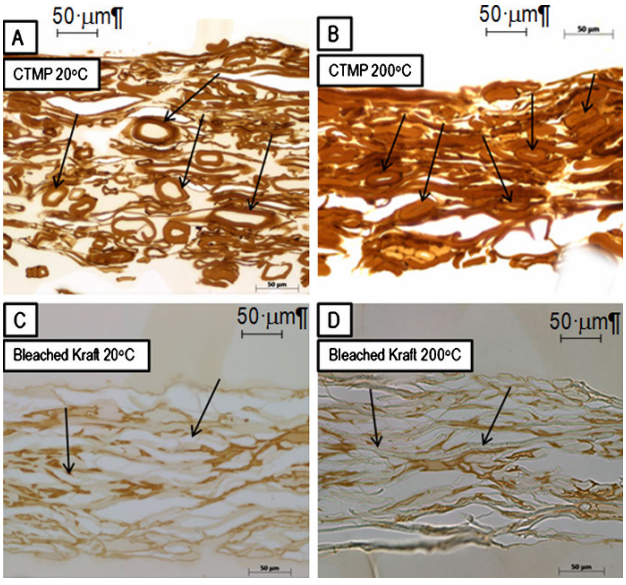

Figure 4: Light microscopy of cross sections of paper sheets at a resolution of 300× with 20× (50 μm) camera lenses, stained with $KMnO_4$ for 6 minutes. (A) CTMP hot-pressed at 20 °C, (B) CTMP hot-pressed at 200 °C, (C) bleached kraft hot-pressed at 20 °C, (D) bleached kraft hot-pressed at 200 °C. Arrows indicate non-collapsed (A) and collapsed (B, C, D) fibres.

Physical properties

The CTMP, HT-CTMP, and TMP based paper sheets all showed a substantial increase in density when the nip temperature increased from 20 °C to 200 °C (180 °C for TMP) (Figure 5). Still, the densities at 200 °C were about

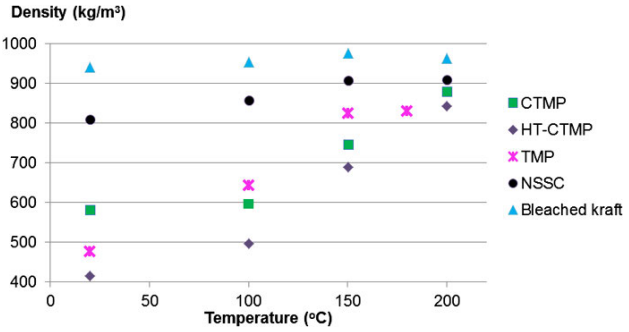

Figure 5: Density as a function of temperature in the pressure nip. Five different pulp mixtures pressed at 20 °C, 100 °C, 150 °C, and 200 °C (180 °C for TMP).

10 % lower for the HYPs than for bleached kraft. The increase in density was 103 % for HT-CTMP, 51 % for CTMP, and 74 % for TMP. The reason for the HT-CTMP gaining more density than the CTMP is probably the initially higher bulk, which in turn is due to the low refining energy needed to reach a certain low shive content compared to conventional CTMP (Table 1). The NSSC based paper showed only a slight increase in density over the temperature interval, probably because the pulp mix of hardwood produced a denser structure even at 20 °C. Bleached kraft pulp did not show a significant increase in density with increasing temperature (Figure 5). The fibres and the fibre structure in the bleached kraft pulp had already collapsed and become denser due to the removal of all the lignin and most of the hemicellulose from the fibre walls, as also seen in the light microscopy pictures.

The tensile strength index for the HYPs increased significantly with the increase in density (Figure 6). CTMP increased by 98 %, HT-CTMP by 153 %, TMP by 82 %, and NSSC by 45 %; conversely, the bleached kraft pulp increased only very slightly (7 %). The tensile index for the CTMP and the HT-CTMP was about 70 kNm/kg, close to the 80 kNm/kg of the bleached kraft despite a 10 % lower density for the former two materials. It is also interesting that the tensile index of the NSSC increased to a very high level of 93 kNm/kg (higher than for the bleached kraft) when hot-pressed at 200 °C.

SCT index is a very important property for measuring how well packaging can withstand crushing. The data in Figure 7 reveal that when the sheet density was increased by means of increasing pressing temperatures, the HYP followed the same increasing trend in SCT. The CTMP increased by 131 %, HT-CTMP by 213 %, TMP by 111 %, NSSC by 63 %, and bleached kraft by 16 %. All the HYPs reached the same SCT index level as the bleached kraft when the nip temperature was increased to 200 °C, but at a 10 %

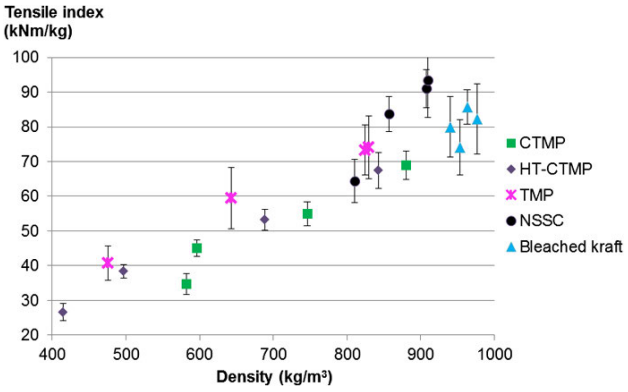

Figure 6: Tensile index as a function of density. Error bars indicate 2SD. The increasing values are nearly linear with the increase in temperature in pressure nip, except for bleached kraft.

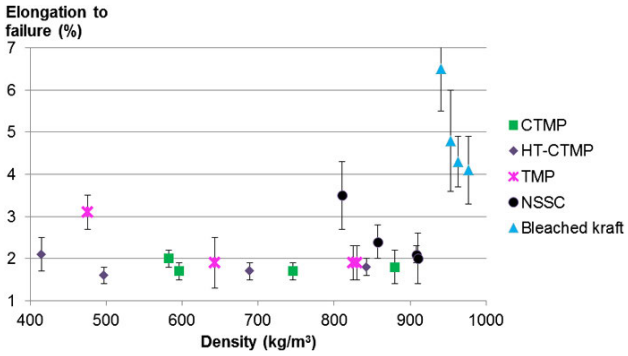

Figure 8: Elongation to failure as a function of density at different nip temperatures. Error bars indicate 2SD.

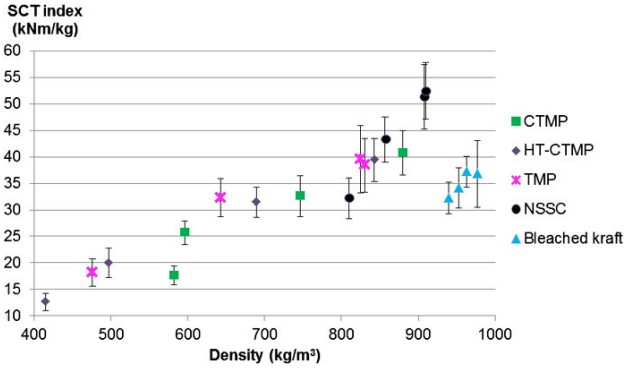

Figure 7: SCT index as a function of density. Error bars indicate 2SD. The graphs show a significant increasing SCT with increasing nip temperature for the HYPs.

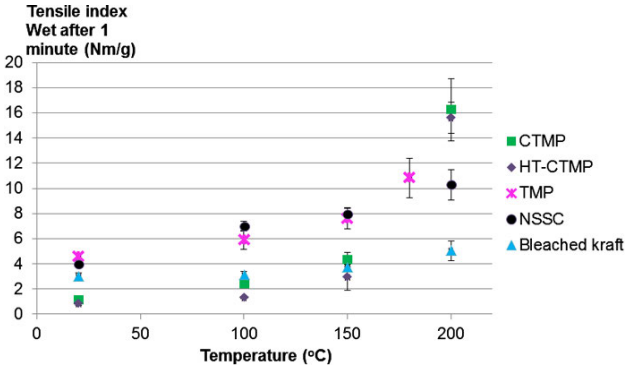

Figure 9: Wet tensile index (1 minute in water) as a function of temperature in press nip. Error bars indicate 2SD. Nip pressure temperatures of 20 °C, 100 °C, 150 °C, and 200 °C (180 °C for TMP).

lower density (except for NSSC, which had a density of 910 kg/m^3). The NSSC pulp reached very high SCT values, well above the bleached kraft (52.4 vs. 37.2 Nm/g).

Elongation to failure is an important property that reflects the brittleness of a material. When the nip temperature was increased, the elongation to failure decreased generally for all pulps (Figure 8), indicating that the material became more brittle as the temperature in the nip increased. The HYPs had low elongation values even at 20 °C, probably due to stiff fibres. The bleached kraft pulp showed the highest elongation to failure as well as the highest drop as the pressing temperature increased.

Resistance against water is of great importance in most packaging materials. The present data demonstrate an interesting development of wet strength when the sheet pressing temperature was raised to levels well above the lignin softening range (Figure 9). It is obvious that the significant development of wet strength will appear between 150 °C and 200 °C. Both the CTMP and the HT-CTMP reached significantly high wet strength levels, over 15 Nm/g, when the sheet nip temperature was increased to 200 °C. The TMP (up to 180 °C) followed the same trend as the CTMP and HT-CTMP, while the development of the NSSC pulp was slightly lower. The bleached kraft did not develop any significant wet strength.

In order to study the persistence of wet strength in the paper sheets hot-pressed at 200 °C, they were observed after immersion in water for 1 minute, 1 hour, and 24 hours. All the samples showed only very small changes over this time interval (Figure 10). The CTMP and HT-CTMP lost remarkably little wet strength over time, which gives these materials a great potential in packaging where wet stability is essential. Papers are considered to have a wet strength effect if the relative wet strength is higher than 15 % (Dunlop-Jones 1991) of the initial tensile strength, which both CTMP and HT-CTMP reached more than adequately.

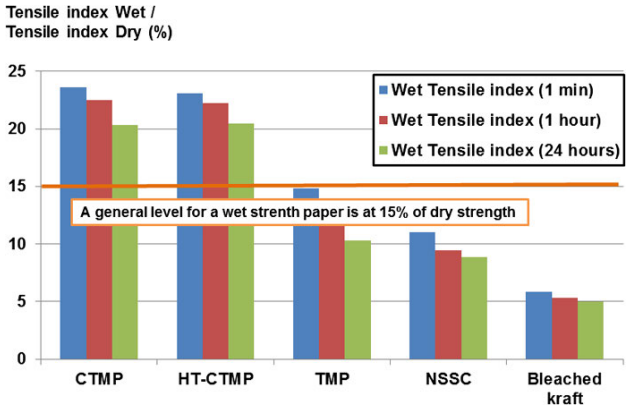

Figure 10: Wet tensile index as a percentage of dry tensile index measured after 1 minute, 1 hour, and 24 hours for paper sheets pressed at 200 °C (180 °C for TMP) nip temperature. The red line indicates the general level above which the paper is considered stable in water.

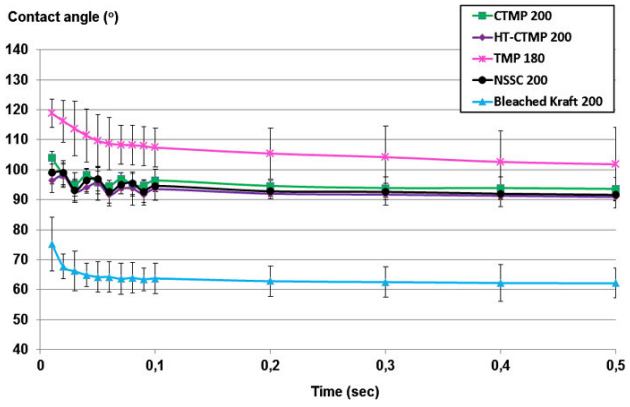

Figure 11: Contact angle for sheets pressed at 200 °C nip temperature (180 °C for TMP). Error bars indicate 2SD.

Contact angle is a measure of hydrophobicity. A surface is considered hydrophobic when the contact angle is greater than 90°. The contact angles for CTMP, HT-CTMP, and NSSC samples hot-pressed at 200 °C indicated a surface hydrophobicity, as all three samples had an initial contact angle of 100° (Figure 11). The TMP sample pressed at a nip temperature of 180 °C gave an initial contact angle well above 100°, indicating a significant surface hydrophobicity. The bleached kraft pulp sheets were not hydrophobic, with a low initial contact angle of 75°.

This large effect of nip temperature on surface hydrophobicity is a significant result (Figures 12 and 13). The higher the press temperature, the higher the contact angle. The TMP showed a slower contact angle setting than CTMP even at the lowest press temperature.

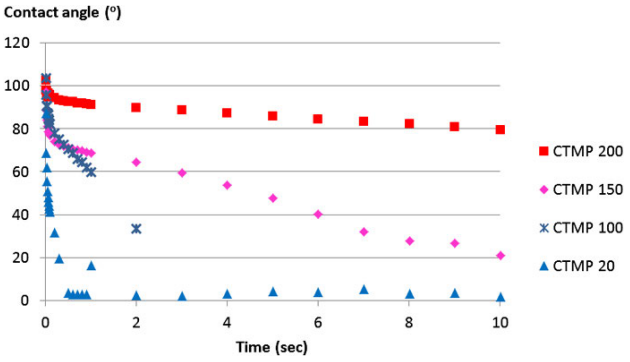

Figure 12: Contact angle for CTMP based sheets pressed at nip temperatures of 20 °C, 100 °C, 150 °C, and 200 °C.

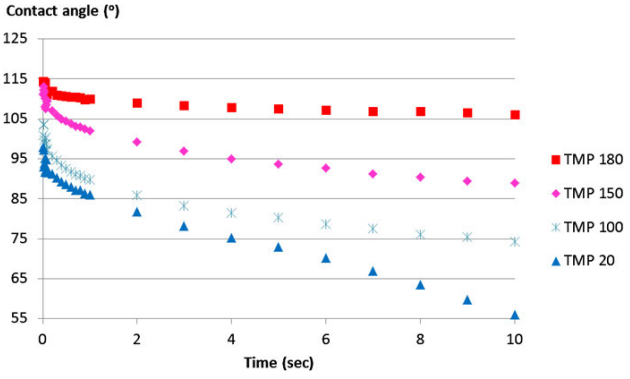

Figure 13: Contact angle for TMP based sheets pressed at nip temperatures of 20 °C, 100 °C, 150 °C, and 180 °C.

Discussion

Rheology studies using SEM and light microscopy on cross sections of paper sheets with fluorescence and $KMnO_4$-staining methods are not new, but here they provide information on how the fibres and fibre structure were affected by the hot-pressing technique used in the experiments. SEM analysis of the CTMP sheet surface showed how the hot-pressing made the fibre structure denser and smoother. Moreover, light microscopy pictures of the paper sheet cross sections indicated that there was a viscoelastic flow of lignin in the fibre structure during hot-pressing, in line with earlier research (Byrd 1979). The lignin distribution, indicated by bright yellowish areas, was enriched around the fibres. This is in accordance with that Scott et. al have shown about how the lignin is enriched on the outer surface of the primary fibre wall (Scott et al. 1969). When fibres collapse, the lignin seems to remain on the fibre surfaces and the contact area between lignin coated fibres increases. The structure of the lignin free and very flexible bleached kraft pulp paper

structure was already highly collapsed at room temperature, and did not change significantly during hot-pressing. It is also obvious from the images that the low freeness TMP contained more fine material (e. g. fibrils, fines) than the CTMP. The much larger proportion of fines contributed to the denser structure of this TMP compared to the CTMP.

The dry strength properties for all HYPs in this study increased with increasing nip temperature, which to a large extent can be explained by the densification that occurs as the fibre structure becomes more collapsible. Norgren et al. (2018) showed that it is possible to increase the tensile index of CTMP and HT-CTMP from about 30 kNm/kg to 70 kNm/kg, and this was also the case in the present study. NSSC pulp is much more densified and has much higher strength values at low nip temperatures. NSSC is a semi chemical pulp made from hardwoods (in this case birch and aspen), in which both the lignin content and the softening temperature are lower in comparison to softwood lignin. Early studies (Gupta et al. 1962) showed that lower Tg results in better fibre adhesion. It has also been shown that the syringyl units in hardwood lignin form bonds through condensation reactions more easily than the guaiacyl units in softwood lignin (Shimada et al. 1997). This, in combination with higher density and the fact that the NSSC in this study was refined to 25°SR, could explain the high strength values even at low pressing temperature in comparison to the CTMP.

High enough moisture content of the sheets is a prerequisite to soften the lignin and hemicellulose in the fibre walls and between the fibres. A moisture content of 50 % was chosen based on previous experiences from studies at FSCN, Mid Sweden University (Norgren et al. 2018, Pettersson et al. 2017). The dependence of strength development on moisture content in hot-pressing of lignin-rich paper sheets was shown by Back et al. in 1979. They tested paper sheets made from a kraft pulp with 60 % yield, and reached the highest tensile strength index at a d. c. of about 50 % at a given density during hot-pressing at 250 °C. It was also concluded that lower initial solid content results in higher paper strength at the same density. However, high initial solid content also meant that a higher nip temperature was needed to reach high paper strength (Back and Anderson 1979).

The highest wet tensile strength level was developed at a nip temperature of 200 °C, which is well above the softening temperature of lignin. This was the case for paper sheets based on very different kinds of lignin-rich pulps without using wet strength agents. Paper sheets from CTMP and HT-CTMP hot-pressed at 200 °C had an extremely large increase in wet tensile strength, comparable to commercial wet strengthened papers where wet strength chemicals are used. CTMP contains lignin with a relatively low sulphonation degree (about 20 % of the sulphonable sites); however, this is enough to soften the wood chips so that pulps with well separated fibres can be produced at low energy demand. Moreover, as the fibre-fibre separation is mainly performed in the mid-lamellae, these fibres are mainly covered by mid-lamellae lignin.

One possible explanation for the extremely high wet tensile index could be that high temperature combined with increased contact area between the lignin covered surfaces could create cross-linking between these lignin surfaces due to condensation reactions. Another possible explanation could be that the lignin surfaces are softened enough (melted lignin) that interdiffusion occurs when the material is hot and plasticized (wet enough), where after the surfaces interlock during drying and cooling. The latter suggestion is partly based on a review on the nature of joint strength in paper (Lindström et al. 2005).

Sulphonation increases hydrophilicity, but the reduced softening temperature in combination with hot-pressing seemed to further improve the development of wet strength. TMP and NSSC with high initial density started to develop increased wet strength at much lower temperatures, but did not reach levels as high as CTMP in the tested temperature interval. The TMP based paper sheets could not be hot-pressed above 180 °C due to delamination problems related to the fact that this pulp was refined to a CSF of 55 ml, which results in a very smooth and sealed surface. This TMP also showed the highest contact angle, probably due to the high surface density together with high lignin content. The NSSC was based on hardwood, and so contained less lignin than the softwood based HYP; moreover, this lignin had a lower Tg due both to its high content of syringyl lignin units (Olsson 1997) and to the higher sulphonation degree. This may be a reason why the wet strength increased but not to the same level as for the spruce based CTMP and HT-CTMP. Another reason might be that condensation reactions probably occur to a larger degree in softwood lignin than in hardwood lignin (Shimada et al. 1997). The bleached kraft pulp, which was nearly lignin free, showed no significant wet strength increase with increasing pressing temperature.

The stability of the wet strength index was studied by comparing strength after 1 minute, 1 hour, and 24 hours soaking in water. Only a minor decrease in wet strength was observed. This indicates that either new covalent bonds are created, or that there is an interlocking phe-

nomenon which protects the hydrogen bonds in a fairly permanent and stable way.

The contact angle was far higher for paper sheets based on HYP compared to bleached kraft when hot-pressed, despite similar high density. This illustrates that lignin plays an important role, and that high density is not enough to provide a hydrophobic surface. The bleached kraft pulp lacked the properties needed for bonding or interlocking that can resist water, probably because the lignin had been removed.

TMP produced the highest contact angle, perhaps due to a denser sheet structure and non-sulphonated lignin on the surface. The surface hydrophobicity of NSSC, CTMP, and HT-CTMP papers was somewhat lower, and seemed to be quite similar between these three pulps. The contact angle measurements also showed that surfaces pressed at low temperature had more open structures, as the contact angle decreased fast i. e. the water droplet was sucked down into the paper sample. As the pressing temperature increased, the contact angle increased due to the ability of the lignin to provide hydrophobicity and according to the compressibility under these conditions.

Hot-pressed materials based on pulp fibres are still biodegradable, since no wet strength agents are utilized. Future studies will deal with aspects of biodegradability, since it is known to us that hot-pressing involves crosslinking and chemical bindings. Wet-strong commercial paper products mainly use fossil based chemical systems, usually combinations of sizing and wet strength agents. The dosages have to be chosen in order to balance the wet strength properties with the runnability as well as with environmental aspects related to product safety, emissions, and health issues. It is therefore desirable to find eco-friendly alternatives to these environmentally questionable wet strength chemical systems, and simultaneously improve both the end product properties and the runnability.

Conclusions

Our results confirm the potential of using high yield pulps to develop high density paper with high tensile and SCT index as well as very good wet strength by means of a hot-pressing strategy.

It is possible to develop very good dry and wet strength provided that lignin rich pulps are used. These strong paper sheets can be produced without adding wet strength chemicals when using the hot-pressing technique.

Hot-pressing also improves the hydrophobicity of paper surfaces, provided that a lignin-rich pulp is used.

Fibre structure can be visualized by light microscopy studies of paper sheet cross sections, resulting in a deeper understanding of how fibres collapse in the hot-pressing nip of the cylinder press at increasing temperature.

HYP could potentially compete with standard chemical kraft pulp in strength when hot-pressed at 200 °C or higher; that is, well above the softening temperature of lignin. The pulps used in these trials varied in terms of their lignin, hemicellulose, and extractive contents as well as their fines and shives contents.

Our general conclusion is that HYPs such as TMP, CTMP, HT-CTMP and NSSC gain enhanced dry and wet strength properties during hot-pressing, while lignin free kraft pulp does not.

Acknowledgments: We gratefully acknowledge financial support from the Knowledge Foundation (KKS) with FORIC (Forest as Resource Industrial Research College, a part of Treesearch), the Kempe Foundation, IPCO AB, MoRe Research Örnsköldsvik AB, and Mid Sweden University. We would also like to thank the laboratory personnel at MoRe for their excellent cooperation.

Funding: Knowledge Foundation (KKS) with FORIC (Forest as Resource Industrial Research College, a part of Treesearch), the Kempe Foundation, IPCO AB, MoRe Research Örnsköldsvik AB, and Mid Sweden University.

Conflict of interest: The authors declare no conflicts of interest.

References

Atack, D. (1972) On the characterization of pressurized refiner mechanical pulps. Sven. Papp.tidn. 75(3):89–94.

Back, E.L. (1984) A review of pressdrying. Tech. Report, D-224, STFI, Stockholm.

Back, E., Andersson, R. (1979) Multistage press drying of paper. Sven. Papp.tidn. 2:35–39.

Back, E., Salmén, L. (1982) Glass transitions of wood components hold implications for molding and pulping processes. Tappi J. 65(7):107–110.

Byrd, V.L. (1979) Press drying – Flow and adhesion of hemicellulose and lignin. Tappi J. 62(7):81–84.

Dunlop-Jones, N. (1991) Wet-strength chemistry. In: Pap. Chem.. Eds. Roberts, J. C. Chapman & Hall, New York, USA. pp. 76.

Goring, D.A.I. (1963) Thermal softening of lignin, hemicellulose and cellulose. Pulp Pap. Mag. Can. 64(12):T517–T527.

Gupta, P.R., Rezanowich, A., Goring, D.A.I. (1962) The adhesive properties of lignin. Pulp Pap. Mag. Can. 63:21–30.

Irvine, G.M. (1984) The glass transition of lignin and hemicellulose and their measurement by differential thermal analysis. Tappi J. 67(5):118–121.

Irvine, G.M. (1985) The significance of the glass transition of lignin in thermomechanical pulping. Wood Sci. Technol. 19(2):139–149.

Klinga, N., Höglund, H., Sandberg, C. (2007) Paper properties of TMP and CTMP handsheets from spruce, as affected by the solids content from pressing. Nord. Pulp Pap. Res. J. 22(4):475–480.

Lehtinen, J. (1998) Condebelt board and paper drying. Dry. Technol. 16(6):1047–1073.

Lindström, T., Wågberg, L., Larsson, T. (2005) On the nature of joint strength in paper – a review of dry and wet strength resins used in paper manufacturing. In: 13th Pulp Pap. Fundam. Res. Symp., Cambridge, UK. pp. 457–562.

Lucisano, M.F.C. (2002) On Heat and Paper: From Hot Pressing to Impulse Technology. Dr. Thesis, K. Tek. Högskolan, ISSN 1104-7003.

Mason, W.H. (1931) Process of making integral insulating board with hard welded surfaces. Patent number: US1812969.

Mason, W.H. (1937) Molding composition and process of making same. Patent number: US2080078.

Mason, W.H. (1938) Process of making ligno-cellulose fiber products. Patent number: US2120137.

Norgren, S., Pettersson, G., Höglund, H. (2018) Strong paper from spruce CTMP – Part II: Effect of pressing at nip press temperatures above the lignin softening temperature. Nord. Pulp Pap. Res. J. 33(1):142–149.

Olsson, A.M. (1997) The effect of lignin composition on the viscoelastic properties of wood. Nord. Pulp Pap. Res. J. 12(03):140–144.

Page, D.H. (1969) A theory for the tensile strength of paper. Tappi J. 52(4):674–681.

Pettersson, G., Norgren, S., Höglund, H. (2017) Strong paper from spruce CTMP – Part I. Nord. Pulp Pap. Res. J. 32(01):054–058.

Rundlöf, M., Sjölund, A., Ström, H., Åsell, I., Wågberg, L. (2000) The effect of dissolved and colloidal substances released from TMP on the properties of TMP fines. Nord. Pulp Pap. Res. J. 15(4):256–265.

Salmén, L. (1984) Viscoelastic properties of in situ lignin under water-saturated conditions. J. Mater. Sci. 19(9):3090–3096.

Scott, J.A.N., Procter, A.R., Fergus, B.J., Goring, D.A.I. (1969) The application of ultraviolet microscopy to the distribution of lignin in wood description and validity of the technique. Wood Sci. Technol. 3(1):73–92.

Shimada, K., Hosoya, S., Ikeda, T. (1997) Condensation reactions of softwood and hardwood lignin model compounds under organic acid cooking conditions. J. Wood Chem. Technol. 17(1–2):57–72.

Stone, J.E., Clayton, D.W. (1960) The use of microtome sections for measuring the change in strength of spruce fibers due to pulping. Pulp Pap. Mag. Can. 46:345–355.

Wahren, D. (1982) Methods and apparatus for the rapid consolidation of moist porous web. Patent number: US4324613.