Stiftelsen Åforsk

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“Hot pressed lignin-rich materials with high wet strength”

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Summary

Addressing society's urgent concern to diminish fossil material consumption and environmental pollution from plastics, this project has focused on overcoming key obstacles hindering the widespread adoption of eco-friendly, renewable materials. Particularly, in sectors dominated by plastics, such as packaging and construction, the need for sustainable alternatives is paramount. The aim of this project was to fundamentally identify why lignin-rich cellulosic materials acquire impressive material properties, with an emphasis on wet strength, after treatment with high temperatures and pressures. Within this project, an extensive experimental work has been carried out to investigate the optimal pressing conditions, as well as the effect of adding certain additives. Also, a theoretical model has been developed to evaluate the collected data. The results have shown that a certain amount of humidity in the material during hot-pressing is required to obtain the best possible properties. We have also found that it is possible to tune, with the help of the theoretical model, the combination of pressing temperature and pressing time in order to get the desired properties. This enables us to design a material with custom-made properties for a specific product with unique requirement specification.

Background

Plastic emissions are one of the world's greatest environmental threats. The amount of these emissions has been steadily increasing for many years and is expected to continue to do so [1]. Plastic pollution is commonly divided into two different size scales, namely plastic and microplastic, the latter of which has recently attracted enormous attention. The effects when this microplastic spreads in the marine environment, plants and human body are largely unknown, making it difficult to predict the causes in the future [2], [3]. Plastics take time to degrade and it can take as long as 1000 years for a plastic bag to fully decompose [4].

Although plastic has been identified as a major environmental threat today, it has played a crucial role in the development of our society since the beginning of mass production in the 1940s [5]. This material allowed the production of products with features and shapes that we did not know before, in a way that was both cheap and fast. Today, it is also possible to produce plastics from renewable resources, and biodegradability has been extensively studied and varies greatly depending on the process [6]. Although the biodegradability of these plastics is improved compared to petroleum-based polymers, they can still be harmful to the environment, limiting their use in products.

Lignin, which is a compound of natural plants (wood), is considered by many to be an abundant polymer. It is said among researchers that "you can do anything out of lignin, except money" [7]. It is often referred as a by-product in industries such as the production of paper, ethanol, biomass, etc. [8]. However, the potential for lignin is huge and research interest has increased greatly in recent years. Nevertheless, there are currently only a few commercial products based on lignin. On the other hand, there are process lines within pulp and paper production where the lignin is not removed and the products produced therefore have a much higher yield, so-called high yield pulps, which then have a high lignin content. Unlike high yield pulp, chemical pulp has the lignin removed. High yield pulp has a yield of up to 95 %, while chemical pulp has a yield of about 50 % [9], making high yield pulp the preferred option from the point of view of better utilisation of raw material. High yield pulp has mainly been used for printing paper, the market for which has declined sharply in recent years, so new markets are needed.

The main reason for removing the lignin, as is done in chemical pulping, is that it can give more desirable properties to the material, such as brightness and strength. However, recent studies have shown that hot pressing of material from high yield (lignin-rich) pulp significantly improves various material properties. Figure 1 shows how wet strength (Tensile index Wet) increases with increasing pressing temperature. The pulps with high lignin content (CTMP, HT-CTMP, and TMP) also show the significantly highest increase in wet strength with increasing temperature [10]. Note that for the Bleached kraft, which is produced from a chemical pulp that contain almost no lignin (0.01 %), this increase is significantly lower. The explanation for this phenomenon so far is that the lignin is softened by these high temperatures and at the same time densified and consolidated, which improves the fibre-fibre contacts. [10, 14] On the other hand, the dry strength, is mostly explained by the density increase [10].

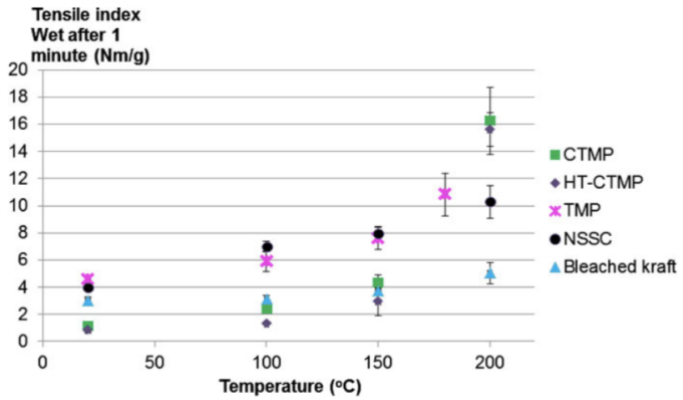

Figure 1. Wet tensile index (1 minute in water) as a function of temperature in press nip. Error bars indicate 2SD. Nip pressure temperatures of 20°C, 100°C, 150°C, and 200°C (180°C for TMP). [10]

The aim of this project was to fundamentally identify why and how lignin-rich cellulosic materials acquire impressive material properties, with an emphasis on wet strength, after treatment with high temperatures and pressures.

Methods and Materials

Within this project, an extensive experimental work has been carried out to investigate the optimal pressing conditions, as well as the effect of adding certain additives in combination with hot-pressing. These pressing conditions include temperature, pressing time, humidity in the sheets prior pressing, and pressure level. The hot-pressing equipment used is a planar press installed in hydraulic MTS^{TM} machine (Figure 2) with a capacity up to 100 kN and a pressing temperature up to 300°C. The pulp-material used is a chemi-thermo-mechanical, CTMP, from SCA Östrand mill (Timrå, Sweden). The pulp was first prepared according to ISO 5263-3, followed by producing hand-sheets with a Rapid Köthen sheets former (PTI, Austria) following ISO 5269-2. These sheets were then pressed in the hot-pressing equipment. The sheets were characterized according to various ISO standards, starting with conditioning at 23°C and 50% relative humidity for at least 24 hours (ISO 187). This was followed by determining the density by measuring the weight and thickness (ISO 534 and 536). Finally, tensile strengths in dry and wet state were carried out according to ISO 1924 and 3781. A theoretical model has been developed to evaluate the collected data.

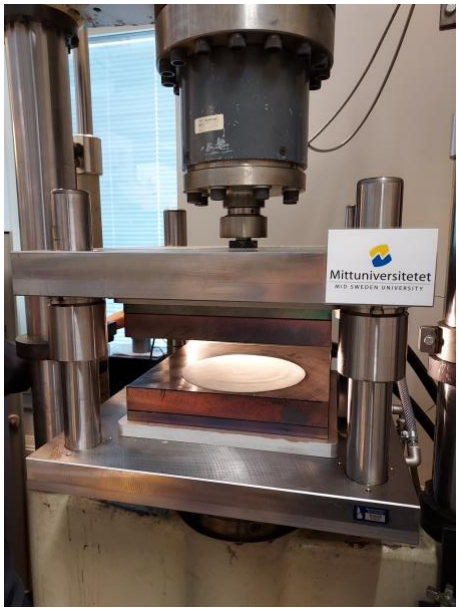

Figure 2. Hot-pressing equipment at Mid Sweden University.

Results

The pressing temperature has shown to be the dominant effect on the increased mechanical properties of the sheets, with a special emphasis on the wet strength [10]. Samples of the sheets after pressing at the different temperatures are shown in Figure 3, where “D” stands for pressed dry, and “W” stands for pressed wet. The higher the pressing temperature, the darker the paper sheet, indicating a certain degree of burned and decomposed components, hemicellulose and lignin, at high temperatures. The tensile properties, dry and wet, of the hot-pressing interval 100°C to 300°C is presented below (Figure 4) for both wet (20% moisture) and dry sheets prior to pressing. As can be seen, both dry and wet strength increases with increasing pressing temperature, particularly the wet strength. This increase for wet strength has been observed earlier, which can be explained by the fact that lignin softens at high temperatures. This softening of lignin occurs earlier for wet lignin, than for dry lignin. At low pressing temperatures, below 180°C, no measurable wet strength was seen. For dry strength at high temperatures, the values tend to decrease at high pressing temperatures due to decomposition of the hemicellulose and lignin of the sheet, making the material both weaker and more brittle. This is, as mentioned, possible to observe in Figure 3. It is important to observe that for both dry and wet strength, higher values are received when the sheets are hot-pressed wet (orange bars).

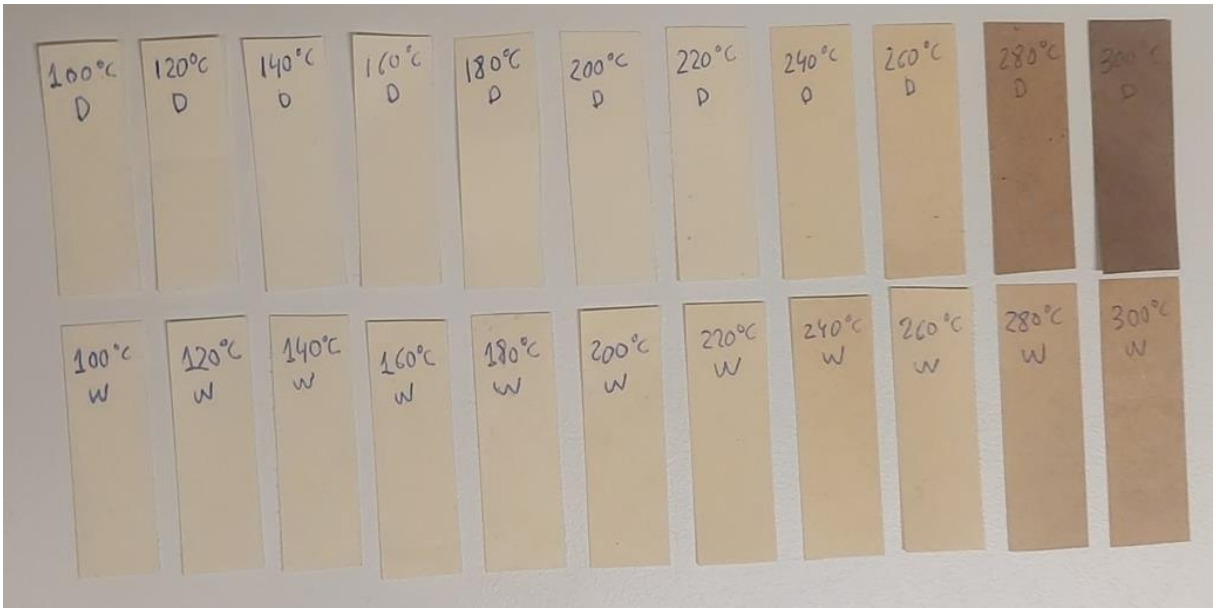

Figure 3. Chart including the hot-pressed sheets after pressing at temperatures from 100°C up to 300°C for both dry (“D”) and wet (“W”) pressed sheets.

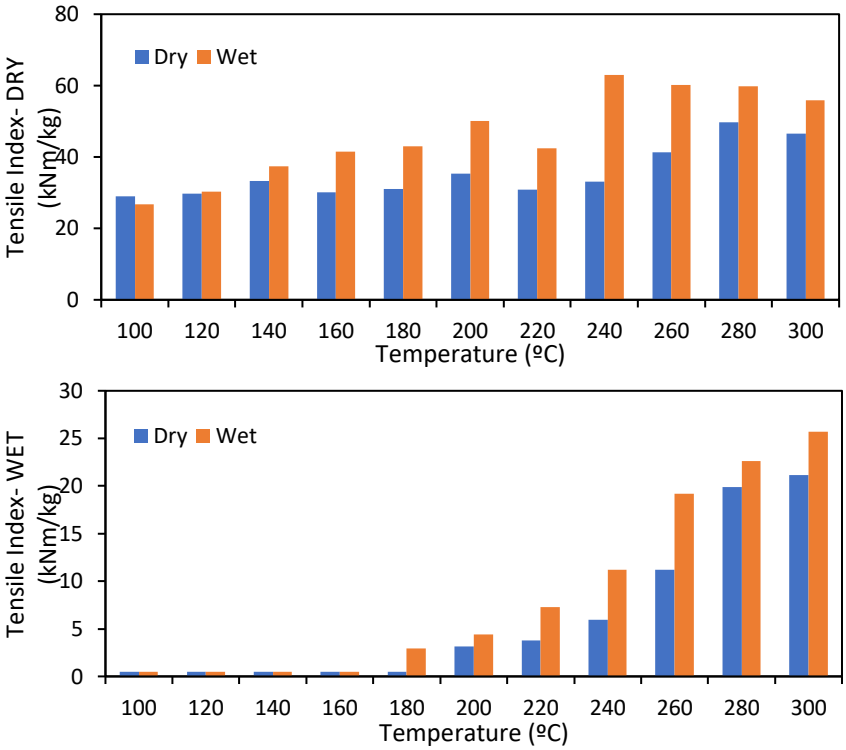

Figure 4. Dry (upper) and wet (lower) tensile strength as a function of pressing temperature for dry and wet pressed sheets.

The effect of different humidity levels can be seen in Figure 5 for both dry and wet strength, for two different pressing times, i.e. 1 sec and 5 sec. The trend is clear that dry pressed sheets does not give as high strength values (both dry and wet strength) as those pressed with wet prior to pressing. However, the values keep on a stable level, or even decreases with increasing amount of humidity (decreased amount of dryness). Therefore, we decided to use a level of approximately 80% dryness of the sheets when hot-pressing the sheets wet. High humidity levels in the sheets (low amount of dryness) prior pressing can cause problem in the hot press due to steam explosion. Additionally, longer pressing times showed higher strength values for both dry and wet strength values, especially the wet strength.

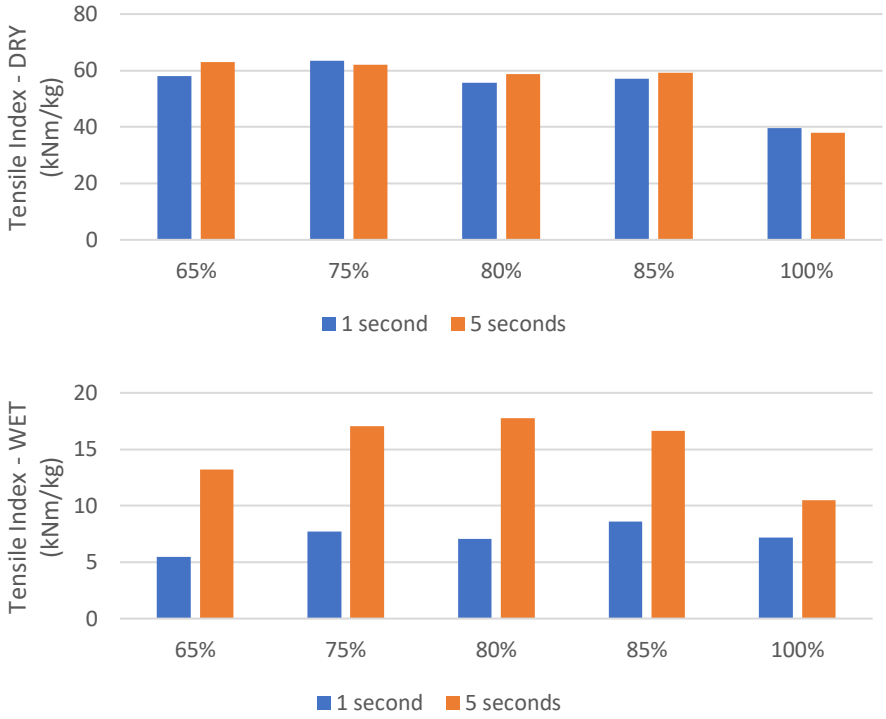

Figure 5. Dry (upper) and wet (lower) tensile strength as a function of the humidity in the sheets, here as dryness (100% means completely dry), prior pressing. This is tested for two different pressing times, i.e. 1 seconds and 5 seconds.

The result for the dry and wet tensile strength for a series of varying hot pressing times, ranging from 50 ms to 60 min, is shown in Figure 6. This is done for two different pressing temperatures, i.e. 180°C and 260°C (only up to 10 min for 260°C due to decomposed samples), as well as for both dry and wet sheets prior to pressing. As can be seen, the dry strength increases with increasing pressing time for both pressing temperatures up to around 30 sec, but after that the values for 260°C decreases whereas for 180°C it continues to increase and plateau. For the wet strength, we observe a rapid increase up to around 60 seconds, after which is starts to decrease for the higher pressing temperature 260°C, but continues to increase for the lower pressing time 180°C. These increases for 180°C are continuing to increase, even up to 60 minutes. Again, we observe higher values for the wet pressed sheets for both the wet and dry strength. Interestingly, it is possible to fit the data from the hot-pressing of both 180°C and 260°C to a master curve by scaling the pressing time so that the curves collapses (Figure 7). These curves seems to collapse very well, indicating that the mechanisms happening at both time scales are similar, but happening at a slower diffusion rate for the lower temperature. The data for hot-pressing at 260°C are scaled by multiplying the values by 50 for the wet pressed sheets and by 1800 for dry pressed sheets. The reason for the much bigger scaling factor for the dry pressed sheet, meaning a bigger difference between the two pressing temperatures, is because of higher softening temperature of the lignin for dry lignin in comparison to wet lignin. Therefore, at pressing temperature 180°C for dry sheets, the lignin has just started to soften and hence the diffusion rate is very slow for that temperature level.

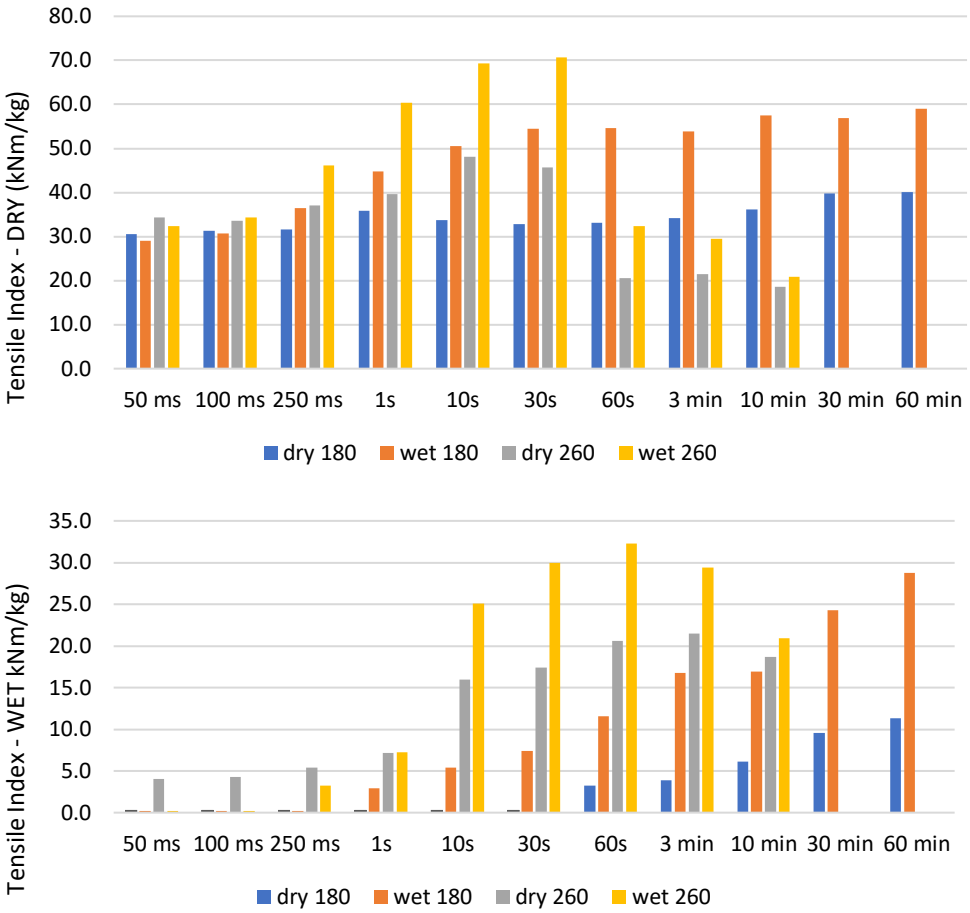

Figure 6. Dry (upper) and wet (lower) tensile strength for pressing times ranging from 50 ms to 60 min. This is done for two different temperatures, i.e. 180°C and 260°C, as well as for both dry and wet sheets.

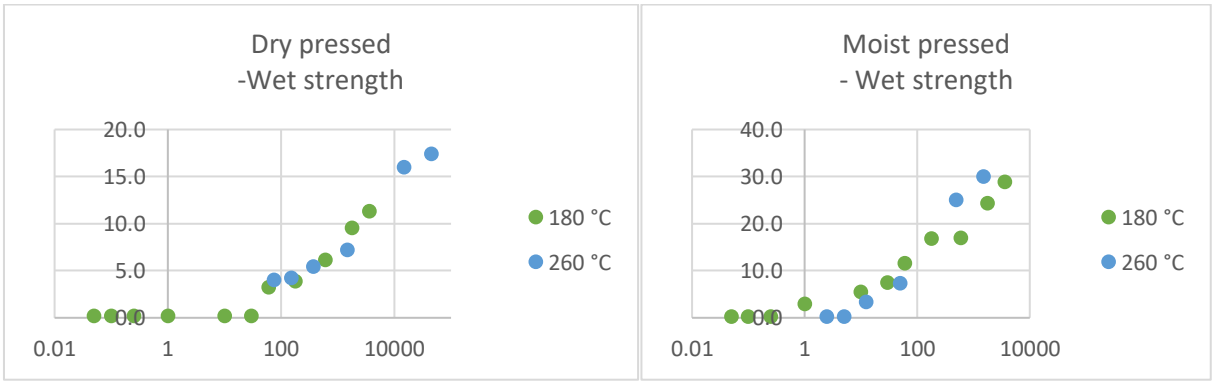

Figure 7. Wet tensile strength for dry (left) and wet (right) pressed sheets as a function of pressing time. The x-axis is now in a logarithmic scale and the data for hot-pressing at 260°C are scaled by multiplying the values with 50 for the wet pressed sheets and 1800 for dry pressed sheets.

Conclusions and future work

This knowledge will help to improve and optimize the hot-pressing processes, which will hopefully soon lead to implementation in production of commercial products. The presented process for hot-pressing the lignin-rich cellulosic material is free of toxic chemicals that are normally used to improve the wet strength of cellulosic materials. The lignin, which is considered a residual component of wood pulp, has the potential here to act like a natural binder and contribute to improved material properties.
Future work in this field would be to try other types of pulp material to investigate if all these trends are general or dependent on a specific pulp. Additionally, we are continuing to investigate the area of moulded and formed products, where the gained knowledge from this project is of great interest.

Outreach and publications

During the International Fibre Moulding and Paper Forming conference in Stockholm 27-28th of September 2023 I, Amanda Mattsson, presented work from this project. The presented data in this report is not yet published, but I wrote an abstract based on this and sent to a conference, International Mechanical Pulping Conference, held in Sundsvall the 27-29th of May 2024, which has now been accepted for an oral presentation. In parallel, an article is being written for publication in a journal. I have also co-authored one article in this subject during the year, where we investigated the synergetic effect of adding micro/nano cellulose and hot-pressing [13].

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